

REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

Please rate the importance compared to published work in this subject area

Reviewer #1: High (Top 20%)

Reviewer #2: High (Top 20%)

Reviewer #3: Outstanding (Top 5%)

Please rate the novelty compared to published work in this subject area

Reviewer #1: High (Top 20%)

Reviewer #2: High (Top 20%)

Reviewer #3: Outstanding (Top 5%)

Which aspects of scholarly presentation require improvement (if any)?

Reviewer #1:

References

Reviewer #2: (No Response)

Reviewer #3: (No Response)

Do the methods, data and analysis (including statistical analysis where applicable) adequately test the hypothesis and support the conclusions?

Reviewer #1: Mostly

Reviewer #2: (No Response)

Reviewer #3: (No Response)

Are the methods, data and analysis described in sufficient detail to be reproduced?

Reviewer #1: Yes

Reviewer #2: None

Reviewer #3: None

Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: (No Response)

Reviewer #3: (No Response)

Please indicate whether you have included attachments

Reviewer #1:

No

Reviewer #2:

No

Reviewer #3:

No

COMMENTS TO AUTHOR:

Reviewer 1: The manuscript of Su, Kong and coworkers presents an interesting constrained geometry complex consisting of a pincer PNP backbone with boron as the central atom. The authors describe the complexes as "T-shaped", and with P-B-P angles in the range 141-146°, this is more or less true. The authors prepare firstly the dicationic species, then, by sequential reduction, the radical monocation, then the neutral species. They show through reactivity studies that the dication is a Lewis superacid, while the neutral species is a Lewis superbases. Thus, the study presents a discrete series of constrained boron species in three different oxidation states and overall charges, and contrasts the reactivity of the two extremes through extensive tests, along with a number of physicochemical tests and DFT calculations. Such extensive studies on reactive boron species are rare, making this an impressive accomplishment and one worthy of publication in *Angewandte Chemie*. The system itself is

also intriguing given the unusual geometry at boron in all three oxidation states, and will no doubt inspire the synthesis of other pincer complexes of boron in the future. I have only a few minor comments for the authors to address.

- One problem I see is that the species 2 is definitively a borylene species, yet the literature for borylene compounds is missing. Bertrand has published at least one review on the topic, and there are many other relevant citations to be added.

- The radical cation is described in detail, however, does it undergo any reactions? Some reactivity of this species would be interesting to see.

- There seems to be a problem with the 6th name in ref 2.

- Fig 3b: "Friedle" should be "Friedel"

- p1: is it Schewesinger or Schwesinger?

- p2: "under heating conditions" - what temperature?

Reviewer 2: Kong et al presented the synthesis of the geometrically constrained boron dication. The stepwise reduction afforded the corresponding boron radical cation and borylene species. The boron dication and borylene have been demonstrated, through both theoretical and experimental assessments, to be Lewis superacid and organic superbases, respectively. The synthesis of tricoordinate boron dications is a challenging task, and the existence of geometrically constrained tricoordinate boron dication as Lewis superacid has rarely been reported thus far. Hence, the results shown in this paper should be of broad interest and I wish to recommend the manuscript for publication in *Angewandte Chemie*.

Some minor points to be addressed prior to publication:

1) The Cp*-substituted boron dication should be cited and calculated for comparison (*Inorg. Chem.* 2016, 55, 12427). A recent cationic boron LSA (*Chem. Eur. J.* 2023, e202301270) should be included in ref 5.

2)- Does [2]²⁺ catalyze the deoxygenation of ketones in the presence of a silane?

3)- The gas-phase proton affinity and basicity as well as the pK value of (CAAC)(iPr)B(CN) could be computed and included in Table 2.

4) TD-DFT calculations of [2]^{*+} and 2 could be performed to explain the UV-vis absorption spectra.

5) The steric properties of [2]²⁺ and 2 should be studied using SambVca 2.1 routine.

Reviewer 3: This article deals with geometrically-constrained boron compounds. Using a PNP pincer ligand, original T-shaped boron derivatives have been prepared, from the dicationic form to the corresponding radical cation, and the neutral borylene structure. All new

compounds have been fully characterized. Their structure, properties and reactivity have been carefully analyzed by experimental and computational means.

Accordingly, the dicationic compound proved to be a Lewis superacid and its synthetic potential in Lewis acid catalysis has been demonstrated in 4 different transformations.

The respective radical cation displays very high spin density at boron, about 80%, and boron-centered radical reactivity has been substantiated with tributyltin hydride.

The 2e-reduced structure, namely the neutral borylene form, turned to be a superbases and to exhibit nucleophilicity at boron.

This is a very original and significant work. It nicely completes and extends the related chemistry reported recently in JACS about a geometrically-constrained bis-silylene stabilized borylene (SiCSi pincer ligand). Here, the PNP ligand is shown to not only impart geometric constraints and to enhance acidity / basicity, but also to bring stability to three different redox/charge states. For me, it makes no doubt this contribution represents a major achievement and will interest a broad audience. I very enthusiastically recommend its publication in Angew Chem and have only a few minor modifications to suggest:

- The impact of the PNP pincer ligand and geometric constraints should be systematically analysed and commented. Nothing is said on this matter for the radical cation, and it seems the impact is less for the neutral borylene than for the dicationic form.
- To help the reader, the structure of O-CBA should be given in Figure 1b.
- Page 2, right column, 1st line: typo NTf2(-)
- Page 4, left column, line 11: typo boronium
- Page 5, right column, line 6: typo protonation
- Ref 10: the ACIE version is given twice