

### Referee 1

Interesting work. However I was a bit confused by the title. In particular the use of the word "phosphagermynylidene" which includes the unusual letter sequence "germynyl" which I could not decipher. The first "y" seems out of place. He needs to explain why he uses it here. Did he mean phosphagermenylidene?

he should also point out that the species in question is "base-stabilized" by a carbene donor ligand (mention in title?).

I don't think there is a problem with his bonding explanation although it is not as clear as it might be. It might be clearer if he added some orbital labels (e.g. HOMO, LMO etc to Figure 3.

In the captions to Figures 2 and 3 he uses the word omitted when I think he means "not shown"

### Referee 2

This manuscript reports the synthesis and characterization of the first base-coordinated phosphagermavinylidene. This compound was stabilized by the coordination of a cyclic (alkyl)(amino)carbene (CAAC) to the terminal germanium atom. The synthetic routes to this compound were thoroughly investigated and its molecular structure, electronic properties, and reactivity were very carefully studied experimentally (XRD analysis, NMR and UV-vis spectroscopy etc.) and theoretically (e.g. IBO/ELF/EDA-NOCV etc.). Considering recent dramatic advances on the chemistry of low-coordinate main group element compounds, this study involves important results and deserves to be published in J. Am. Chem. Soc. The referee recommends publication after consideration of the following points by the authors.

1. Is the name of the title compound correct? Is it phosphagermenylidene?
2. The title compound was isolated as a base-coordinate form and should be therefore expressed as a base-coordinate phosphagermenylidene.
3. Please provide the yields of all compounds **2-11**. This is important for the readers to understand if the reaction proceeded cleanly or not.
4. Although the steric effects of the CAAC may be important for stabilizing **3**, are there any possibility that the CAAC could stabilize more electronically than NHC?
5. In the discussion of the  $^{31}\text{P}$  NMR spectrum of compound **3**, please provide  $^{31}\text{P}$  chemical shift values of hitherto-known typical phosphagermenes in addition to those of the related P=B and P=C species on page 2.
6. Regarding the reaction of **3** with  $\text{NH}_3$ , is it possible to detect the initial product if the reaction is carried out at lower temperatures?
7. The reaction of **3** with  $\text{GeCl}_2(\text{dioxane})$  providing **2** and **4** may not be good evidence for the dative bond character of the C-Ge bond in **3**, as the coordination of  $\text{GeCl}_2(\text{dioxane})$  to **3** may facilitate the dissociation of CAAC. In this regard, if compound **3** is treated with an excess amount of another CAAC, can the CAAC be converted to another CAAC?

### **Referee 3**

This manuscript by the Liu research group describes the synthesis of the CAAC-stabilized N-heterocyclic boryl-substituted phosphagermynylidene and its reactivity. The electronic nature of the title compound has been examined by the X-ray crystallographic analysis data together with DFT calculations (ELF, NBO, MOs, IBOs, EDA-NOCV).

Starting material N-heterocyclic boryl-functionalized phosphide **1** can be easily converted into compound **5** by the reaction with CAAC-GeCl<sub>2</sub>, which led to the thermal TMSCl elimination upon heating, producing compound **3** (Scheme 1). Treatment of **1** with GeCl<sub>2</sub> yielded the 4-membered Ge<sub>2</sub>P<sub>2</sub> ring that can also be transformed into compound **3** by adding CAAC. In the use of Me<sub>2</sub>IPr as a Lewis base, only compound **7** was obtained via **6**, as well as **2**. Molecular structures of **3** and **5** were determined by X-ray analysis (Figure 2). The reactivity of **3** (MeI, <sup>t</sup>BuPTE, NH<sub>3</sub>, AgOTf) was also presented (Scheme 2). Molecular structures for compounds **8**, **9**, and **10** derived from the X-ray analysis were also shown (Figure 4).

The study concept with the successful isolation of Lewis base stabilized phosphagermynylidene is properly presented. The reviewer would support the publication of the current manuscript,

however, the following points need to be considered for the improvements of the manuscript:

1. page 1, right, line 7: in the paper on the synthesis of compound **B** (ref 14), the generation of phosphagermynylidenes and their cycloaddition products are also reported. This point should be highlighted.
2. page 2, left, line 7: this NHB ligand should possess the pi-acceptor ability which should also influence the thermodynamic stabilization.
3. page 2, left, line 13: the details for the calculations of parent model compounds H<sub>2</sub>B-PGe and H<sub>2</sub>B-GeP should be provided in the supporting information (i.e. MOs, bonding nature, structures).
4. page 2, right, line 4: in the sentence, compound **7** is described first and then compound **6** is mentioned, afterward compound **3**, **4**, and **5**. This is a bit confusing for the readers and should be fixed.
5. page 2, right, line 4: The addition of two equivalents (or a bit more excess) of small NHC (Me<sub>2</sub>IPr) to compound **6**, NHC-stabilized phosphagermynylidene species could also be formed. Information about the treatment with sterically bulky NHC should be provided, in order to enhance the importance of the use of CAAC with strong electronic perturbation.
6. page 3, left: the B-P bond lengths in compound **3** should also be discussed, and also relevant contribution of the lone pair electrons donation from P to B can also be found by IBO. In fact, the WBI is 1.13 for the B-P bond in compound **3** indicating somewhat multiple bonding character (page 4, left).

7. page 4, right: while the reaction with AgOTf yielded compound **8** (P coordinates to Ag), the reaction with <sup>n</sup>BuPTe gives the compound **9** (Te interacts with both Ge and P). This different coordination mode should be clarified and explained.

8. page 4, right: The reaction mechanism of NH<sub>3</sub> activation should be discussed. Also, the experimental evidence for the postulated [GeNH]<sub>n</sub> can be provided.