

## REVIEWER REPORT(S):

Referee: 1

Recommendation: Encourage transfer to another [RSC journal](https://pubs.rsc.org/en/Journals/). Please suggest a suitable journal in the box below.

### Comments:

This manuscript by Kong and coworkers describes the synthesis and reactivity of a cationic terminal iminoborane with a formula of  $[\text{Mes}^*-\text{N}\equiv\text{B}\leftarrow\text{NHC}][\text{AlBr}_4]$  ( $3^+$ ), where the  $\text{Mes}^*$  and NHC groups are sterically bulky 2,4,6-tri-tert-butyl phenyl and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene. The synthesis of the salt of  $3^+$  was successfully done by the halide abstraction of  $\text{Mes}^*-\text{N}=\text{B}(\text{Br})\leftarrow\text{NHC}$  (compound 2) with  $\text{AlBr}_3$ . The molecular structure of  $3^+$  is closely related to the previously reported cationic iminoborane  $[\text{Me}_3\text{Si}-\text{N}\equiv\text{B}\leftarrow\text{CAAC}]$  (ref. 11, compound VII in Figure 1c). The authors conducted a thorough investigation on the chemical reactivity of  $3^+$  with various reagents, where  $3^+$  displayed a typical reactivity of a highly polarized B–N multiple bond species and undergoes complexation with Lewis bases at boron, 1,2-addition, or cyclization with 1,3-dipoles to form a five-membered ring.

My opinion on this work here for Chemical Science is mixed. This is a nice synthesis albeit a reasonable extension from prior works. However, in addition to the analogy of  $3^+$  with the previously reported iminoborane-CAAC adduct, chemical reactions of  $3^+$  can be rationalized on the basis of the accumulated knowledge of iminoborane and related chemical species. It seems to me that there is not enough demonstration of novelty and usefulness for this paper to warrant publication in Chemical Science. I think this paper would be most appropriate for Eur. J. Inorg. Chem., Dalton Trans. or Inorg. Chem.

### Specific comments:

- 1) I think that the authors should describe more about the chemistry of neutral iminoborane and highlight what can be expected for its cationic counterparts in the introductory part.
- 2) An important example (Lin and Branschweig et al., JACS 2020, 142, 1065) related to the formation of compound 11 is missing in the reference.
- 3) Supporting Figures: In the caption of all NMR spectra, add the deuterated solvent used for the measurement.
- 4) Fig. S15: In  $\text{CH}_2\text{Cl}_2$ , absorption profile below 250 nm is not reliable since the spectrum should be saturated in most cases.
- 5) Some of the intensity of  $^{11}\text{B}$  signals are too weak to be convinced that there is a single pure product, there seems to be other peaks. E.g., Figs. S30, S35, S51.
- 6) As for the formation of intramolecularly cyclized product  $7^+$ , it is worth to mention the ability of a neutral three-coordinate borane to cause intramolecular

C-H activation (Knochel et al., JACS 1999, 121, 6940.)

Additional Questions:

Are the conclusions drawn in this manuscript scientifically sound? Please provide details to support your reasoning in the comments below.: Yes

It is the responsibility of authors to provide fully convincing evidence for the homogeneity, purity and identity of all compounds they claim as new. Is adequate supporting information provided to support the claims made in this manuscript?: No

What level of significance or novelty does the work have in its field?: Average (top 25– 50%)

As Chemical Science is a multidisciplinary journal a high level of wider interest is expected. What level of wider interest does the work have in the chemical sciences?: Average (top 25– 50%)

Based on the above criteria how would you rate the current version of this manuscript? (1 = poor; 10 = outstanding; only articles rated 9 or 10 are suitable for Chemical Science). If you feel that the score could change after revision please indicate in your comments below.: 7

Do the references contain appropriate and balanced citations?: Yes

Referee: 2

Recommendation: May be suitable for Chemical Science after revisions

Comments:

The manuscript by Kong and co-workers describes some intriguing chemistry of NHC-stabilised iminoborane 3+, which has been fully characterised including X-ray crystallographic analysis. DFT calculations indicate the triple bonding character of the B-N bond in 3+ and these can also be reflected by its reactivity. Lewis base coordination at boron, 1,2-addition reaction, and cycloaddition reaction were observed and corresponding products were also isolated.

Authors presented a nice piece of main group chemistry and thus this manuscript is worth to publish in Chemical Science after following points are addressed.

(i) A little more comparison to the similar system by Bertrand (compound VII) should be undertaken (structural features, reactivity, etc.) in order to clarify

the electronic effects of NHC and CAAC.

(ii) The bond length of 3+ can also be compared with neutral complexes (2 and 4).

(iii) does compound 3+ react with H<sub>2</sub>?

(iv) In the reaction with PMe<sub>3</sub> (Scheme 2), the reversible coordination was observed. To estimate and compare the binding energy (or BDE) of the NHC→B vs Me<sub>3</sub>P→B in complex 6+ would be interesting. This may bring the idea why NHC stays at B atom whereas Me<sub>3</sub>P shows dissociation and association.

(v) In the reaction with TMSCHN<sub>2</sub> (Scheme 4), TMS group is migrated from carbon atom to nitrogen atom. How this migration be rationalized? The intermediate (non-migrated product) could be observed?

Additional Questions:

Are the conclusions drawn in this manuscript scientifically sound? Please provide details to support your reasoning in the comments below.: Yes

It is the responsibility of authors to provide fully convincing evidence for the homogeneity, purity and identity of all compounds they claim as new. Is adequate supporting information provided to support the claims made in this manuscript?: Yes

What level of significance or novelty does the work have in its field?: High (top 10–25%)

As Chemical Science is a multidisciplinary journal a high level of wider interest is expected. What level of wider interest does the work have in the chemical sciences?: High (top 10–25%)

Based on the above criteria how would you rate the current version of this manuscript? (1 = poor; 10 = outstanding; only articles rated 9 or 10 are suitable for Chemical Science). If you feel that the score could change after revision please indicate in your comments below.: 9

Do the references contain appropriate and balanced citations?: Yes

Referee: 3

Recommendation: Accept

Comments:

The authors describe the synthesis and characterization of a rare (if not the only) two-coordinate boron cation incorporating B-N multiple bond and stabilized by carbene. These species are shown to Lewis acidic and undergo 1,2 and 2+3 addition reactions. The work is well characterized and thoroughly described. I believe this work will be of general interest and is suitable for publication in Chem Sci following attention to the minor points below.

1. The authors might consider coordination of the Et<sub>3</sub>PO to the cation so as to provide a comparison with literature data using the Gutman-Beckett test of Lewis acidity.
2. Similarly the authors could consider computing the fluorophilicity or GEI as a measure of Lewis acidity.

Overall an excellent paper.

Additional Questions:

Are the conclusions drawn in this manuscript scientifically sound? Please provide details to support your reasoning in the comments below.: Yes

It is the responsibility of authors to provide fully convincing evidence for the homogeneity, purity and identity of all compounds they claim as new. Is adequate supporting information provided to support the claims made in this manuscript?: Yes

What level of significance or novelty does the work have in its field?: Outstanding (top 10%)

As Chemical Science is a multidisciplinary journal a high level of wider interest is expected. What level of wider interest does the work have in the chemical sciences?: High (top 10–25%)

Based on the above criteria how would you rate the current version of this manuscript? (1 = poor; 10 = outstanding; only articles rated 9 or 10 are suitable for Chemical Science). If you feel that the score could change after revision please indicate in your comments below.: 9

Do the references contain appropriate and balanced citations?: Yes