

The first round:

REVIEWER REPORT(S):

Referee: 1

Recommendation: Revisions required

Comments:

This is an interesting paper that describes the 1,3 additions of arene and CO₂ fragments across BNN fragments. The compounds are well characterized and the chemistry is discussed in the light of computations. The work is well done. This work extends 1,3 dipolar additions to BNN fragments. This is a significant advance and should be published following attention to the points below.

1. The first sentence of the introduction should be deleted.
2. Noticeably absent from the discussion of BNN linkages are the recent works of Stephan et al. (Angew. Chem. Int. Ed. 2017, 56, 16588, , Angew. Chem. Int. Ed. 2019, 58, 18487, Dalton Trans. 2020, 49, 901).
3. The analogy between the intermediate IN3 and the compounds reported by Braunschweig in Science begs the question can the present chemistry be reproduced by reduction under N₂.
4. It is also noteworthy that 1,3. additions across boron azides have been described (Dalton Trans. 2015, 44, 5045).
5. pg 3 "co-workers" and "moeity"
6. p4 "propargyl-type form weight of 16.5% and allenyl-type form weight of 66.1%." are the sig. figs to 0.1% meaningful?

Additional Questions:

How would you rate this article?: Very significant (top 10% - suitable for publication in Chemical Science)

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

Do the references contain appropriate and balanced citations?: No

What contribution does this article make to the subject area it addresses? (1 = poor; 10 = outstanding; only articles rated 9 or 10 are suitable for Chemical Science, articles rated 8 or lower suggest the work is unsuitable for Chemical Science): 9

Referee: 2

Recommendation: Revisions required

Comments:

The authors report on very exciting novel iminoborane derivatives where the substituent at the nitrogen atom is an amine group. This substitution pattern has never been as convincingly demonstrated as in this contribution. The isolation of iminoboranes is already limited to very sterically crowded derivatives, and the addition of an N-N bond to the molecule makes things even more challenging, as can be seen by its very unusual (if not unique) reactivity involving dearomatization addition to a pendent aryl ring. The article is well written except for some minor points listed below. The article will be of high interest to the Main-group community, especially so to boron chemists. Because of the extremely unusual reactivity of the novel iminoboranes, yielding dearomatization addition products, and because of the strong (isosteric) analogy between iminoboranes and alkynes, the article would be highly relevant across the subfields of chemistry.

The literature is properly cited (although a very relevant paper for discussion has been left out : K. Bode, U. Klingebiel, M. Noltemeyer, H. Witte-Abel, Z. Anorg. Allg. Chem. 1995, 621, 500-505. A noteworthy and slightly related dearomatization reaction was also mentioned in D. Prieschl, G. Belanger-Chabot, X. Guo, M. Dietz, M. Muller, I. Krummenacher, Z. Lin, H. Braunschweig, J. Am. Chem. Soc. 2020, 142, 1065-1076.)

The experimental work seems to have been, in general, competently performed (see however the minor points below).

My main issue with the results is the disappointing amount of transparency involved in the reporting of the structural data, which is one of the pillars of demonstrating the existence of the exciting compounds reported here. The SI contains very generic statements on the restraints used and does not allow to trace back the steps used to get to the model reported in the main article (which is one of the purposes of the SI). A closer look into the cifs reveals that not much more effort was done there to add critical details on the use of SQUEEZE, for example. Without looking at the cifs, the reader would never know that that the structure of 7 is heavily disordered, for example. This allows more weight to be given to the structural data than there should be. In general, the following needs to be addressed:

-the data_ field in the cif submitted to the database should bear a more useful name than a compound number, which is only appropriate for the cifs in the supporting information of the article. Check a few issues listed in the checkcif (wavelength is given as .71000). The wavelength used for each structure should also be indicated in the tables or in the paragraph on crystallographic details.

Specific issues:

Data_1

Several indications of data quality problems are noticeable: large second weight parameter, somewhat misshapen ellipsoids (which was cosmetically fixed by applying a very strong ISOR restraint, which is not very appropriate in the absence of a disorder model, but rather serves the purpose of hiding underlying problems with the model and/or data), large number of omitted

reflections, large positive and negative difference peaks (one of those located near a nitrogen atom).

Although the N-H proton should be “freely” refined, the distance should be restrained to a sensible value.

As it stands now, the model needs either many excuses and qualifiers in order to be used as proof or is otherwise not at all usable.

Data_2

Consider “freely” refining the N-H with restrained N-H distances.

Data_3

The residual density is quite high because a disordered phenyl ring was cosmetically hidden by the use of a strong simu restraint without modeling the disorder (again a misuse of the restraint).

Data_4

Check number of reported hydrogen atoms (triggers an alert in checkcif).

Data_5

SQUEEZE was used but there is no mention of it anywhere. There needs to be, in the cif file, an explanation of the void volume and the electrons “found” in that volume.

It is preferable to submit a non-squeezed version where the disordered moiety is tentatively refined to convince the reader that the SQUEEZE is warranted and does not affect the chemistry of the model. When details on SQUEEZE are properly included in the cif file, the errors associated to solvent accessible voids should disappear from the checkcif. Disorders should be discussed in the SI, especially the rather peculiar wagging motion of the B-Br bond... The disordered t-butyl groups were not refined as disorders but as half-occupancy orientations. This is rather non-standard and leads to poor display when viewing the molecule.

The various problems with this structure, if mentioned in the SI and properly justified, would likely not affect the use of the structure as qualitative proof for the existence of the compound.

Data_6

Again, disorders refined as partial occupancy fragments and not refined as two-part disorders. Twin refinement performed but not mentioned in SI. The negative BASF parameter doesn't make much sense. Depending on how this is handled, the data could be unusable.

Data_7

The molecule is fully disordered over two conformations about an inversion center. The use of part -1 instruction would have been appropriate here, otherwise tools like the mercury software display a confusing partial superimposed disorder model with the main molecule. The heavy disorder should be mentioned in the SI to qualify the reliability of the model (which is heavily restrained).

Although I find these problems aggravating, I do believe that, with proper discussions and revisions, the structural data will support the claims of the paper. If these rather serious issues and those less serious ones listed below are properly addressed, I will enthusiastically recommend this contribution for publication in this journal.

Additional minor points that need fixing:

-A sentence from the template found its way in the article :
"The main text of the article should appear here with headings as appropriate."

-In Fig. 1 a) there is a somewhat out-of-place "etc"

- I don't like the word "achieved" for a compound, as in "a compound was achieved".

- "Multiple resonance" A multiplet?

"is endergonic by

11.8 kcal mol⁻¹, the precipitation of [ItBuH][Br] over the course of the reaction provides driving force for this conversion." I don't like the use of "driving force" for an equilibrium shift.

- I would like that the byproducts of the "HBr" elimination reactions (carbene-HBr, I presume) be drawn in the reaction schemes. Same goes for TMSBr (because at first glance one could expect HBr and its salts with the hydrazine starting material.) As things are now, one must read quite a bit of text before one knows for sure what is going on in the reactions.

- "The

absence of ItBu is spontaneously destructive to the tetracyclic framework leading to the base-free 1,2-

diboraneylidenehydrazine DppB=N=N=BDpp upon an

unrestricted geometry optimization." : This is an important observation. Would you care to provide a rationale for this behavior?

- "In the absence of either the C24-C25 or

B2-C19 linkage, re-aromatization is favourable via a [3 + 2]

cyclo-reversion with an activation barrier of less than 27 kcal

mol⁻¹." : It is not clear what is meant here. A scheme illustrating the compounds "without the linkages" from which the value of 27 kcal/mol was obtained would need to be in the SI.

- "forging bonds" is a bit of a strong metaphor for a scientific publication.

- Typo : 1,3,2,5-diazadiborinine

- "Mixing a 1:3 molar ratio" A bit too colloquial

- "in which species 6 was

isolated in 31% yield after work-up" : from which

- "significantly short B1-N1 bond" : "significantly short" doesn't work. What do you mean?

- "mode results from" : vibrational modes don't result from frequencies. Please rephrase.

-typo : "Comparision"

- "electronic property of 6 was " : properties were

- "two abnormally low energy frequencies" : abnormally low for what? For that type of compounds? There are a lot of deformation and bending modes around 500 cm⁻¹, so it is not clear what is meant here. What would be "normally low" in your opinion?

-“and such facile bending is essential to the high cycloaddition reactivity” : depending on how the preceding point is addressed, this point might not be relevant anymore.

SI

-“¹³C NMR data was not obtained because of its limited solubility in C₆D₆, C₆D₅CD₃ and THF-D₈ and instability in CD₃CN, CD₂Cl₂, and CDCl₃ “ : “its” -> whose (rephrase)? What kind of instability? Also, are you sure that the ¹H spectrum is indicative of the bulk of the material?

- In Figure S3, phasing will change the shift significantly and it seems off in that spectrum (check phasing throughout).
- Fig S12: The middle signal is significant. Can you comment on what it is? At any rate it suggests that the isolated compound is severely contaminated.

-S21: borosilicate peak picked?

Additional Questions:

How would you rate this article?: Very significant (top 10% - suitable for publication in Chemical Science)

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Do the references contain appropriate and balanced citations?: Yes

What contribution does this article make to the subject area it addresses? (1 = poor; 10 = outstanding; only articles rated 9 or 10 are suitable for Chemical Science, articles rated 8 or lower suggest the work is unsuitable for Chemical Science): 10

Referee: 3

Recommendation: Revisions required

Comments:

The manuscript by Kong and co-workers reported the synthesis of ArBNNB(NHC)Ar and the intramolecular cycloaddition with Ar. Although iminoboranes have been studied for a long time, the compounds described in this work are novel in that two BN fragments are conjugated, leading to unusual reactivity. The authors also isolated the BNNB compound with a more bulky

terphenyl substituent and found that it reacted with CO₂, leading to double cycloaddition. DFT calculations strongly support the proposed cycloaddition pathway. Overall the work is interesting and novel, this reviewer recommend to publish the work with some modifications listed below:

(1) the resonance structures in Fig 6 should be carefully analyzed. Inspection of the electronic structure of 6, the N₂ atom appeared to be very nucleophilic. In this case, the charge from the NHC should also be included in the resonance forms. The charge distributions in the BNNB should be rechecked. The title "BNN 1,3-dipole" may not be proper and should not be emphasized since it may not represent the central discovery in this work.

(2) the mechanism for the cycloaddition could be nucleophilic addition via the N₂ atom (Fig 4), thus the use of very electron deficient benzene derivatives may lead to intermolecular cycloaddition?

(3) what would happen if the reactions in schemes 1 and 2 employed pyridines instead of NHC?

(4) For compound 6, X-ray single crystal analysis and calculations should have information on the interactions of two BN fragments, these should be discussed and emphasized in the text. The unique reactivity is due to the interactions.

Additional Questions:

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Referee: 4

Recommendation: Revisions required

Comments:

It was a pleasure to receive this paper to review. In this contribution, the author disclose the preparation and reactivity of an isolable ArBNNB(NHC)Ar compound. In comparison with azines, azo compounds, etc., the chemistry of 'dinitrogen' boron compounds is unfortunately underdeveloped, notably because of the lack of reliable methods to prepare such complexes.

In this work, using the reaction between a bis-trimethylsilylhydrazine, a variety of dibromoboranes ArBBr₂ and a NHC, Kong, Ke and coworkers access ArBNNB(NHC)Ar compounds. Three examples of such compounds are presented. To the best of my knowledge,

such a BNNB motif in which one of the boron atom is only dicoordinated is unprecedented and, as expected, it is highly reactive.

Interestingly, the ArBNNB(NHC)Ar is stable and isolable if Ar = 2,4,6-tritertbutyl-phenyl, which will allow its reactivity to be studied. The authors already show its reaction with CO₂, through which it readily forms bicyclic a compound. I am convinced that this compound and its derivatives will display a rich reactivity in the future. Have the authors already exposed compound 6 to alkynes?

Because of the high reactivity of the ArBNNB motif, if the Ar group is instead a terphenyl group (2,6-diphenyl-phenyl or 2,6-dimesityl-phenyl), an intramolecular [3+2] cycloaddition takes place in which a RBNN fragment acts as a 1,3-dipole and adds across a C=C bond of one of the side aryl groups of the the terphenyl group.

These new boron compounds are novel and well-characterized and I thus recommend publication in Chemical Science, with the following revisions:

- the first sentence of the article is a leftover from the template and should be removed.
- in Fig. 1, the use of two-ways arrows to denote an isoelectronic analogy is easily confused with resonance arrows. Another notation would be preferable. Furthermore, the BNN and the nitrile ylide are not isoelectronic because of the bonding pattern at the Ar(NHC)B=N- nitrogen atom.
- p1, last sentence of the first paragraph: 'prohibitively harsh conditions' should probably be changed to the more neutral, precise and scientific 'flash vacuum pyrolysis conditions'.
- the authors should find a more concise term than diborane-ylidenehydrazine for their class of compounds, probably in analogy with organic chemistry. In any case, the current term should be spelled with one fewer 'e': diboranylidenehydrazine.
- since the authors describe the solid-state structure of 2 in such details, they should include it in a figure.
- the B2-N2 bond length in 6 is not given correctly (it does not appear to be 1.365) in the SI data.
- according to the mechanistic studies, the fact that no retro-cycloaddition (cycloreversion) is observed is ascribed to the high energy barrier (kinetics). However, while it is true that the energy barrier is too high to expect a cycloreversion to occur, the authors would in any case not observe it by heating at 70 °C because of thermodynamic considerations (the cycloaddition is strongly exergonic). Arguing purely from kinetics thus seems superfluous. They take the exact same argument (kinetics of the reverse reaction) to explain why no intermolecular cycloaddition could be observed with benzene or toluene, suggesting that the reaction is easily reversible. Their data, however, clearly demonstrates that the intermolecular reaction is 1) strongly endergonic (non-spontaneous) and 2) kinetically inaccessible with barriers of 34-40 kcal.mol⁻¹. There is thus no ground to hint at a reversible reaction in this case and the whole picture should be shown in the text.
- Considering that the reaction is purely intramolecular and that the authors' data show the impossibility of it being intermolecular, the arene in Fig. 1 and the TOC graphic should be connected to the boron atom with a solid and (not dashed) linker.

In the SI, the NMR spectra should be labelled in full with the conditions stated in the caption. The products are well-characterized (NMR, XRD, HRMS), but for some of them, the level of purity in the isolated product is below the standards I would expect for a top journal like Chemical Science. For example:

- compound 1 shows a large resonance at 2.1 in the ^1H NMR. What does that correspond to?
- compound 3 shows an important broad signal in the ^{11}B NMR at around 30 and a smaller one around 0 ppm. What do these peaks correspond to?
- in the ^1H spectrum of compound 4, I find a large unassigned signal at around 1.2.

The baseline of the ^{11}B NMR spectra look different from one spectrum to the next, with the glass signal being sometimes shifted. Have the spectra been processed similarly?

Finally, more as a matter of opinion, I question the fact that the paper is constructed around the concept of Huisgen 1,3-dipolar addition, for a variety of reasons listed below. It seems to me that this does not put the exciting results in their proper context and does not focus on what is the most interesting about them. As can be seen in the beginning of my review, I find that the new BNN species, especially the isolable compound 6, are very interesting in terms of unusual nitrogen-rich main group molecules with a promising reactivity. Their contribution in terms of insight on 1,3-dipolar cycloaddition reactions is, in my opinion, secondary.

- For one thing, as the author note, intramolecular (or even intermolecular in some cases) dearomative additions of unusually reactive main group complexes to aromatic groups is not exactly uncommon or unexpected. I don't find that the 1,3-dipolar aspect of the reactivity in this case to be the especially provide deep new chemical insight, especially considering the precedents in FVP. Neither do I expect this method's synthetic potential ('in organic synthesis, catalysis, materials science, and biomedical research') to be far-reaching.
- Considering the above, as well as the precedents of 1-3 DC to arenes from FVP (cited by the authors), it seems to me that the label of an 'Unprecedented cycloaddition reactivity of transient BNN-1,3-dipoles' (discussion subtitles and repeated in the paper) becomes blurry. Some aspects of the reaction are 'unprecedented', but as a whole, the process has a lot of precedents. As described above, the most unprecedented component of the paper is the BNN molecule itself. With the reaction also being fundamentally limited to an intramolecular process (as shown by computations), it also gives the term 'unactivated arene' a very specific meaning.
- The sentence 'Notably absent from this list [of previously studied 1,3-dipoles] are boron-containing analogs of 1,3-dipoles' (p.1) is also confusing, considering that the authors subsequently note that: 'To date, the only one example of a stable propargyl/allenyl-type BNP-1,3-dipole I was described by Nöth et al. in 1999', which shows that boron-containing analogs of 1,3-dipoles are not absent from the list. The authors might also want to look at Figueroa's (boryl)iminomethanes that possess a 1,3-dipolar reactivity with CO_2 (Chem. Commun. 2015, 541).

In conclusion, while I had to highlight a need for a number of revisions, my assessment of this

work is very positive and I recommend publication in Chemical Science. Before the paper is finalized, some issues regarding the purity of the new compounds and the interpretation of computation data is needed. As a possible addition, I would encourage the authors to consider not presenting the results primarily as relevant to Huisgen cycloaddition, which would allow them to drop some of the hyperbolic language that can be found in the introduction.

Additional Questions:

How would you rate this article?: Very significant (top 10% - suitable for publication in Chemical Science)

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Do the references contain appropriate and balanced citations?: Yes

What contribution does this article make to the subject area it addresses? (1 = poor; 10 = outstanding; only articles rated 9 or 10 are suitable for Chemical Science, articles rated 8 or lower suggest the work is unsuitable for Chemical Science): 9

The second round:

REVIEWER REPORT(S):

Referee: 3

Recommendation: Accept

Comments:

The manuscript was revised following the reviewer's comments and the present version is suitable for the publication

Additional Questions:

How would you rate this article?: Very significant (top 10% - suitable for publication in Chemical Science)

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Do the references contain appropriate and balanced citations?: Yes

What contribution does this article make to the subject area it addresses? (1 = poor; 10 = outstanding; only articles rated 9 or 10 are suitable for Chemical Science, articles rated 8 or lower suggest the work is unsuitable for Chemical Science): 9

Referee: 2

Recommendation: Accept

Comments:

I am generally happy with the revisions. The data reporting is more transparent and the shortcomings of the crystallographic data/models are somewhat better treated. However, the following points should be addressed:

-I think the output of the SQUEEZE treatment of structure 5 should be used to propose a tentative explanation (one of the solvents used, usually) for what is in the voids. If no solvent occupancy can be conceived of that would roughly occupy the volumes and account for the electron "count" found by SQUEEZE, then the voids could be occupied by chemically significant moieties, like anions or cations, for example, which would invalidate the interpretation of the model as that of a neutral molecule (a protonated amine could perhaps, although unlikely, be hidden within the electron density smear of the disordered bromine atoms).

-Structure 7: Because the full pentalene-analogous ring is generated by symmetry (the N-N bond sits on a symmetry element), the part -1 instruction should be used. Instead, a confusing mix of parts is used which is very hard to track. The main problem, however, is that it makes no sense to refine occupancies independently (variable 5 and 6) for one conformer (there has to be exactly 50% of each conformer, and within one conformer, all atoms need to be there exactly once) -Capital letters for titles (SI) -In the SI, the statement "Note that omission of these reflections did not affect the structural Reliability" equates to saying that it is fine because you say so. I would just not comment on the OMIT instruction, although removing a large amount of outliers is indicative of problematic crystal or data.

-« showed disorderly » ... maybe "showed evidence of disorder" or "were disordered" is less metaphorical.

-The work of Klingebiel et al. was cited somewhat out of context. Their paper describes efforts in the direction of what the authors have accomplished in this contribution, so it would have been advantageous to discuss this a little bit more.

-I would remove the statement that equates the frequency of the bending mode to flexibility altogether. Bending modes are usually at low frequency (check out CO₂), and vibrational frequencies do not exclusively depend on bond strengths. The energy of bending is a better and less misleading indication of the flexibility to be showcased.

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Referee: 4

Recommendation: Revisions required

Comments:

In this revised manuscript, the authors have significantly improved the scholarly presentation of their results and present better data, notably with higher purity for some compounds. For the most part, my concerns have been properly addressed (with some exceptions that I comment on below) and those of other reviewers as well. Some new minor issues have surfaced, however, and I recommend publication of the paper in Chemical Science only after they are taken care of:

- First, I still think figure 1 needs some work:
- The one-way arrow now suggests reactivity, which is not what is expressed here. How about dropping arrows completely and using labels under the species? I also still don't agree with the calling these species analogues. How about simply saying 'dipolar moiety' in green?
- It would be useful to express the two types of 1,3-dipoles (Propargyl / allyl) in Figure 1a, since it is discussed in the text, simply by grouping the examples under a designation.
- On p. 2, we read that 'that of 1 is a formal Z,Z-configuration probably due to crystal packing forces.' I would refrain from making a claim about crystal packing forces unless some evidence ruling out other factors (e. g. calculations) is provided. In addition, the calculated geometry of 1 in the gas phase is also Z,Z, which suggests that crystal packing is not the reason for the geometry or that if it is, the wrong geometry is used for thermodynamic calculations.
- In my previous assessment of the mechanistic studies using DFT calculations, I commented on the discussion on the importance of the intramolecular character of the cycloaddition reaction. I feel that this section, although revised, still does not clearly present the logical conclusions of the DFT studies. These conclusions are clear: the dipolar cycloaddition is exergonic when intramolecular and endergonic (thermodynamically unfavored) with intermolecular substrates. This has to be spelled out clearly in the text and would probably benefit from being included in Fig. 3 (including part of Fig. S.25 in fig. 3). Furthermore, associating the unfeasibility of an

intermolecular cycloaddition with the barrier of the reverse reaction is irrelevant (written now as: 're-aromatization is favourable via a [3 + 2] cycloreversion with an activation barrier of less than 27 kcal mol⁻¹(Fig. S25)') because a low reverse reaction barrier is a simple consequence of having an endergonic one-step reaction.

- On p.3 the first sentences of the 'Synthesis and characterization of an isolable BNN 1,3-dipole' are unclear.

- P. 4: 'Single crystals... were obtained from...'. Should be 'were obtained by...'

- p. 4 'N₂ chemistry by Braunschweig and Stephan groups'. Should be : 'N₂ chemistry by the Braunschweig and Stephan groups'. Furthermore, unless I am mistaken, the Stephan group has published main group chemistry with diazomethanes that is relevant to N₂ chemistry and to this paper, but that is not actual dinitrogen chemistry. The text seems to imply dinitrogen chemistry in both cases.

The authors might want to also cite here Braunschweig's second N₂ paper (Science 2019) which also features BNN moieties.

-The discussion on the bending of 6 according to DFT calculations ('Interestingly, a vibrational analysis of 6 shows that the B-N-N bending mode involves a low energy frequency of 532 cm⁻¹, therefore indicating a flexibility of the molecule along this coordinate. In fact, bending the B-N-N angle up to 155° from 172° in 6 has negligible energetic cost (2.7 kcal mol⁻¹.)') is confusing and, without comparison with other systems, not very important to the paper. I would suggest removing it, or at least clarifying it and discussing why it is interesting.

-beginning of p.5: 'Compound 6 exhibit an absorption maxima': Should be 'maximum'.

- As needed, some products have now been dried and purified. I am wondering, however, how the yields of the syntheses changed with the purification? Do we have updated yields?

- Captions of Fig. 2 and Fig. 4: the details 'Hydrogen atoms ... probability level' should not be in parentheses.

- Throughout the ESI, the captions of the NMR figures should give the conditions (solvent, frequency). Also, since HRMS is invoked in the text, would it be possible to include the mass spectra in the ESI?

- I would also suggest that the authors remove some of the priority claims ('this is the first...') from the manuscript. There are a lot of them and they are sometimes redundant. I think the novelty of the work will speak for itself.

After these issues are addressed, I recommend that the paper would be published in Chemical Science.

Additional Questions:

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