

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: Very important (top 5%)

2. Please rate the citation of previous publications

Reviewer #1: Appropriate

Reviewer #2: Appropriate

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: Fully consistent

Reviewer #2: Fully consistent

5. Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2:

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6. Please indicate whether you have included attachments

Reviewer #1:

- No

Reviewer #2:

- No

COMMENTS TO AUTHOR:

Reviewer 1: The manuscript of Liu, Kong and coworkers presents reactions of aldehydes (and CO₂) with aryliminoboranes, which undergo [4+2] cycloaddition with the BN triple bond and one C=C bond of the aryl substituent, thus deromatizing the latter. They test this reaction on a wide scope of aldehydes, with remarkably high yields. In most cases, the substituent at the aryl group is retained, while in a few cases it is lost. When R = H, the H migrates to the N atom, while with R = tBu, isobutene is lost, leaving an H that also migrates - in both cases rearomatizing the ring. The reaction seems to be quite robust and general, and I am unaware of any like it in main-group chemistry. Furthermore, the work is comprehensive, the compounds are well characterized, the SI is detailed and reliable, and the manuscript is concisely written. Thus, I believe this unique reaction has the novelty required for publication in *Angewandte Chemie*, and apart from a few suggestions, I am in favor of publication.

I have one thematic suggestion: I understand what the authors are saying about the Diels-Alder reaction, but given that the BN unit is isoelectronic with an alkynyl CC unit, wouldn't a better comparison be to the well-known [4+2] cycloaddition of enynes with alkenes? Just like in the current manuscript (e.g. compounds 8 and 9), this reaction subsequently undergoes an H-migration to reestablish aromaticity. This seems to me to be a more logical comparison. For instance, just from a quick google search I found this example, DOI: 10.1016/j.catcom.2020.106117, but there are likely many more. To be clear, I don't think this detracts from the novelty of the manuscript, and maybe the authors don't need to completely change the text, but it might be a good idea to acknowledge these reactions, and also change the descriptions from "Diels-Alder" reactions to "Diels-Alder-like" reactions.

Minor points:

- Fig 1a caption: "Selected dearomative HDA reactions" - no reactions are shown in Fig 1a, only compounds. The figure or the caption should be altered.
- The caption of Fig 5 doesn't really describe the contents of the figure.
- Scheme 1: It would facilitate understanding of the reactions in parts a and b if "- isobutene" or something similar could be added under the arrows.
- SI: There are many doublets in the NMR data of 4n that are missing coupling constants.

Reviewer 2: In the manuscript submitted by the Liu and Kong groups the authors report a very interesting observation of a dearomative [4+2]-cycloaddition that takes place between aldehydes (as 2e component) with "BNCC hetero-diene" as 4e component. Owing to unique polarization of the B-N bond, even highly sterically hindered aryl groups undergo a facile cycloaddition reaction. The authors report that the reaction is concerted, and they provide reasonable kinetic and DFT analysis of the reaction. They also report the scope of the reaction, which tolerates a wide variety of aromatic and heteroaromatic aldehydes. Unfortunately, ketones and aliphatic aldehydes do not seem to be viable reaction partners.

I believe that the present manuscript is an important addition to the field of main group chemistry. Most of the authors' claims are well supported by experimental or computational data. I recommend that the paper be considered for publication with minor revisions, that are listed below.

1. The authors did a good job collecting experimental kinetics of the reaction, however I would have liked to see more interpretation of the data obtained:
 - 1.1. The reaction is concerted, but highly asynchronous (as evidenced from the computed TS geometry). I believe that the authors could analyze the consequences of this asynchronicity in the following aspects:
 - 1.1.1. What is the consequence of B-O bond to be formed first?
 - 1.1.2. Why does the reaction possess high and positive rho value? Could the charge redistribution be corroborated by DFT? I am not understanding the positive value of Hammett rho value in context of a transition state in which the B-O bond formation is advanced.
 - 1.1.3. The entropy of activation was obtained through the Eyring plot but was neither discussed nor compared with the computed value. I think that it may be very valuable to compare the entropy of activation with other Diels-Alder reactions, if possible.
 2. Diastereoselectivity of the reaction is not explained. The difference between

exo and endo transition states have not been analyzed computationally.

3. The authors provide compelling evidence that their reaction is concerted, but the scheme 1 shows two examples of species 5 and 6 that one would consider very different from the iminoboranes 1, and possibly going through alternative mechanisms. An explanation or, preferably, calculation is requested.

4. High resolution mass spectra provided in the SI feature no visible natural abundance isotopic distribution, which would be visible to the naked eye given large fraction of carbon and boron isotopes in the molecules. Please, explain and revise.

Minor comments:

5. I believe that the orbital depiction on Figure 2c is too shiny and nearly impossible to analyze. Please, provide more classical renderings in which it is possible to see the phases of the wavefunction.

6. I believe that the SI should feature full reaction schemes and structures of the products.

7. Typos and language inconsistencies found:

7.1. "Wildly used approaches" (page 1 line 41)

7.2. "... as analogous reactions with ... were inert" (page 3 line 56). (The reactions cannot be inert, only the reagents can.)

8. Please, explain what is the mysterious IPr₂Me₂ reagent (page S2)