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Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Reconsider after major revisions.

Comments:

Stephan and coworkers have done a sublime job in obtaining a stable phosphanorcaradiene. The experimental work is well done and complete, but the theoretical support is modest. The manuscript is well-written, crisp, and supported with spectroscopic data and X-ray structures. The study is suited for a communication in JACS provided that the following points are addressed:

1. The study homes in on the valence tautomerism  $1 \rightleftharpoons 2 \rightleftharpoons 3$ , which are both pericyclic reactions. The first is a cheletropic ring closure, the second a [1,3]-sigmatropic shift. The last process is properly addressed in the introduction, but is not considered in the remainder of the study. This is an omission in the focus on 2E as P-derivatives of both 1E and 3E are known and referenced.
2. The loss of a phosphinidene from phosphanorcaradiene is also a pericyclic reaction, a retroaddition, which is implied in the introduction, but not explicitly stated. This retroaddition also happens in the case of IN1, but because of the additional linkage (i.e., C-N bonding) the departure of the phosphinidene is not optimal and therefore results only via a prohibitively high barrier in the addition to its carbon substituent ('3' in Figure 2). This could be emphasized in the text and visualized by the computed difference in pathways for free (2-E) and bicyclic (1) phosphanorcaradiene, because it is the underlying reason why 2 is obtained as stable product. a. The numbering has to be adjusted throughout the manuscript and the SI. Number 3 is associated with the norbornadiene structure (Figure 1). In Figure 2 it relates to the phosphinidene dissociation product. In other words, 3 in Figure 2 should become 4 and all subsequent numbers must be adjusted.
3. The reason for the conversion  $2 \rightarrow 3$  by both  $h\nu$  (or sunlight) and  $\text{Ru}(\text{PPh}_3)_2\text{Cl}_2$  deserves to be addressed more comprehensively. a. The DFT energy scheme in Figure 5 is a wonderful basis for the Ru-complex, but it would be helpful to provide the reason why the barrier for dissociation of the Ru-complexed phosphinidene is lowered. This should be very simple. Further, why does the [1,3]-sigmatropic shift to a phosphanorbornadiene not become competitive. This can be addressed computationally in the Supporting Information. b. The explanation for the  $h\nu$  induced conversion is too simplistic. It is wonderful that the SI provides the UV spectrum and the main

orbital components of the DT-DFT calculations, but it is not a satisfactory or adequate explanation. It requires some more attention.

4. The last section in which reactions of 2 are described (Scheme 2; the same appears to be the case for 3 as stated in the text) are for my feeling somewhat exaggerated. Of course, the reactions are fine and so is the experimental description. a. That 2 (or cyclized 3) reacts with the dione to give '4' is obvious because of the P-oxophilicity but also underscores the formation of an incipient phosphinidene. b. The reaction with Bertrand's carbene is elegant, but adds little and can even be questioned because '6' is not rigorously characterized and is neither needed to explain the formation of '7' and '8'.

5. I am satisfied that MS (ESI) values are given instead of elemental analyses for the new compounds in the SI, but do note that not all spectra look equally clean. The NMR spectra show, besides the obvious solvents, some impurities. Could the samples not be purified better or does it indicate to some degree rearrangement products or other addition products? There are a few minor points:

6. Page 2, left column, line 49: "concerted" should be "concentrated".

7. Page 2, right column, Figure 4. I would prefer the current (c) and (d) above (a) and (b), because it is more natural to have the LUMO above the HOMO and HOMO-1.

8. Page 2, right column, lines 43-44: "is known readily equilibrates" should be "is known to readily equilibrate"

9. Page 3, left column, line 28: remove "occurs".

Additional Questions:

Significance: Highest (top 5%, suitable for JACS)

Novelty: Highest (top 5%, suitable for JACS)

Broad interest: Moderate (not suitable for JACS)

Scholarly presentation: High (suitable for JACS)

Are the conclusions adequately supported by the data?: Yes

Are the literature references appropriate and correct?: Yes

Reviewer: 2

Recommendation: Publish in JACS after minor revisions.

Comments:

The manuscript from Stephan and coworkers reports the synthesis of the first phosphanorcaradiene, an isomer of the known (but also very rare) phosphanorbornadienes. The phosphanorcaradiene is formed by removing the Au fragment from a phosphacycloheptatriene derivative, with the phosphorus de-inserting, and this reaction can be controllably reversed by adding the gold back. The phosphanorcaradiene can then be rearranged to form a three-membered ring species, and undergoes further phosphinidene chemistry with carbenes and orthoquinone-type reagents.

Overall, the work amounts to a considerable synthetic achievement, which is comprehensively explored both experimentally and theoretically. Thus, I am in favor of its publication in JACS, after a few minor points have been addressed:

- There are numerous English mistakes throughout the paper - it should be edited.
- The use of compound number 3 for the phosphanorbornadiene in Fig 1, and later in Fig 2 for a different compound, is confusing.
- The authors could calculate compound 6 to see what its likely structure is, and maybe compare its NMR data. There are also many Carbene=PR species known with which the authors could compare data.

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