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REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

1. Please rate the importance of the reported results

Reviewer #1: Highly important (top 20%)

Reviewer #2: Highly important (top 20%)

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2. Please indicate whether the results discussed justify publication as a Research Article

Reviewer #1: Publish as a Research Article

Reviewer #2: Publish as a Research Article

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3. Please rate the citation of previous publications

Reviewer #1: Insufficient

Reviewer #2: Appropriate

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4. Please rate the length of the manuscript

Reviewer #1: Concise

Reviewer #2: Concise

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5. Please rate the verification of hypotheses and conclusions by the presented data

Reviewer #1: Fully consistent

Reviewer #2: Fully consistent

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6. Please indicate which other journal you consider more appropriate

Reviewer #1: ----

Reviewer #2: ----

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7. Please indicate whether you have included attachments

Reviewer #1: No

Reviewer #2: No

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8. Please rate the quality of the Supporting Information

Reviewer #1: Satisfactory

Reviewer #2: Satisfactory

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COMMENTS TO AUTHOR:

Reviewer 1: This paper by Li and coworkers describes the synthesis, isolation and reactivity studies of a new distonic radical cation. Reaction of the biradicaloid bis-phosphorous compound 1 with PQ gives rise to an O-O bridged species that rearranges upon 1e oxidation to form the distonic radical cation, in which both O-donors coordinate to the cationic P-atom (P1), while the radical resides at the other P-atom (P2). The compound is well-characterized with x-ray diffraction and EPR, and the electronic structure was investigated with DFT. The compound reacts with RS-SR and 1,4-cyclohexadiene, confirming the radical nature of P2. Overall this is certainly an interesting paper, showing interesting properties of unusual compounds. Some minor changes are needed before this paper can be accepted though:

- Unlike what is claimed by the authors, this is not the first report of an isolated distonic radical cation. See for example: Chem. Commun. 2002, 1192. Quite a few cationic transition metal complexes with noninnocent ligands are known, where the charge and spin are also spatially separated. In a way, the aminyl radical complex reported by one of the authors is also a distonic radical cation. The latter species also contrasts with the statements in the introduction about pnictogen-centered radicals. Several (trivial but) stable distonic radical cations are also listed and used in this paper: Isr. J. Chem. 2018, 58, 343. Please revise this statement.

- Ref [22] seems to have a wrong author list. Please check.

- Conclusions: bench-stable (not sable).

- TOC text: Species, not specie.

Reviewer 2: the mss of Grützmacher, Li and co-workers describes a highly interesting finding, that is the synthesis, characterization and reactivity of a room-temperature-stable distonic phosphorus radical cation. the paper is well written and the compounds thoroughly characterized.

some comments:

-p3, l3: "oxidation process followed by a chemical reaction (EC process)". could the authors provide some insight here? To me this chemical reaction seems surprising as the 3 radical cation (title compound) is thermally stable, also in THF. Could it be over-oxidation instead, as also the chemical oxidant Fc-BARF needs to be added very carefully, and 3\*+ also reacts with additional oxidant.

-p3, l7, 2nd column: "Surprisingly, 3\*+ was shown to contain a four-coordinate P center (P1) and two-coordinate P phosphorus center (P2) as a result of an unexpected skeletal rearrangement (Figure 2d)." I suggest to reformulate this sentence, as thus far the story is written towards the desired synthesis of DRCs, so rewording surprisingly & unexpected is suggested.

-minor detail: i suggest to rename model 3a\*+ (H replacing one of the Dipp substituents of 3) to 3H\*+

-the conclusion states "bottle-sable" instead of bottleable or bottle-stable

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