
Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish in JACS after minor revisions.

Comments:
The authors present the synthesis of a deprotonated derivative of an aryliminoborane. Although many research groups have been investigating BN-chemistry in general for decades, an anionic derivative of the here presented iminoborane [Ar-BN]– is, to the best of my knowledge, unknown. The presented synthesis is straightforward, and the chemistry of the nucleophile shown in the paper should be of interest to the broad community of people working in the field of BN molecules and materials.
To this referee data of elemental analysis of the new compounds should be presented. Furthermore, NMR spectra of compound 4 were recorded in the solid state. The 119Sn solid state NMR should be presented. A solvent which could be used in the case of compound 4 is 1,2-difluorobenzene.
Otherwise this nice chemistry should bepresented to the broad readership of JACS .

Additional Questions:
Significance: High (suitable for JACS)

Novelty: Highest (top 5%, suitable for JACS)

Broad interest: Highest (top 5%, suitable for JACS)

Scholarly presentation: High (suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes

Reviewer: 2

Recommendation: Publish in JACS after minor revisions.

Comments:
The communication from Guo et al. is, from my point of view, an important piece of work. As aptly described by the authors, the the isosteric nature

of the BN unit has the potential to imbue a range of new materials with novel properties, and therefore may be useful to a wide range of researchers should it become more generally employable. This communication is a step in this direction. At the current time, many in the wider community might find this work to be a clever bit of synthesis of interest in the main group community, but this is taking the short view.

The paper followed a tried-and-true organization, which is effective. The computational work, from a non-expert's point of view, is sufficient and compelling, though if you're already doing DFT on these novel molecules, GIAO predictions of 11B NMR shifts are simple to carry out and are a useful confirmation of obeerverables. The handful of reactions demonstrated by the authors is a good starting point for further work. There are a few points that I would be remiss if I did not point out.

1) A minor editorial point: The manuscript periodically suffers from disagreements in number (singular vs. plural). For example, in the first sentence, "reactivity" should be reactivities. In the last sentence of the first paragraph "synthesis" should be syntheses. I would urge the authors or the editorial staff to comb through for such errors. They do not affect the quality of the paper in a real way, but should be fixed if possible!

2) In the paragraph straddling the columns on page 2, a citation is needed for the B-N bond lengths of the other "B-aryl iminoboranes" that are not A and B. These should include the Paetzold and Braunschweig non-metallic compounds.

3) In the second full paragraph of page 2 the discussion of the IR frequencies of the compounds should be expanded somewhat. This is a particularly useful value for these types of compounds, and will only become more important if these authors' hopes are realized and the compound leads to this unit's inclusion in more varied environments. How does this value change in compared to non-ionic compounds? How does it change compared to
compound 4? There is just a bit of discussion that may be useful.

3) The authors should address the idea that this particular structure is stabilized by pi-Li interactions stemming from the large aryl protecting groups. This kind of interaction is not unknown and may be of particular importance in this instance. The DFT work already carried out on the compounds should enable speedy analysis of these.

4) In the discussion of the thermal breakdown of the compound (end of page 2) no 11B NMR is reported. The relevant proton spectra are given. Perhaps

this is because the 11B is not observed to change, but this should be noted. These large unsaturated boron structures are frequently thought to degrade by bond-activations at boron, which would lead to a less unsaturated boron atom observable by 11B nmr, especially if the hybridization is increasing.

5) The concerted transition state for the formation of 9 (Fig s52) has an energy I tend to think of as unattainable at room temperature. I wonder if there isn't a multi-step sequence that fits more appropriately. This would seem more realistic.

Additional Questions:
Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: Moderate (not suitable for JACS)

Scholarly presentation: High (suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: In Part

Reviewer: 3

Recommendation: Publish in JACS after minor revisions.

Comments:
This was an exceptional manuscript detailing the first synthesis of an boraiminolithium reagent, a BN isotere of the well-known alkynyl lithium reagents. Given the growing interest in incorporating p-block elements (especially B and N) into organic molecules, this manuscript is very timely. What is beautiful about this work is the simplicity that the authors have found to generate the desired compound, e.g. simple dehydrohalogenation/deprotonation. What further strengthens this manuscript is the several examples of reactivity that the authors have already revealed for this new species. I can't wait to see what the authors come up with next.

I enthusiastically recommend publication in JACS.

Additional Questions:
Significance: Highest (top 5%, suitable for JACS)

Novelty: Highest (top 5%, suitable for JACS)

Broad interest: High (suitable for JACS)

Scholarly presentation:

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes

Reviewer: 4

Recommendation: Publish in JACS after minor revisions.

Comments:
The authors present a BN analogue to lithium acetylides. The polarized B≡N triple bond with an anionic N center and the reactivity related to a new BN containing building block is discussed.

The analytical data presented are fit and sufficient for all assumptions.
The IBO analysis is consistent with a triple bond between boron and nitrogen, while the NBO and Wiberg bond analyses indicate a double bond. A comparison between the different results and a detailed discussion should be added.
The crystal structure of 7 shows a significant angle between the nitrogen-boron and nitrogen-silicon bonds, which should be mentioned and discussed.

The authors present a nice example of an isoelectronic relationship for a potential important compound class.

Additional Questions:
Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: High (suitable for JACS)

Scholarly presentation: High (suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes
