Borylenes

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The Parent Borylene: Betwixt and Between[**]

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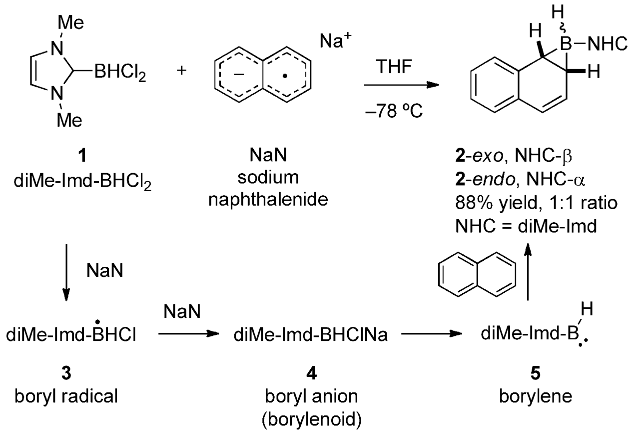
In memory of Daniel Belluš (1938–2011)

N-Heterocyclic carbenes (NHCs) are effective at stabilizing unusual bonding patterns on boron.[1,2] Rare boron-based reactive intermediates including NHC-boryl radicals,[3] boryl anions,[4] and borenium cations[5] have all been generated and directly observed by spectroscopy and sometimes even crystallography. Very recently, evidence for NHC-borylenes has appeared. Bertrand and co-workers just reported a trivalent borylene bearing two carbenes.[6] Isoelectronic with an amine, this fascinating molecule can also be viewed as a borylene–Lewis base complex.

Prior to that, Braunschweig and co-workers reported tantalizing evidence for "Trapping the Elusive Parent Borylene".[7] Specifically, addition of 2 equiv of sodium naphthalenide (NaN) to diMe-Imd-$BHCl_2$ (**1**; diMe-Imd = 1,3-dimethylimidazol-2-ylidene) provided a 1:1 mixture of stereoisomeric boriranes (boracyclopropanes), **2**-*exo* and **2**-*endo*, in 88% yield (Scheme 1). The isolation of these novel, stable boriranes galvanized NHC-borylene research.

The authors concluded that boriranes **2** formed from cycloaddition of parent NHC-borylene **5** and naphthalene. Borylene **5** is isoelectronic with a carbene. Though the boron atom has only six valence electrons, it still has a formal negative charge. This is offset by a formal positive charge on the NHC ring, so **5** is neutral.



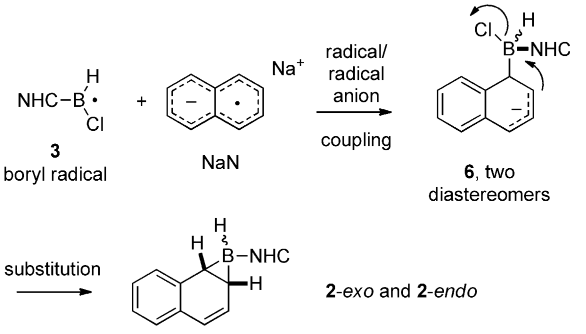
Scheme 1. Formation of novel boriranes (boracyclopropanes) **2** (top) through a suggested borylene mechanism (bottom).

The lower part of Scheme 1 shows a plausible route to this borylene through sequential electron transfer reactions of NaN to provide a boryl radical **3**, then boryl anion **4** (a boron analogue of a carbenoid). These two steps have precedent in NHC-borane chemistry.[1c,4b] α-Elimination of chloride from **4** provides **5**, whose cycloaddition with naphthalene has a low calculated activation barrier ($< 3\ \text{kcal mol}^{-1}$).[7]

Here we suggest a "radical–radical anion coupling" path to **2** that does not involve a borylene intermediate. This mechanism is supported by literature data and by isolation of a coupled product from NaN reduction of a related carbene-borane. We then change the reduction partners to discourage radical–radical anion coupling, and we observe instead products of C–H insertion. We speculate that these products indeed arise from trapping of the elusive parent NHC-borylene.

Braunschweig and co-workers commented in their Supporting Information that naphthalene was the uniquely successful trap for borylene **5**. Various alkenes and alkynes did not trap it, even when used in excess. This contrasts with carbene chemistry, where cyclohexene is a better trap than naphthalene.[8] Extending the B/C analogy, carbenes can be generated by reductions of dihaloalkenes with NaN, but they are further reduced by NaN more rapidly than they add to naphthalene.[8,9] This analysis questions the viability of **5** as an intermediate.

Since borylene **5** was not observed directly, its existence is necessarily a mechanistic conclusion. We suggest that the mechanism shown in Scheme 2 may instead account for the formation of **2**. Here, **1** is again reduced by sodium



Scheme 2. A mechanism based on radical–radical anion coupling also accounts for the formation of **2** and explains why the reagent NaN (not naphthalene) is a unique trap that cannot be outcompeted by added molecules.

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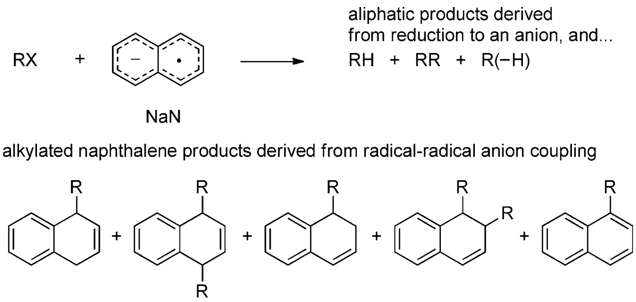
naphthalenide and the resulting boryl radical **3** again reacts with a second equivalent of sodium naphthalenide. However, we suggest that radical–radical anion coupling occurs in this second encounter rather than electron transfer. This provides anion **6**, which undergoes intramolecular substitution to give the products **2**. Recent studies on diverse substitution reactions of NHC-boryl halides and triflates provide precedent for this last step.[10]

The reaction between **3** and sodium naphthalenide is effectively a radical–radical combination whose rate could approach the diffusion-controlled limit. This explains why external traps cannot "outcompete" the reagent for trapping. Radical–molecule reactions cannot compete with radical–radical reactions when one of the radicals (here NaN) is present in high concentration. The negligible barrier of this reaction also accounts for the lack of stereoselectivity in formation of the two diastereomers of **6** and hence **2**.

This mechanism has precedent in the reactions of sodium naphthalenide with alkyl halides summarized in Scheme 3. These reactions have low preparative value because they give complex product mixtures.[11] For example, treatment of alkyl halides with sodium naphthalenide provides aliphatic products of reduction (RH), coupling (RR) and disproportionation (R(-H)) along with assorted naphthalene coupling products.[12] All the aliphatic products are said to arise directly or indirectly from alkylsodium intermediates. The ratio of naphthalene-derived products to aliphatic products increases in order of R−X primary < secondary < tertiary.[12a,13]



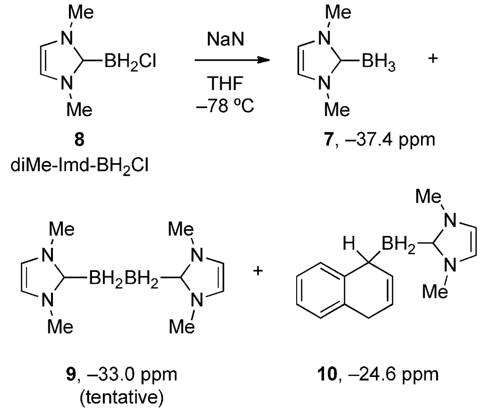
Scheme 3. Reductions of alkyl halides with NaN provide complex mixtures of aliphatic and naphthalene-derived products. (R(−H) is an alkene formed from disproportionation.)

This trend originates from a competition in the reactions of alkyl radicals with sodium naphthalenide between electron transfer (reduction) and radical–radical anion coupling. As the radical $R^{\bullet}$ becomes more difficult to reduce to an anion (primary < secondary < tertiary), the radical–radical anion coupling takes over and the amounts of naphthalene-derived products increase. Tellingly, chemical and electrochemical reduction studies have shown that NHC-boryl radicals are easy to oxidize[5a,14] but difficult to reduce.[4b] So boryl radicals are prime candidates for coupling.

To start, we repeated the experiment to prepare **2**.[7] Looking for minor side products, we recorded an ^{11}B NMR spectrum of the crude product mixture. As expected, the major peaks at −33.2 and −36.9 ppm are from the two diastereomers of **2**.[7] We also observed a small quartet at −37.4 ppm that corresponds to the doubly reduced, protonated product **7** (diMe-Imd-BH_3, <5%) and an intriguing sharp triplet at −24.6 ppm (15%).

The formation of **7** suggested that our reaction medium had traces of a proton source (water?) that was not present in Braunschweig's experiments. This in turn suggested that some diMe-Imd-BH_2Cl (**8**) was formed during our reaction. Could the triplet at −24.6 ppm be due to a coupling product derived from **8** and NaN?

To answer this question, we prepared **8** (see Supporting Information) and reduced it with sodium naphthalenide. The results of two key experiments are shown in Scheme 4. The ^{11}B NMR spectrum of the reaction product resulting from the addition of 2.5 equiv NaN in THF to **8** showed no resonances for **2**. There were three resonances: the sharp triplet at −24.6 ppm (about 25%), the quartet for **7** (about 25%), and in between a new, very broad triplet at −33.0 ppm (about 50%). This last product might be diborane **9**,[15] but it did not survive flash chromatography.



8
diMe-Imd-BH_2Cl

7, −37.4 ppm

9, −33.0 ppm
(tentative)

10, −24.6 ppm

Crude product ratios from ^{11}B NMR spectra

equiv NaN	addition	7	9	10
2.5	normal	25%	50%	25%
7.5	inverse	35%	–	65%[a]

[a] Isolated in 24% yield by flash chromatography

Scheme 4. Reduction of mono-chloroborane **8** gives stable coupled product **10**.

Inverse addition of **8** to excess NaN (7.5 equiv) provided a cleaner crude product; the broad triplet resonance was absent and the sharp triplet resonance predominated over the quartet of diMe-Imd-BH_3 (**7**) (about 65% to 35%). Flash chromatography provided the new product **10** in 24% isolated yield. The initial structure assignment by an HH COSY experiment was confirmed by X-ray crystallography (Figure 1).

We suggest that **10** arises from the coupling of the boryl radical derived from **8** with NaN followed by protonation.[16] Although this radical (diMe-Imd-$BH_2^{\bullet}$) is not the same as the previous radical **3** (diMe-Imd-$BHCl^{\bullet}$), it is similar. So this result provides additional evidence that the radical–radical anion coupling mechanism for formation of **2** is viable.

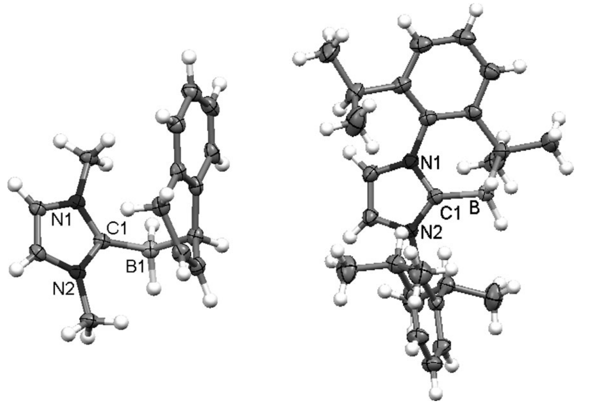
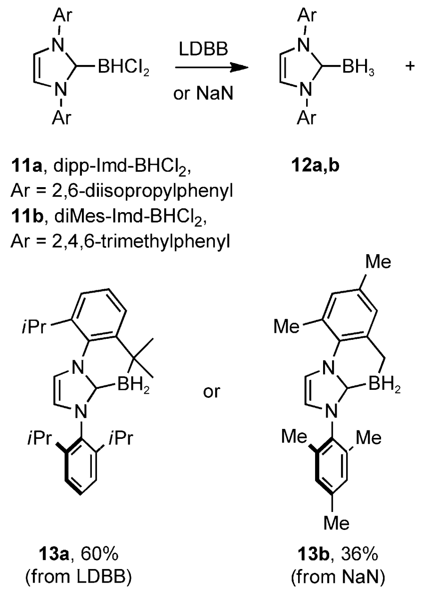


Figure 1. Crystal structures of **10** (left) and **13a** (right).

Preparatively, the problems of arene alkylation shown in Scheme 3 were solved by the introduction of lithium di-*tert*-butylbiphenylide (LDBB).[13] This reagent was designed to block radical–radical anion coupling (every ring carbon has a large substituent either *ipso* or *ortho*). Indeed, we showed that LDBB reduced a boryl radical to a boryllithium reagent by both ^{11}B NMR studies and product analysis.[4b] No radical–radical anion coupling products were observed.

To discourage radical–radical anion coupling, we reduced two more hindered boryl dichlorides **11a,b** with LDBB. The results of two experiments are shown in Scheme 5. Addition of **11a** to LDBB (2.5 equiv, THF, −78 °C) provided a relatively clean crude product containing 18 % of doubly reduced product **12a** and 82 % of a new C–H insertion product **13a**. This insertion product was isolated in 60 % yield by flash chromatography.

Similar addition of **11b** to LDBB provided a product mixture containing resonances for **12b** and **13b** along with other broad resonances (see Supporting Information). A cleaner crude product (40 % **12b** and 60 % **13b**) was formed by adding NaN to **11b**. The new C–H insertion product **13b** was isolated from this reaction in 36 % yield by flash chromatography. The crystal structures of both **13a** (Figure 1) and **13b** (Supporting Information) were solved.



Scheme 5. Reductions of hindered boryl dichlorides provides stable C–H insertion products **13a,b** after flash chromatography.

Robinson and Braunschweig have just described the formation of related C–H insertion products from potassium graphite reductions,[17] so such insertions may be general. If so, then is the formation of C–H insertion products a reliable signature of the borylene? Perhaps, but other mechanisms for insertion must also be considered.[18]

Where does this leave the elusive parent NHC-borylene? Betwixt and between the various product types, apparently. Currently, we hypothesize that products **2** are formed from radical–radical coupling, not cycloaddition of borylene and naphthalene. Likewise, **10** is also formed from coupling. On the other hand, we hypothesize that products **13** are formed by C–H insertion of either a free borylene or another reactive intermediate (borylenoid) with borylene-like reactivity. Methods to test these hypotheses, especially by direct observation of borylenes, are important objectives.

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[15] Compare this value to (dipp-Imd-$BH_2)_2$, $\delta = -31.6$ ppm, and (diMes-Imd-$BH_2)_2$, $\delta = -31.2$ ppm. See reference [1b,c].

[16] Substantial (40 %) deuteration was observed when a ring-deuterated analog of **8** was used; see Supporting Information.

[17] a) See Figure 5 in reference [1a]; b) P. Bissinger, H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kupfer, K. Radacki, K. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 19044 – 19047.

[18] For other possible mechanisms, see: a) the discussion in the Supporting Information; b) reference [17b]; c) A. Prokofjevs, E. Vedejs, *J. Am. Chem. Soc.* **2011**, *133*, 20056 – 20059.