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1,2-Migratory ring expansion of a BN-naphthalene

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Organoboranes hold an undeniable value in modern organic chemistry and show ever-growing potential in polymer design and functionalization. Azaborines, in particular, are still being explored as a promising class of organoboron compounds. We investigated the reactivity of a 1,2-azaborine towards Matteson homologation, a cornerstone of organoborane transformations. The azaborine was shown to be reactive towards nucleophiles. Addition of *n*-BuLi led to exchange of the R group, while addition of chloromethyl-lithium formed the desired tetracoordinate intermediate. However, rather than homologation, the complex readily underwent ring expansion via migration of the adjacent C(sp²), followed by deborylation. Computational analysis revealed a stable geometry of the azaboronate in which the migrating carbon is antiperiplanar to the leaving group, and which we propose as being responsible for the observed reactivity. This finding suggests a unique role for azaborines in molecular transformations which may be unachievable with other organoboron frameworks.

Introduction

Organoboranes are a versatile functional group in the organic chemist's toolbox, due to the ability to convert the C–B bond into a variety of other functional groups including C–O,^{1,2} C–N,^{3,4} and C–C⁵ bonds, often with high stereospecificity. This arises from the ability of groups to migrate from a tetrasubstituted, anionic boronate in a 1,2-rearrangement, a mechanism with ongoing synthetic utility^{6–9} and implicated in such established reactions as stereoretentive oxidation of organoboranes and the Matteson homologation (Scheme 1). The Matteson homologation is the insertion of a single CH₂ or CHX (X = halogen) group into a C–B bond, which can be employed iteratively and in combination with other organoborane functionalizations.^{10–14}

While a variety of organoborane functional groups have been reported, an important emerging class are 1,2-azaborines, aromatic compounds in which one C=C double bond has been replaced with the isoelectronic B–N bond (Fig. 1a). These unusual aromatic heterocycles have been widely investigated as biological isosteres, in materials science, and in catalysis,¹⁵ but far less work has focused on their utility as synthetic intermediates. This is despite the exciting potential of azaborines to solve synthetic challenges, particularly in the context of polymer chemistry. Due to its aromatic character, the monomer BN 2-vinylnaphthalene (BN2VN, Fig. 1b) has styrene-like reactivity and versatility, allowing for controlled

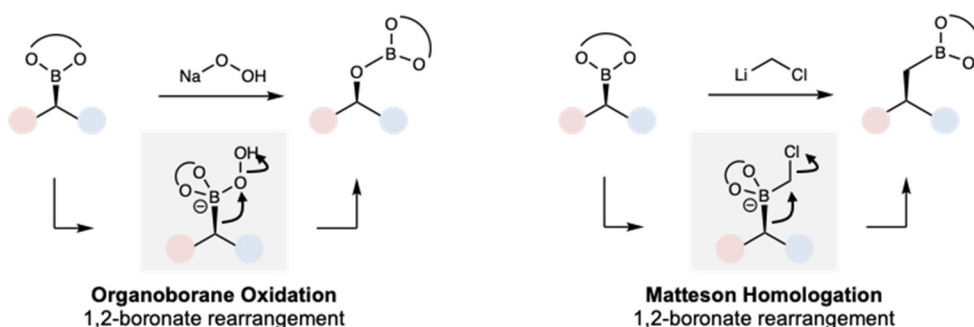
radical, free radical, and syndioselective coordination polymerization and co-polymerization.^{16–23}

We became interested in whether polymeric materials derived from BN2VN could also undergo a Matteson homologation, considering the similarities in mechanism between hydrogen peroxide mediated oxidation and Matteson homologation. Achieving this functionalization would not only facilitate polymer synthesis but could also impact molecular synthesis. If Matteson homologation of 1,2-azaborine systems were possible, existing heterocycles^{24–32} could be rapidly further diversified without requiring *de novo* synthesis of the sometimes challenging heterocyclic core.

Therefore, in considering the feasibility of the proposed homologation of B-alkyl azaborine derivatives, two different steps must occur (Fig. 1b): (i) addition of chloromethyl-lithium (or related carbenoid) to the boron of an azaborine ring to form an azaboronate complex **I** and (ii) selective migration of the exocyclic bond labeled "a" from azaboronate complex **I**. Migration of either the amine or the bond labeled "b" would lead to ring expansion and loss of BN aromaticity. While prior work from our group supported the feasibility of organolithium addition to the boron of BN naphthalene,²⁴ the relative migratory ability of varying groups on boron has been incompletely elucidated. Existing experimental and theoretical work suggests that endocyclic migration is uncommon due to conformational constraints of the migration.^{33–36} However, in the last 5 years, several methods for ring-contractive endocyclic migration have been developed.^{37–42} As such, and additionally considering the unique electronic and conformational context of these aromatic azaboronates, the expected decomposition pathway for complex **I** was unclear.

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Scheme 1 1,2-Boronate rearrangements in organoborane oxidation and the Matteson homologation.

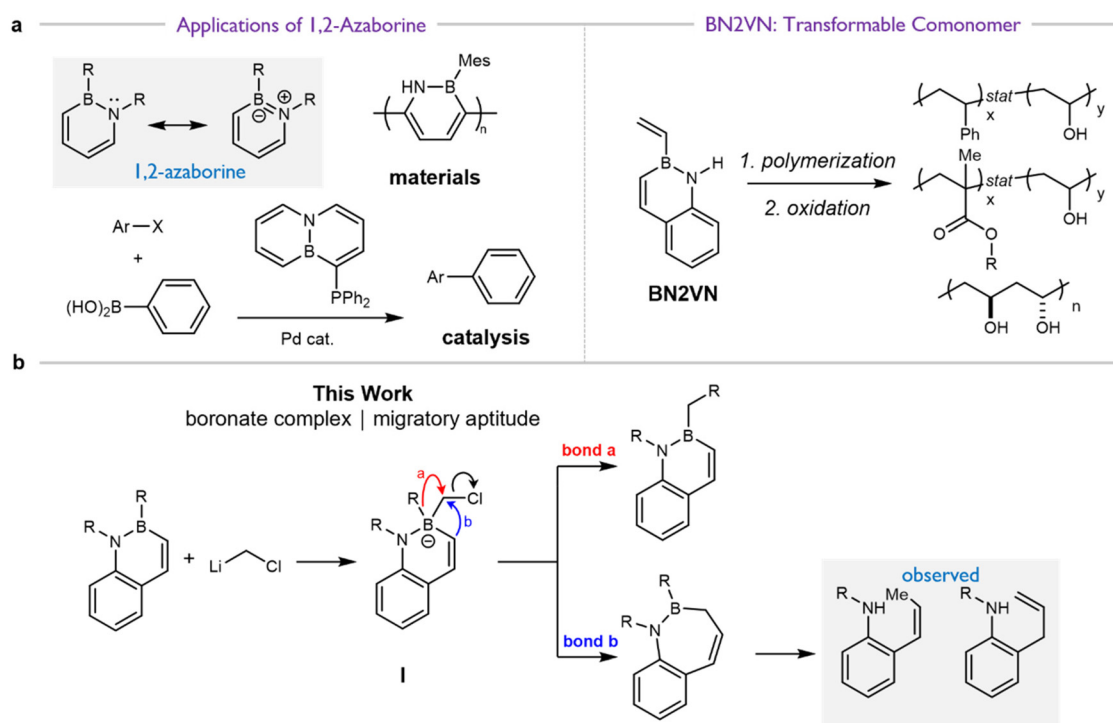


Fig. 1 (a) Previous research: applications of azaborines as benzene mimics, as synthetic intermediates in polymer synthesis, and as electronically modular ligands for Suzuki cross-coupling reactions, adapted from Sun et al. (2015).¹⁵ (b) This work: investigation of migratory aptitude in the rearrangement of BN naphthalene-derived azaboronate complexes.

Here, we report our attempts to perform the Matteson homologation on B-isopropyl functionalized BN naphthalenes. We observed a novel ring-expansion *via* migration of the C(sp²) adjacent to the boron in the naphthalene core. Extensive characterization supports assignment of the major products to deborylated variants of this ring-expanded structure (Fig. 1b).

Results and discussion

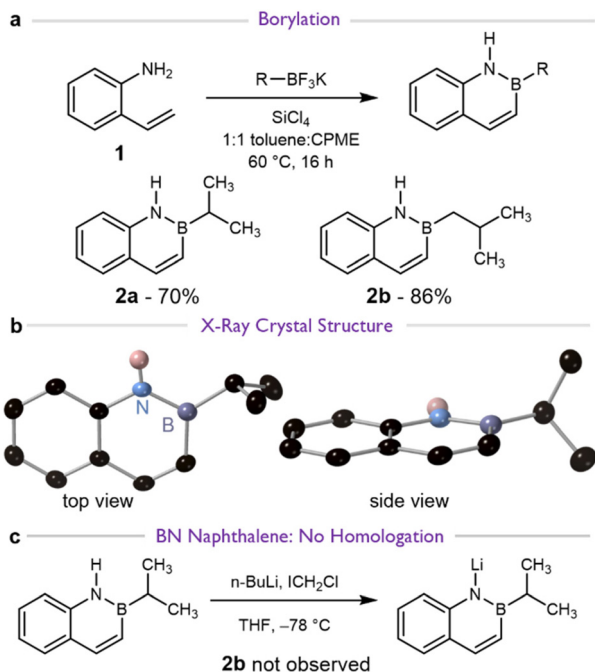
We began by synthesizing examples of BN naphthalenes with different alkyl substituents on boron. We initially targeted compounds **2a** and **2b** (Scheme 2a), with an isopropyl and isobutyl side chain respectively, because Matteson homologation

of **2a** would yield **2b**. Known 2-vinylaniline⁴³ (**1**) was a common precursor *via* Molander's procedure²⁹ for borylative annulation. Borylative annulation proceeded in high yields and an X-ray crystal structure confirmed the planar structure of **2a** (Scheme 2b).

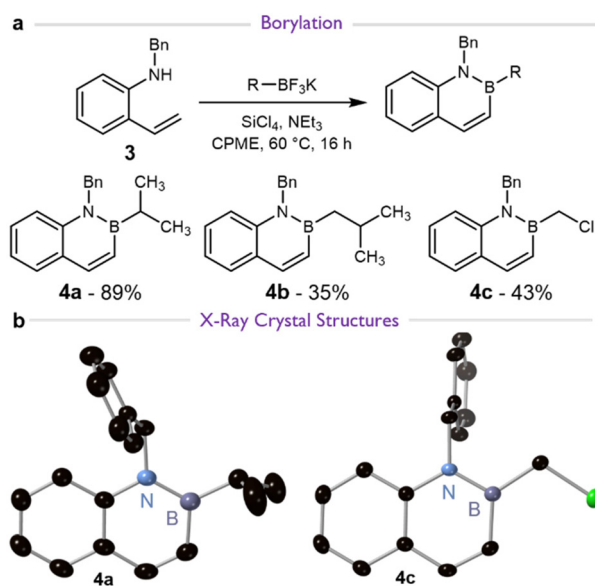
Attempted Matteson homologation of **2a** did not yield the desired **2b** (Scheme 2c). The one-pot reaction conditions employed lithium-halogen exchange of chloriodomethane (I-CH₂-Cl) and *n*-butyllithium (*n*-BuLi) in the presence of **2a**. The only observed reaction was partial deprotonation (Scheme 2c and Fig. S1). Reaction with 2 equivalents of the carbenoid did not afford any additional products.

We therefore synthesized *N*-benzyl protected BN naphthalenes **4a-c** (Scheme 3a), a common and facile derivatization of





Scheme 2 (a) Synthesis of BN naphthalenes **2a–b**. (b) X-ray crystal structure of **2a** determined at 110.00(10) K. Thermal ellipsoids set at the 50% probability level with most hydrogen atoms omitted for clarity. Black = carbon, blue = nitrogen, purple = boron, pink = hydrogen. (c) Deprotonation of **2a** observed instead of Matteson homologation.



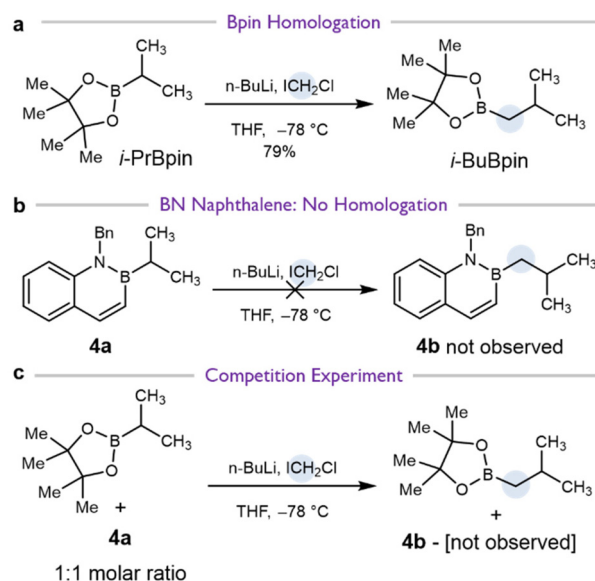
Scheme 3 (a) Synthesis of BN naphthalenes **4a–c**. (b) X-ray crystal structures of **4a** and **4c**, determined at 243.00(10) and 110.00(10) K, respectively. Thermal ellipsoids set at the 30% probability level with hydrogen atoms omitted for clarity. Black = carbon, blue = nitrogen, purple = boron.

1,2-azaborines which renders it unable to undergo the observed deprotonation.^{9,14,15} An X-ray crystal structure confirmed the structure of **4a** (Scheme 3b). The synthesis of **4b**

has not previously been reported and could be prepared by similar reactions as have been described elsewhere.^{20,24,29} However, our 35% yield on preparative scale was significantly lower than observed for similar compounds. We attributed this to the formation of ¹H NMR-silent inorganic byproducts which required multiple purification steps to fully remove, as described completely in the SI.

Reaction of **4a** with chloromethyl lithium produced no measurable quantity of the homologation product **4b** under the same conditions which transformed pinacol boronic ester *i*-PrBpin to the homologation product *i*-BuBpin in 79% yield (Scheme 4a vs. Scheme 4b). Instead of cleanly forming **4b**, a complex mixture of products was obtained, the assignment of which will be described later (*vide infra*). As a first hypothesis, we considered if the azaborine ring of **4a** might inhibit the lithium–halogen exchange reaction of *n*-BuLi and ICH₂Cl, preventing formation of chloromethyl lithium. We therefore tested if *i*-PrBpin could still undergo homologation in the presence of **4a**. Treatment of a 1 : 1 mixture of **4a** and *i*-PrBpin with chloromethyl lithium resulted in complete conversion of *i*-PrBpin to *i*-BuBpin with no formation of **4b** detected by NMR or mass spectrometry (Fig. S2). This experiment indicates that the lack of homologation observed with **4a** cannot be attributed to inhibition of the lithium–halogen exchange reaction between chloriodomethane and *n*-BuLi.

Having established that chloromethyl lithium was formed under the reaction conditions, we next considered if failure of nucleophilic addition to the boron atom of **4a** might account



Scheme 4 (a) Successful homologation of *i*-PrBpin with standard conditions (2.5 equiv. ICH₂Cl, 2.1 equiv. *n*-BuLi, 0.5 equiv. ZnCl₂, 0.6 M THF, –78 °C to rt, 16 h). (b) *N*-Benzyl protected **4a** does not homologate under standard conditions. (c) Competition experiment: an equimolar combination of *i*-PrBpin and **4a** results in only homologation of the pinacol boronic ester and no recovery of **4b**, demonstrating that lithium–halogen exchange of *n*-BuLi and ICH₂Cl to form chloromethyl lithium does proceed in the presence of **4a**.



for the lack of homologation. We began by understanding what reactions **4a** does undergo with alkylolithium reagents generally. Previous research from our laboratory has shown that vinyl BN naphthalene reacts with *n*-BuLi in a substitution reaction, resulting in the formation of *n*-butyl BN naphthalene **4d** (Table 1, entry 1) and ethylene, which was hypothesized to arise from protonation of vinylolithium.⁹ Because the formation of a more stable C(sp²) carbanion from C(sp³) *n*-BuLi was thought to contribute to a favorable exchange reaction, elimination of 2-propyllithium was not initially considered to be a concern for **4a**. However, treatment of **4a** with *n*-BuLi yielded measurable conversion to **4d**, as estimated by ¹H NMR, and high conversion to **4d** could be observed with excess *n*-BuLi (Table 1, entries 2, 3 and Fig. S3, S4). We found that the more sterically hindered *tert*-butyllithium (*t*-BuLi) did not result in substitution (Table 1, entry 4 and Fig. S5). These data suggest that direct nucleophilic attack by LiR² on **4a** could yield an azaboronate complex such as **II**, which can either regenerate starting materials or yield the exchange product. The lack of substitution with *t*-BuLi is consistent with slow nucleophilic attack to form azaboronate **II** due to the greater steric hindrance of the *t*-Bu group.

These results suggest that the reaction between **4a** and ICH₂Cl/*t*-BuLi should cleanly generate complex **I** as the only boronate in solution (Fig. S4), a key step towards homologation. However, the ultimate product distribution would depend on the relative rates of *i*-Pr migration and exchange, leading to products **4b** or **4c**, respectively (Fig. 2a). Prior work has shown that Lewis acids can accelerate 1,2-migration.^{44–46} Therefore, we hypothesized that addition of ZnCl₂ to our synthetic protocol could accelerate *i*-Pr migration over exchange.

The reaction of **4a** and LiCH₂Cl under this revised protocol was reinvestigated. Independent synthesis of **4b** and **4c** (Scheme 3a) provided authentic samples for comparison. However, analysis of the ¹H NMR spectrum of the unpurified reaction mixture suggested no evidence of either the homologation product **4b** or the substitution product **4c** (Fig. 2b). Instead, we identified the products as **5a** and **5b** (Fig. 2c),

which could be isolated after column chromatography in 58% combined yield (**5a**:**5b**, *ca.* 1:2). The isomeric products were challenging to separate, but after a second purification by preparatory thin layer chromatography, small quantities of pure samples of both (*Z*)-**5a** and **5b** could be obtained, which, combined with mass spectrometry, confirmed the structural assignment. (*E*)-**5a** is known^{47,48} and our spectroscopic data match, with exception of the coupling constants for the vinyl protons ((*Z*)-**5a**, *J* = 11.2 Hz; (*E*)-**5a**, *J* = 15.4 Hz).⁴⁹ Allylbenzene **5b** is a known compound and our spectroscopic data match the reported characterization data.^{50,51}

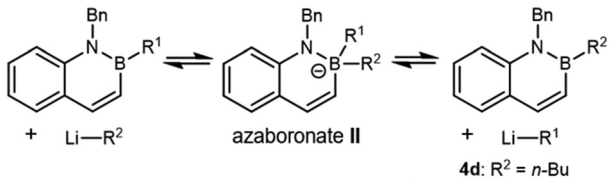
Formation of **5a** and **5b** from **4a** under a variety of conditions (Table 2, entries 2–4) is consistent with an unprecedented alternative decomposition of azaboronate **I**. Rather than exchange (dominant in the reaction of **4a** and *n*-BuLi, see Table 2, entry 1) or migration of the *iso*-propyl group (dominant in the reactions of *i*-PrBpin and LiCH₂Cl, see Scheme 4a), we hypothesize that migration of the endocyclic alkenyl group results in ring-expansion product **6** (not isolated, Fig. 3). Intermediate boracycle **6** was unable to be isolated, and instead (*Z*)-alkene **5a** and allylbenzene **5b**, which are related by isomerization, are observed. Without the stabilizing effect of aromaticity, which is expected to be around 20 kcal mol⁻¹,⁵² we suggest that **6** readily undergoes deborylation prior to or upon quenching to yield the shown products. This is in line with the mechanistic understanding of deborylation reactions^{53–56} and with established lability of the B–N bond under the given conditions.^{57–61}

We appreciated that if azaboronate **I** is the key intermediate leading to **5a** and **5b**, then azaboronate **I** should also be accessible from the reaction between **4c** and *iso*-propylmagnesium chloride (*i*-PrMgCl, Fig. 3). Indeed, the reaction of **4c** and *i*-PrMgCl exclusively yielded ring-opened products **5a** and **5b** (Table 2, entry 5). Neither the starting material **4c**, the exchange product **4a**, nor the homologated product **4b** were observable by either NMR or mass spectrometry. **5a–b** were also observed as the major products in the reaction of **4c** with *n*-BuLi (Table 2, entry 6). These data strongly support ring-expansion of azaboronate **I** as the pathway leading to **5a** and **5b**.

Ring-expansion *via* O-migration in pinacol-derived boronates has been long known to compete with exocyclic migration. For various reasons, including conformational demands, it is typically a minor or unobserved product.^{41,62} Observation of exclusively an endocyclic migration product and dearomatization prompted further investigation.

To support ring expansion and compound **6** as a plausible intermediate towards the formation of the isolable **5a** and **5b**, we performed computational analysis at the B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP (SMD, THF) level of theory. Complex **I** is shown coordinated to ZnCl₂ (**I**·ZnCl₂), which was present in the reaction conditions with the highest yields of **5a** and **5b**. Of the two possible diastereoisomers, the favored one has the carbenoid and ZnCl₂ in a *syn*-relationship, which facilitates halide abstraction, as previously reported in related studies on the Matteson homologation.⁶³ The starting material

Table 1 BN anthracene substitution reactions with butyllithium reagents



Entry	R1	R ²	Equiv. LiR	Conv. (%) ^a
1 ^b	CHCH ₂	<i>n</i> -Bu	1.0	85
2	<i>i</i> -Pr	<i>n</i> -Bu	1.0	72
3	<i>i</i> -Pr	<i>n</i> -Bu	2.5	96
4	<i>i</i> -Pr	<i>t</i> -Bu	2.5	n.r.

^a Conversion estimated by ¹H NMR spectroscopy. ^b Previously reported by Wakefield and co-authors.²⁴



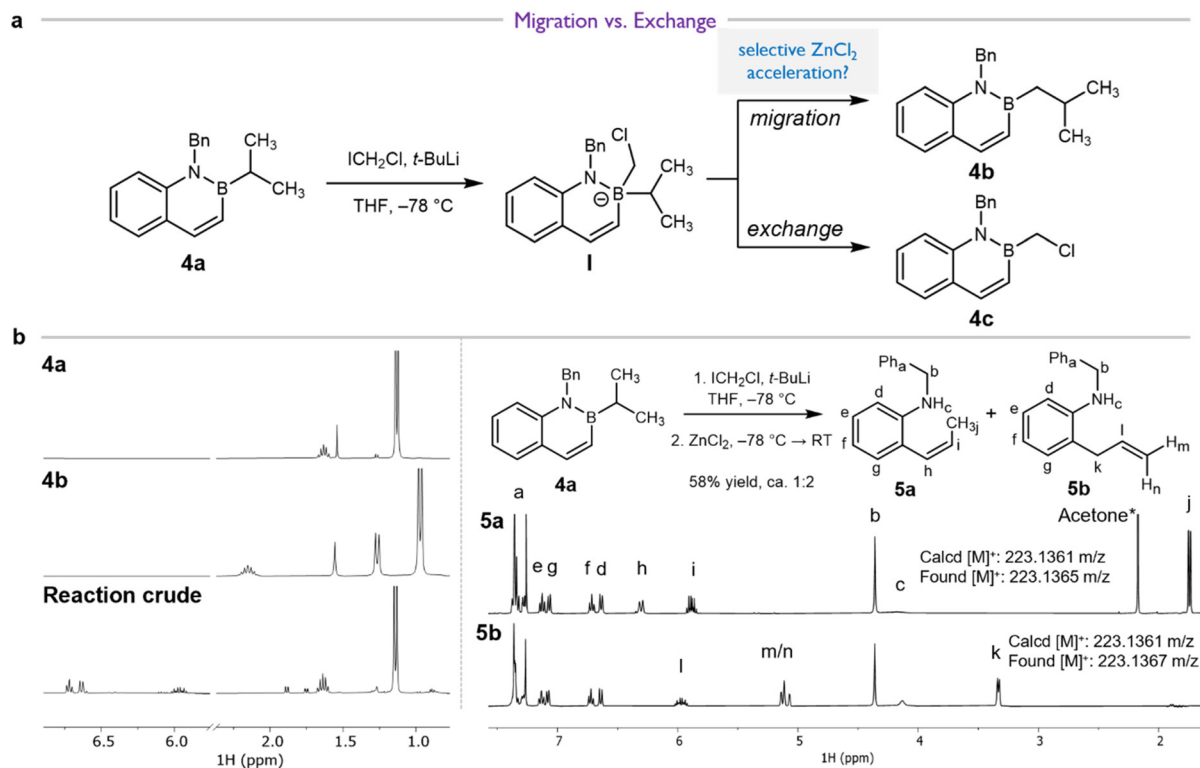


Fig. 2 (a) Azaboronate complex I as a common intermediate in migration or exchange pathways. (b) (left) Cropped ^1H NMR (400 MHz, CDCl_3) spectra of the unpurified reaction mixture compared to independently synthesized **4a** and **4b** as well as purified samples of **5a** and **5b** (right) identification of **5a** and **5b** as the major products of azaboronate rearrangement of **4a**.

Table 2 Distribution of observed products formed from the decomposition of azaboronate complexes I generated from either **4a** or **4c**, estimated by ^1H NMR and EI-MS

Entry	Starting material	Carbanion	ZnCl_2	Migration	Exchange	Ring expansion
1	4a ($\text{R}^1 = i\text{-Pr}$)	<i>n</i> -BuLi	—	n/a	72–96%	0
2	4a ($\text{R}^1 = i\text{-Pr}$)	LiCH_2Cl	—	0	0	20%
3	4a ($\text{R}^1 = i\text{-Pr}$)	LiCH_2Cl	0.5 equiv.	0	0	58%
4	4a ($\text{R}^1 = i\text{-Pr}$)	LiCH_2Br	0.5 equiv.	0	0	33%
5	4c ($\text{R}^1 = \text{CH}_2\text{Cl}$)	<i>i</i> -PrMgCl	0.5 equiv.	0	0	>99%
6	4c ($\text{R}^1 = \text{CH}_2\text{Cl}$)	<i>n</i> -BuLi	0.5 equiv.	0	0	>99%

1,2-azaborine does not strongly bind ZnCl_2 , but addition of a nucleophile to form azaboronate complex I breaks aromaticity by preventing interaction of the N lone pair with B. This means that the N in complex I is much more Lewis basic than in azaborine **4a**.

We observed a low-energy rotational conformation of $\text{I}\cdot\text{ZnCl}_2$ in which the $\text{Cl-C-B-C}(\text{sp}^2)$ dihedral angle is 179.99° . This orients the internal carbon perfectly for ring-expansion *via* 1,2-metallate migration, which occurs in an antiperiplanar fashion (Fig. 4). The barrier to the subsequent migration is low

($5.4 \text{ kcal mol}^{-1}$). The exocyclic *i*-Pr group is not antiperiplanar (torsion angle = 56.03°) suggesting that migration of the exocyclic substituent is less favorable. Low but observable formation of **5a** and **5b** in the absence of ZnCl_2 could be due to coordination to the lithium counterion in a similar fashion.⁶⁴ While further experimentation and calculations would be necessary to thoroughly compare the possible decomposition pathways of azaboronate complex I, these data support ring-expansion as a kinetically plausible pathway under experimentally-relevant conditions.



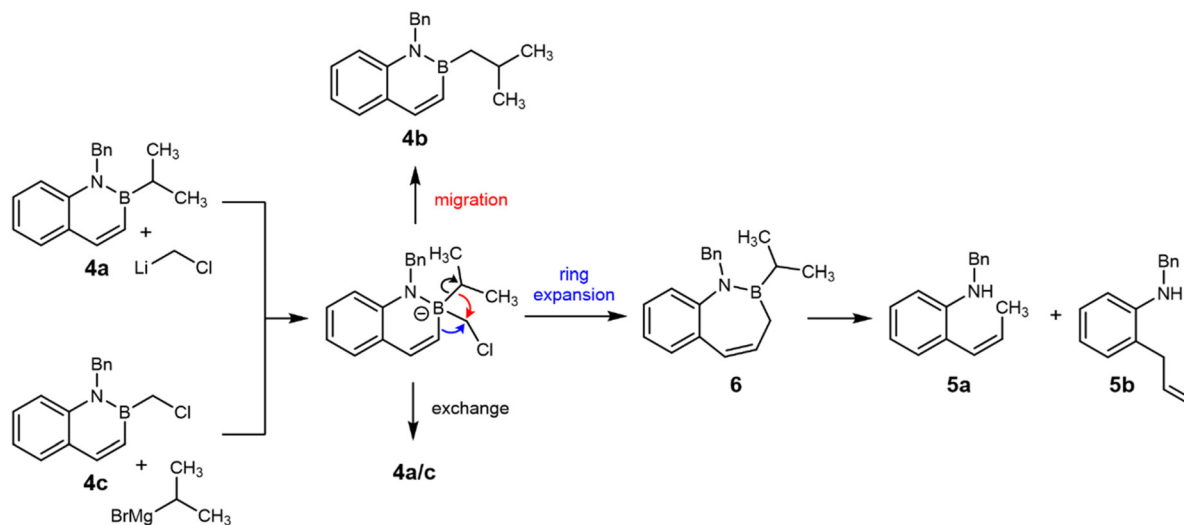


Fig. 3 Overview of the three potential decomposition pathways for azaboronate complex I, formed by reaction of 4a with chloromethyl lithium or 4c with isopropylmagnesium chloride. Ring expansion product 6 is not isolable, but 5a and 5b can be recovered.

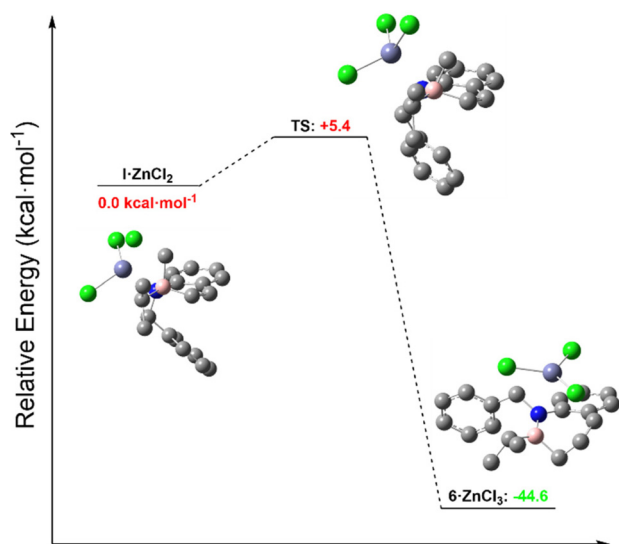


Fig. 4 Calculated relative free energies (ΔG , kcal mol⁻¹) for the ring-expansion migration pathway of I-ZnCl₂ to form 6-ZnCl₃ at the B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP (SMD, THF) level of theory.

Conclusions

Here we describe the observed behavior of alkyl-substituted azaborines towards the formation and decomposition of a tetra-coordinate azaboronate complex *via* addition of a carbon-based nucleophile. We found that the starting azaborine was readily deprotonated upon addition of butyllithium, so an *N*-benzyl variant was synthesized. However, this structure readily underwent nucleophilic addition and exchange with *n*-BuLi, which was not desired but nonetheless demonstrated susceptibility of the boron to nucleophilic addition. Upon

treatment with conditions which generated chloromethyl lithium as the sole nucleophile in solution, we isolated products which indicated that the azaboronate complex was decomposed by an unexpected C(sp²)-migration. This hypothesis was further substantiated by forming the same azaboronate by a different method, which yielded similar results, and by computational analysis which identified a stable conformation of the intermediate which was geometrically aligned to perform the observed ring-expansion.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5ob01286d>.

CCDC 2471064–2471066 contain the supplementary crystallographic data for this paper.^{65a–c}

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