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## REVIEWER REPORTS(S):

Referee: 1

Recommendation: Reject - encourage submission in another <a href="https://pubs.rsc.org/en/Journals/" target="\_new">RSC journal</a>. Please state in your report which RSC journal would be suitable and what, if any, revisions are required

### Comments:

This manuscript "Facile Oxidative Addition of E–H bonds to Dicarbondiphosphide via Fluctuation of  $\pi$ -Electrons" by Zhang et al. describes oxidative addition reactions of a  $6\pi$ -electron C<sub>2</sub>P<sub>2</sub>-ring compound **1** reported earlier by Grützmacher and coworkers in 2017. The reactivity of this singlet diradicaloid **1** is comparable to that of the Schulz's (A, Fig.1). In fact, in the same manuscript, Grützmacher et al., also described the homolytic dihydrogen splitting with **1**. Later, further reactivity of **1** has been also reported in Dalton Trans. 2019, 48, 2549 and Chem. Eur. J., 2018, 24, 4849. For a manuscript to be considered for publication in a first-class general chemistry Journal like Chemical Science, I would expect some new outcomes/ insights/ or interesting molecules. Unfortunately, this is not the case with this manuscript.

While all compounds have been satisfactorily characterized and corroborated with theoretical studies, the results are not unprecedented. The splitting of polar bonds to form stoichiometric products as reported in this manuscript may be interesting for specialized (Dalton Trans.) readers.

### Additional comments:

- (1) The introduction is excessively long and unfocused (see in particular para 2).
- (2) The use of the term "fluctuation" instead of "delocalization" is inappropriate. Note, the contribution of a zwitterionic resonance form to the electronic structure of **1** has been already documented.
- (3) Much emphasis is given to "transition-metal species" but the important findings in bond activations by main-group species have been overlooked.
- (4) Concerning main-group diradicaloids, others four-membered compounds featuring Group 13/14 elements should be discussed (Fig. 1).
- (5) The notion " $L \rightarrow (C_2P_2) \leftarrow L$ " is wrong and misleading, and must be updated throughout the manuscript.
- (6) Whenever possible, the NMR signals should be properly assigned to the respective nuclei.
- (7) The reported UV-vis absorptions should be assigned to the electronic transitions.
- (8) Some compounds contain impurities (see NMR plots) and need be purified and remeasure.
- (9) The mass spectra are missing and may be included.

### Additional Questions:

How would you rate this article?: Routine (25-50% - not 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?:

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): 5

Referee: 2

Recommendation: Reject - encourage submission in another <a href="https://pubs.rsc.org/en/Journals/" target="\_new">RSC journal</a>. Please state in your report which RSC journal would be suitable and what, if any, revisions are required

Comments:

This manuscript by Liu, Li and co-workers describes the reactivity of an NHC-stabilized dicarbonyldiphosphide towards a series of reagents featuring polar E–H bonds (E = C, N, and O) including phenylacetylene, malononitrile, 2-iodo-2-methylpropane, activated anilines and alcohols. The authors demonstrate that these substrates add to the phosphorus atoms of the dicarbonyldiphosphide core to afford 1,3-diphosphetanes or 1,3-diphosphetanium ions depending on the reagents in question. Throughout the manuscript the authors allude to these reactions as “oxidative-additions”, which is an erroneous descriptor as such reactions imply the formal increase (by two) of oxidation state and coordination number at a single element site. The transformations reported in this manuscript are certainly not “oxidative additions” but rather reactions involving two ambiphilic centers (a formal zwitterion). This concept has already been explored in the field, including by the authors. The title compound was first reported by Frenking, Su and Grützmacher (*Angew. Chem. Int. Ed.* 2017, 56,5744–5749) and its electronic properties and reactivity have been studied in depth by Li since then. The reactivity of the compound towards acetylenedicarboxylate, diphenylsulfide, elemental sulfur and selenium, boranes, copper and gold chlorides has been reported (*Chem. Eur. J.* 2018, 24,4849–4855). Further reactivity of this compound as a 6- $\pi$  donor towards metal carbonyls has also been reported (*Angew. Chem. Int. Ed.* 2020, 59, 4288–4293). The dicarbonyldiphosphide species studied in this manuscript is valence isoelectronic with compounds such as the diphosphadiazanediyl  $P_2(\mu\text{-N}^-\text{Ter})_2$  biradicaloid studied by Schulz. For the most part, these species react in an analogous manner. The results reported in this manuscript are largely incremental and, in my opinion, lack the novelty or broad interest to warrant publication in Chemical Science. I recommend publication in Dalton Transactions subject to the completion to the corrections requested below.

1) The technical work has been carried out to a relatively high standard and all compounds are, for the most part, thoroughly characterized. I note that there are no elemental analyses

reported for the compounds, and thus no evidence of the compositional purity of the reported species. The authors should provide these data.

2) Please remove the term “oxidative addition” from the text. It is incorrect.

Additional Questions:

How would you rate this article?: Routine (25-50% - not 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?: No

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): 7