

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%)

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

Reviewer #1: High (Top 20%)

Reviewer #2: High (Top 20%)

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

Reviewer #1: (No Response)

Reviewer #2: (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: Partially

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

Reviewer #1: Yes

Reviewer #2: Yes

Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: Other (please include in your report)

Please indicate whether you have included attachments

Reviewer #1:

- Yes, for the author
- Yes, for the editor

Reviewer #2:

- No

Reviewer 1 (R1)

Comments: This manuscript by Liu and co-workers describes the synthesis of a compound with a two-centre, three-electron π -bond between two phosphorus atoms. The authors synthesized the title compound, $[(\text{HCNDipp})_2\text{Si}]_2\text{P}_2]^{-}$, by reduction of $[(\text{HCNDipp})_2\text{Si}(\text{CN})(\text{PCN})]^{-}$ with potassium graphite. $[(\text{HCNDipp})_2\text{Si}]_2\text{P}_2]^{-}$ features a planar Si_2P_2 four-membered ring and is a phosphorus/silicon analogue of the bicyclo[1.1.0]butane radical ion. The compound was investigated by X-ray crystallography, EPR spectroscopy and DFT calculations. This compound is closely related to a similar radical anion reported last year by Iwamoto and co-workers (Angew. Chem. Int. Ed. 2022, 61, e202117584). It differs in that two Si-R groups have been replaced by valence isoelectronic phosphorus atoms. Overall, this is an interesting finding, however, given the similarities with Iwamoto's work, I would have expected to see further chemistry on the title compound in order to justify publication in

Angewandte Chemie. As written, this manuscript simply reports the structure of two new compounds, with a focus on $[\{(HCNDipp)_2Si\}_2P_2]^-$ which, as stated, is very similar to a compound that has already been reported in Angewandte Chemie. It is also worth noting that Iwamoto and colleagues characterized their compound much more carefully. Overall, I think that this manuscript might ultimately become suitable for publication in this journal subject to the completion of some major corrections and several additional experiments.

To summarize, this is an interesting manuscript, that reports the isolation of a new compound the likes of which are very rare. That being said, there are some deficiencies in the thoroughness of the work, and additional experiments are strongly recommended prior to publication. I recommend major revisions of this manuscript.

1) The authors should conduct electrochemical measurements on $[\{(HCNDipp)_2Si\}_2P_2]^-$ in order to assess whether a neutral diamagnetic species is accessible. If so, the authors should attempt to chemically access such a compound. This has been shown to be viable in Angew. Chem. Int. Ed. 2022, 61, e202117584.

2) I am surprised by both the lack of colour and of any observable transitions in the UV-Vis spectrum of the $[\{(HCNDipp)_2Si\}_2P_2]^-$. This needs to be explained. Can this be justified using TD-DFT calculations? The authors state that the compound is both beige and pale yellow. If the latter, I would have expected a band in the UV-Vis spectrum.

3) In the SI the authors state that the 1H -NMR spectrum of $[\{(HCNDipp)_2Si\}_2P_2]^-$ indicates "no paramagnetic compounds except the crown ether of the cation". Presumably, they mean no diamagnetic compounds. Also, an inspection of the NMR spectrum provided in the SI suggests the presence of several other compounds in the 1H -NMR spectrum. All of these species should be accounted for.

4) $[K(18-C-6)][\{(HCNDipp)_2Si\}_2P_2]$ should be characterized by elemental analysis. The authors report high resolution mass spectrometry data but observe the title ion as a

protonated species, i.e. $[M + H]$. The spectrum should be provided in the SI. Surely, negative ion mode ESI-MS should allow them to observe the molecular ion. This experiment would also be welcome.

5) Related to my previous point, can the authors unequivocally rule out the presence of a protonated species? Attempts to synthesize the neutral compound $[(HCNDipp)_2Si]_2P_2H_2$ should be made. Again, Iwamoto and colleagues were able to demonstrate the formation of such a compound in their work.

Reviewer 2 (R2)

The article by Liu and co-workers entitled: An Isolable Radical Anion Featuring a 2-Center-3-Electron Pi-Bond without a Clearly Defined sigma-Bond describes a new radical anionic Si_2P_2 ring compound. The electronic structure of the compound was carefully investigated by various methods that give strong evidence for the proposed electronic situation. While reviewing the article I noticed one thing that deserves further investigation. The synthesis of the radical anion with KC_8 using **2** as a precursor is rather complicated and includes release of two CN units. However, the Si-P bond is probably the weakest bond in **2** and might be cleaved by the reaction with KC_8 as well or at least partially. Furthermore, the molecular structure of the radical anion **3** in Figure 2 has large ellipsoids at the P atoms in comparison to the adjacent silicon atoms. Therefore, I suggest to the authors to carefully verify with mass spectrometry and elemental analysis if really two P atoms are included in the radical anion **3**.

Furthermore, in reference 15 two further Si_4R_4 species could be cited as well such as ACIE 2017, 56, 13866 and Chem Eur. J. 2021, 27, 17361. Although they do not explicitly contain an unsupported pi-bond, these ring compounds are very similar to those cited in ref 15 and contain an elongated transannular sigma bond with very high p-electron character.

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