

Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Reconsider after major revisions.

Comments:

The manuscript by Li, Su et al. expands the scope of the earlier published P2C2 rings. The results are of interest to the wide inorganic chemist community, and I find them interesting. The main point is the unusual inversion via redox chemistry, which I think deserves publication.

However, several points should be addressed:

- 1) The T-shaped TS of inversion of phosphines is not even mentioned. I strongly suggest to do so.
- 2) Page 5 line 38: What is the  $^1\text{H}$  NMR chemical shift of an R group? This should be clarified.
- 3) Of importance: I am not convinced by the DFT results at all. The level in the SI is markedly different from that in the main text. This is very suspicious, especially that it is marked yellow in the SI. I do not understand why PBE was used for such large molecules. The level should be tested with different functionals with dispersion correction. If the authors wish to speculate on relative stability in the ranges reported (0.9 or 7.6 kcal/mol) one should at least check how this changes with the method. If we consider that the error of such calculation can be several kcal/mol, this should be addressed.
- 4) Did the authors consider the correction of hindered rotations for the G values? This may result in large errors. Please include the relative energies as well. How are the trends in the optimized energies?
- 5) Scheme 5: Where does the iodide ion come from? Which PES was studied? This is very unusual, please clarify.
- 6) Some of the references are clearly consider only selected groups (Kwon, Stephan) in the field by citing several papers from them, even though the chiral P centers is very well known in the literature. Please reconsider. Especially the effect of cyclization on the barrier should be extended.
- 7) I suggest to include the structure of 2a in the main text and compare it to the other species.
- 8) Please comment on the purity of the compounds? Did you try EA?
- 9) The conditions should be clearly indicated with yields in Scheme 3.
- 10) Please indicate how the DFT calculations on Page 15 line 6 were done.
- 11) Could you comment why the cis and trans isomers have different stability as neutral or cationic species?
- 12) What formed in the 2e oxidation in the CV?

Additional Questions:

Significance: Above Average

Novelty: Above Average

Broad interest: Above Average

Scholarly presentation: Above Average

Are the conclusions adequately supported by the data?: No

Are the literature references appropriate and correct?: No

Have all unexpected, new, and/or significant hazards or risks been appropriately emphasized?: Yes

Reviewer: 2

Recommendation: Publish after minor revisions.

Comments:

Chen et al reported the highly stereoselective synthesis of cis-1,3-diphosphetanes, which cannot be transferred to trans- at RT, while cis- can be turned to trans upon one-electron oxidation and returned after reduction. Inversion has been reported for trivalent P radical cations, but not for a cyclic rings P radical cations. The work is of sufficient significance to warrant publication in Inorg. Chem. after minor revisions that more examples of cyclic P radical cations should be cited than Ref. 13.

Additional Questions:

Significance: Top 10%

Novelty: Above Average

Broad interest: Above Average

Scholarly presentation: Above Average

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: In Part

Have all unexpected, new, and/or significant hazards or risks been appropriately emphasized?: Yes

Reviewer: 3

Recommendation: Publish after minor revisions.

Comments:

This manuscript by Li, Su, and co-workers outlines the oxidation-induced pyramidal inversion at phosphorus within a series of 4-membered cyclic cis-1,3-diphosphetanes. These results build on this group's exploration of the parent dicarbonyldiphosphide and represent the first purported examples of cis/trans stereo-inversion at cyclic phosphorus centers building on Radosevich's previous example of cis/trans inversion at acyclic trivalent phosphorus centers. The work here is clearly presented and well executed and should be of broad interest to the inorganic chemistry community. I support publication in *Inorg. Chem.* after considering the following revisions and comments:

1. The only significant revision that needs to be addressed is with respect to the electrochemistry. The CV on Fig. 2 lacks many details. For instance, no current (y axis) values are reported and no electrochemical experimental details are provided in the experimental section of the SI. Electrodes used should be stated in the caption, as well as in the SI. No open-circuit potential is stated. This, or the presence of an arrow on the CV indicating the starting potential, needs to be included in Fig. 2. This is a must, otherwise the reader has no idea what is a reduction or oxidation. There is also a large (capacitive) background current in the inset CV that can and should ideally be corrected for. Have the authors performed multiple scan rates? This could also help in showing the likely EC mechanism at play in the oxidation-induced cis/trans isomerization. With additional detail provided in this figure, the preceding paragraph can be adjusted accordingly.

2. Page 8, Line 43: I believe I understand what the authors are attempting to convey when discussing the loss of aromaticity and increased pi-bonding upon alkylation. However, since the alkylation shifts the P lone pairs away from the four membered ring, is it correct to state "pi-back donation from the ring to L." Rather, shouldn't it be increased donation from C to L?

3. Page 14, Line 22: There is a lack of DFT detail provided in the SI. In particular, as the authors are investigating radical species by DFT, a depiction of the alpha and beta spin densities should be provided. I state this because the assessment of the unsymmetrically distributed spin density may be inaccurate. I may be wrong, but the authors should further clarify this. I don't understand the asymmetry given the nominally C<sub>2v</sub> symmetry at the radical cation of 3a.

4. Last paragraph before the conclusion: The authors may want to clarify this further. I had to read it several times to understand what was (likely correctly) stated. Also, I would change the work "reducible" to "oxidizing."

5. I would urge the authors to use spell check prior to submission. The manuscript is riddled with typos. Examples: P3-L5; P5-L42; P9-L20; P10-L32; P12-L33 (among others).

6. Scheme 1b: c-Hex in B and cyclohexyl in C. What's the difference?

7. Figure 1d: Difficult to see Et group in current orientation.

8: Figure S14 is very badly locked and/or shimmed. Fig. S18 should be better phased.

9. Other small modification to text include: 1) Isn't BARF normally written as BArF with F as superscript? 2) P2-L33: "developments showcase"; 3) P2-L53: "skeleton has been shown"; 4) P6-L37: "spectra" not "spectrum"; 5) P8-L47: "planarity of the ring is maintained"; P14-L3: "located".

Additional Questions:

Significance: Top 10%

Novelty: Above Average

Broad interest: Top 10%

Scholarly presentation: Above Average

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes

Have all unexpected, new, and/or significant hazards or risks been appropriately emphasized?: Yes

Reviewer: 4

Recommendation: Reconsider after major revisions.

Comments:

This manuscript concerns the stereochemical and redox reactivity study of

several 1,3-diphosphetanes and their radical cations. It is reported that 1,3-diphosphetanes are formed preferentially in their cis configuration by sequential alkylation of Grutzmacher's biradicaloid NHC-bound dicarbondiphosphide. Upon one electron oxidation, the radical cations are formed and found to adopt a trans configuration. Reduction back to the neutral 1,3-diphosphetanes is attended by return to the cis configuration.

Strengths:

- 1) The authors advance Grutzmacher's biradicaloid NHC-bound dicarbondiphosphide by sequential alkylations (first Me-I, then ZnMe<sub>2</sub>) to access a little-studied class of 1,3-diphosphetanes.
- 2) The neutral (cis) and radical cation (trans) derivatives of compounds 3a-c are all crystallographically characterized, giving unambiguous proof to the structural assignments.

Weaknesses:

- 1) There are many connections to other small-ring phosphacycle literature that is not explored in the present manuscript. Much of the relevant literature on cyclodiphosphazanes is not cited. For instance, the differential redox reactivity of cis and trans cyclodiphosphazanes is known (J. Chem. Soc., Chem. Commun., 1980, 982-983). The relative ground state and inversion barrier energies of these related compounds is not provided, which would assist the reader by providing useful and well-known points of comparison.
- 2) An explanation is not offered as to why inversion is observed in the present system, but not with cyclodiphosphazane and cyclotetraphosphine radical cations (ref 13).
- 3) A rationale is not offered as to why the neutral compounds prefer the cis configuration but the radical cations prefer the trans configuration. What structural effects dominate the conformational potential energy surface, and how are these reflected in the relative energy differences between cis and trans?
- 4) The difference in the EPR spectrum of 3c(BARF) (i.e. doublet of doublets) relative to 3a/3b(BARF) (apparent triplet) is not explained. What does this indicate about the differences in electronic structure and do the DFT models reflect the experimental observation?

In short, this manuscript describes some interesting synthetic observations, but does not offer much in the way of scholarly analysis. With revision and improvement on this latter point, I think that the manuscript could be made suitable for Inorganic Chemistry.

Additional items for revision:

- 1) Pg 6, ln 40 and ln 42: should read 2JPP
- 2) Experimental errors should be included in the tabulated crystallographic data (Table 1)

- 3) Table 1 has table footnote indicators ([a] and [b]) but no table footnotes are included.
- 4) Figure 2 caption: 0.1 M n-Bu<sub>4</sub>(BARF) should be 0.1 M n-Bu<sub>4</sub>N(BARF)
- 5) Neither mass spectrometry nor elemental analysis is provided for any of the compounds.
- 6) Numerous additional typographical errors and misspellings should be corrected.

Additional Questions:

Significance: Above Average

Novelty: Above Average

Broad interest: Above Average

Scholarly presentation: Average

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

Are the literature references appropriate and correct?: In Part

Have all unexpected, new, and/or significant hazards or risks been appropriately emphasized?: Yes

-----