
REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

1. Please rate the importance of the reported results

Reviewer #1: Highly important (top 20%)

Reviewer #2: Highly important (top 20%)

2. Please rate the citation of previous publications

Reviewer #1: Appropriate

Reviewer #2: Insufficient

3. Please rate the length of the manuscript

Reviewer #1: Concise

Reviewer #2: Concise

4. Please rate the verification of hypotheses and conclusions by the presented data

Reviewer #1: Minor inconsistencies

Reviewer #2: Minor inconsistencies

5. Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: (No Response)

6. Please indicate whether you have included attachments

Reviewer #1: No

Reviewer #2: No

COMMENTS TO AUTHOR:

Reviewer 1: Liu, Kong and coworkers report the first adducts of diboriranes, which are structural surrogates of cyclopropanes. The authors report both hydride- and proton-mediated ring-opening reactions, the formal "hydrogenation" of an intraring B-B bond with ammonia borane, and the formation of chalcogenoborirane heterocycles from the addition of S and Se to a diborirane (compound 3). Computational investigations show evidence of bent sigma-bonds throughout the diborirane ring scaffold and ring strain was estimated via isodesmic reactions. Overall, this is an interesting addition to the area of boron chemistry and warrants publication in *Angewandte Chemie* after minor revisions.

* Does compound 4 react with $\text{H}_3\text{N}^*\text{BH}_3$ to yield the same hydride/proton addition product (compound 7) as derived from 3? More specifically, does the formation of 7 from 3 transpire via the formation of the boron hydride 4?

* In the reaction of 3 with chalcogens (Ch), do the authors see NMR evidence for dimeric $[\text{NHC}^*\text{B}(\text{Br})\text{Ch}]_2$ co-products? Related species have been prepared by Braunschweig and coworkers, as documented in ref. 26.

* I am wondering if the ring-opened product 5 can undergo dehydrogenative coupling in the presence of metal catalyst, since acidic C-H and hydridic B-H units are present in 5. Such a reaction would enhance the level of impact of the study considerably.

If the authors repeat the reaction of Li[AID4] with 3, I am wondering if a C-D bond will be formed in the ring-opened analogue of 5? Based on a possible hydride-addition ring-opening mechanism, the formation of 5 could require a proton source to form the C-H linkage (from residual water? NHC ligand activation?).

- * ESI: The chemical suppliers of commercially obtained reagents (e.g. Br3B*SMe2) should be listed as part of the supporting information.
- * Synthesis of 1: How much n-hexane was used to wash the crude product?
- * ESI (and elsewhere): replace "13C" by "13C{1H}"
- * Synthesis of 2, 1H NMR (and elsewhere): list multiplet resonances as ranges; change "5.825" to "5.83" and give J values for all septet resonances.
- * Synthesis of 3: replace "100 %" yield by "quantitative"
- * Synthesis of 4: How much toluene was used to extract the product?
- * Synthesis of 5: How "hot" was the n-hexane used to extract the product and how much of this solvent was used? Please provide specific experimental details related to the formation of compound 5 from 4.
- * Synthesis of 6: replace "ether" by "Et2O"; delete extra ", " before "ArH" in some of the peak listings.
- * NMR spectra: please label residual solvent and vacuum grease on the spectra provided (where applicable).

Reviewer 2: This work reports the synthesis and chemistry of the first diboron analogues of cyclopropane. The results are of great importance and the manuscript is written in a good style. A number of interesting reactions are presented. In principal, I therefore recommend acceptance of this nice work, but there are several points that the authors must address first before a final decision could be made.

- 1) According to the EA, compound 6 is not pure.
- 2) Compounds 3 and 4 are yellow. The authors discuss the frontier orbitals. However, no UV-vis spectra were recorded and discussed.
- 3) For compounds 3 and 4, two isomers are possible. Is only one of them formed in solution and why? Please comment.
- 4) Compound 3 was reacted with an excess of H3N BH3. The authors should

also study reaction between 4 and (less) $\text{H}_3\text{N BH}_3$.

5) Why do the authors not study the chemistry of compound 4 at all?

6) The authors report a protonation experiment, giving compound 6. The first step of this protonation presumably is B-B bond protonation. The authors should repeat the protonation with only one equivalent of acid (maybe a weaker acid such as NH_4^+ is better) to check this.

7) In the introduction, the authors should mention the extensive work on three-membered rings with electron-deficient bonding. (Starting with compound C shown in Figure 1c). See, for example, the following review article: *Angew. Chem. Int. Ed.* 2019, 58, 11600.

In summary, I congratulate the authors to their interesting results. After some revision, the manuscript should certainly become suitable for publication.
