

Referee 1 (R1)

Recommendation: Publish in JACS after minor revisions.

Liu and coworkers present in this manuscript the first stable and structurally confirmed phosphaborene. The authors use a clever strategy to independently construct sterically bulky B and P units containing N-heterocyclic imine and diazaborole groups, respectively. After connecting the two units, thermolytic loss of Me₃SiBr provides the phosphaborene. This species is bent at the P atom, indicating that the P-B bonding is probably more like a double bond, but on the other side the B-N bond seems like essentially a single bond. Thus, the PBN unit does not really resemble a cumulene, which means it is quite a "pure" example of a phosphaborene.

This is a major achievement, and one that has eluded researchers for a long time. It is not often that you get to review a paper that reaches a long-awaited goal of the community. The manuscript is clearly written and seems to be technically sound. In fact, I could find very few things to complain about. I have a few points to mention, but once these are addressed, I believe the paper will make a great addition to JACS. See below:

1. A number of years ago, Marder and Weber showed that diazaborole groups (or at least the one they used) were in fact net pi donors to an attached group, although relatively weak (DOI: 10.1002/chem.201102059). This goes against the usual assumption of tricoordinate boron as a pi acceptor. In contrast, however, the current manuscript discusses this group as a pi acceptor to the P atom (see Figures 1 and 4). The authors should address the possibility that their diazaborole group could in fact be a pi donor rather than an acceptor. They will likely be able to find computational data that can shed light on the matter.

2. I find the treatment of iminoboranes (RNBR) in the introduction to be very superficial, given their very close relationship to phosphaboranes (RPBR). There is by now a substantial amount of literature on iminoboranes, and some reviews, but they are only very briefly mentioned. In my opinion, much better coverage of the literature around these species is needed. Similarly, some comparisons of data between phosphaboranes and iminoboranes in the R&D parts would be good to see (e.g. 11B NMR, P-B/N-B bond indices, angles at P/N and B, reactivity).

3. p3: "Et₃CP(Cr(CO)₅)=Btmp" - the "C" in the phosphine should probably be deleted as this should be the phosphine Et₃P.

4. The arrow drawn from P to B in the Lewis structures strikes me as overstating the bonding between P and B. This electron donation appears from the calculations to be very weak, and the authors themselves even describe it as "feeble". I would suggest that the authors either remove the arrow completely or make it a dashed arrow.

5. p3: "This was evidenced in ^{31}P NMR and ^{11}B NMR spectra by the appearance of three new resonances at -291.9, 53.3, and 38.6 ppm". This is a very confusing way to present data from two different spectra, as it is difficult to determine which shifts are for which nuclei. I would maybe put it into parentheses and put the nucleus in front, e.g. (^{31}P : -291.9; ^{11}B : 53.3, 38.6 ppm).

Additional Questions:

Significance: Highest (top 5%, 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?: In Part

Referee 2 (R2)

Recommendation: Publish in JACS after minor revisions.

This is a beautiful work by Liu and co-workers presenting the synthesis, characterization and reactivity studies of a genuine phosphaborene.

In modern main group chemistry, one of the recent representative approaches to synthesizing heavy p-block elements-containing multiply bonded species relies on the stabilization effect of the Lewis acid/base to form the corresponding complex. However, this protocol frequently results in a significant change in the bonding situation, which impedes the experimental analysis of the essential bonding nature in detail.

In this study, the authors have employed N-heterocyclic boryl and N-heterocyclic imino group, which is a very clever strategy, and successfully isolated the hitherto unknown Lewis base/acid-free phosphaborene. Not only the title compound is fully characterized by the standard spectroscopy and x-ray diffractometry, but also the theoretical study for the PB bonding analysis is comprehensively done, which reveals the genuine PB triple bond character arising from a sigma-bond, 3c-2e bond and a slipped pi-bond. The presence of a "slipped pi bond" in a plane is reminiscent of heavy Group 14 alkyne analogs.

In the last part of the manuscript, the authors demonstrate the reactivity of phosphaborene (5) towards aldehyde, ketone, and CS_2 , which underwent [2+2] cycloaddition, CH activation, and C=S bond cleavage, respectively, confirming the diverse reactivity of the PB triple bond species.

Overall, the first isolation of a Lewis base/acid-free phosphaborene derivatives will enrich the preparative toolbox of the molecular chemistry of boron and phosphorus substantially. The technical and computational parts are done in a high-standard quality and the manuscript is well written and an enjoyable read. This study should attract a wide readership in JACS. I highly

recommend the acceptance for publication after the minor points indicated below are addressed during the slight revision.

---Fig 4f is a bit confusing as the arrows for both π -electron push and pull direct toward the left whereas the dashed arrows in the structure are drawn from N to B and P to B (as if as a push-push system).

---Product (6) contains two chiral centers (P and C) in the four-membered ring assuming no lone-pair inversion at the P, but it seems only one diastereomer is obtained. The authors could comment on the stereochemistry for the selective formation of (6).

---Complete scission of the C=S bond of CS₂ to give (8) and (9) is interesting but there is no description regarding the reaction mechanism. Any comments would be highly appreciated. What happens if only one equivalent of CS₂ is used? In addition, have the authors checked if a similar reaction takes place with CO₂?

---Fig S2-9/S2-16/S2-20/S2-24/S2-30/S2-37. The baseline/phase adjustment should be done properly (maybe better to use a quartz NMR tube?).

Additional Questions:

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

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

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

Scholarly presentation: Highest (top 5%, suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes

Referee 3 (R3)

Recommendation: Publish in JACS after minor revisions.

This paper presents the synthesis of a phosphaborene without any intermolecular donor coordination, and its interesting bonding features. As described in the introduction, the targeted compound seems to be a very fascinating compound with hetero multiple bondings, and its electronic situations have been revealed based on the experimental/theoretical investigations. In addition, the interesting reactivities of the phosphaborene were demonstrated. The newly obtained compounds seem to be fully characterized based on the spectroscopic analyses and the X-ray

crystallographic analyses with reliable data/analytic skills. Thus, the reviewer recommends the publication of this manuscript in *J. Am. Chem. Soc.* as a communication. Please take account the following comments into consideration before the final acceptance.

1&2. The author should draw a phosphaborene as not “R–P≡B–R” but “R–P⁺≡B⁻–R”, where the formal charges should be shown.

The reviewer doubts the PB triple bond character in compound 5. The authors argued that the orbital shown in Figure 4(b) should be similar to the in-plane slipped π -bond as in the case of group-14 dimetallynes. However, the orbital configurations should be totally different from those of the corresponding dimetallynes, since the components of the orbital seem to be almost located on the phosphorus atom (91.5%). Thus, the orbital in Figure 4(b) would be interpreted as a lone pair at the P atom (n orbital). As well, the orbital shown in Figure 4(d) should correspond to the lone pair at the N atom of the NHC moiety. Though the depiction in Figures 4(f)/5 should be an appropriate expression of the bonding situation, it would not be interpreted as the triple bond character, but as delocalized π -bondings. Thus, the authors should not emphasize that compound 5 features PB triple bond character.

3. The authors argued that ¹¹B NMR spectrum of compound 5 showed signals at 53.3 and 38.6 ppm, which should correspond to B(2) and B(1). However, it is difficult to assign the broadened signals, because the baseline of the spectrum would be seemingly very waving. The authors should show much clear spectrum after baseline corrections or the differential spectrum between those of compound 5 and the blank sample.

4. Compound 5 showed two absorptions at $\lambda_{\text{max}} = 348$ and 378 nm in the UV/vis spectra. The ϵ values corresponding to the absorptions should be shown, because the ϵ values should indicate whether the absorptions would be assignable to the π - π^* transitions or LMCT/MLCT transitions. In Figure S2-39, the vertical line of the spectrum should be not absorbance but ϵ value

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

Referee 4 (R4)

Recommendation: Reconsider after major revisions.

The manuscript by Liu and coworkers presents synthesis and isolation of a phosphaborene 5 without additional Lewis-base stabilisation. The study comprises carefully designed/selected ligand system (N-heterocyclic boryl & N-heterocyclic imino ligands) to stabilize the title compound. The isolated products are characterised by standard analytical methods including X-ray analysis. The synthetic work is well carried out and isolated donor-free phosphaborene 5 is a nice example of this compound class and it is indeed laudable result. However, the referee holds the opinion that the presented description/interpretation of the bonding situation in the title compound contains several concerns, as follows:

Authors introduced the N-heterocyclic boryl ligand (NHB) at phosphorus atom and N-heterocyclic imino ligand (NHN) at boron atom. While NHB acts accepts the electron from the P atom (π -acceptor), NHN donates electron to the B atom. This push-pull effect will enhance the NHB=P multiple bonding character as well as NHN=B multiple bonding character. In fact, the shortening of the P1-B1 & B2-N1 bonds were seen and authors described that "these imply the presence of the delocalization of π -electron over the BPBNC chain". This does not match the compound depicted in the Scheme 1. Also, authors discussed the central P1-B2 bond length (1.7788 angstrom) and stated as shorter than other reported Lewis based stabilised P=B bonds and related compounds. However, this is only slightly shorter than that of $t\text{BuP}(\text{AlBr}_3)=\text{Btmp}$ (1.787 angstrom, reference 12b). More importantly, they ignored the fact that the P=B bond length (1.743 angstrom) in Lewis base stabilised $\text{Et}_3\text{CP}[\text{Cr}(\text{CO})_5]=\text{Btmp}$ (reference 12a) is shorter. According to the computation (e.g. Figure 4 and related text), the triple bonding nature with the slipped π bond is almost negligible or very few (if there is). NBO analysis was discussed, but not in this orbital. Also, calculated WBI values showed B1-P1 (1.14), P1-B2 (1.73), B2-N1 (1.03), and B-C (1.39) which are not supportive for depicted triple bonding nature, and rather heterocumulene nature.

EDA-NOCV was also calculated and discussed, yet the triple bonding nature is not well supported. NRT can also shed light on this bonding situation (see also reference 22). Second Order Perturbation Theory could bring another insights. Although selected ligand system in this compound class may contain the triple bonding nature (ref 22), it seems that this push-pull ligand system (NHB & NHN) supports rather cumulene type structure.

Additional Questions:

Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: High (suitable for JACS)

Scholarly presentation: Moderate (not suitable for JACS)

Are the conclusions adequately supported by the data?: In Part

Are the literature references appropriate and correct?: Yes

Responses to the editorial office:

1) All graphics should be cited within the manuscript text. Please note that you are missing in-text citations for the following graphics: Figure 1c.

2) Include a TOC graphic illustrating the significance of the paper. The TOC graphic should be something that is representative of your entire work. Color schemes or illustrations typically make good choices. The TOC graphic must be original and free from any copyright issues. The TOC graphic should be approximately 3.25 in. x 1.75 in. (8.25 cm x 4.45 cm) and should have adequate resolution and clarity. Confirm that all text is legible at this size. Present the TOC graphic on the last page of the manuscript by itself. Please label the TOC graphic as "TOC Graphic". A caption describing the TOC graphic is not needed. Detailed guidelines can be found at https://pubsapp.acs.org/paragonplus/submission/toc_abstract_graphics_guidelines.pdf

3) Your Communication is too long. Please either shorten your manuscript if you are able to do so while addressing the other requested revisions, or the manuscript can be converted to an Article at revision.

A Communication must convey the scientific findings concisely in abstract, main text, and graphical elements as determined by word count not exceeding 2200 words, including titles/footnotes/captions of approximately five graphics (typically 2 inches long in a single column). References are not included in word count to allow article titles to be included at submission. All graphics and tables must be placed near the point of first mention in the text of the manuscript (not grouped at the end of the document) and must be sized according to current guidance. Long notes are not permitted in the References section; information not directly germane to the Communication can be included as Supporting Information.

The current Communications template remains available to help with estimated length; however, word count is the defining limit for a JACS Communication. Authors need not fit the manuscript to four strict pages by the template measure. To calculate word count within the word processing application, select all text from abstract through end of main text (excluding title, authors, affiliations, and content after main text) and view the word processor's word count data. Communications exceeding the word count limit must be shortened before acceptance.