
Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish in JACS without change.

Comments:

A very interesting chemistry. All of the mechanisms are carefully supported by DFT calculations.

Additional Questions:

Significance: High (suitable for JACS)

Novelty: Highest (top 5%, suitable for JACS) Broad interest: High (suitable for JACS) Scholarly presentation:

Highest (top 5%, suitable for JACS) The conclusions adequately supported by the data?: Yes Are the literature references appropriate and correct?: Yes

Reviewer: 2

Recommendation: Publish elsewhere.

Comments:

Reaction of a DAC with tBuCP affords a rare 2H phosphirene which was characterized including X-ray crystallography.

Page 2, the authors state that 1 is the first crystallographically characterized 2H-phosphirene. If it is so significant that this molecule was the first of its kind to be structurally characterized, then I do not know why the authors use ball-and-stick diagrams for the molecular structure drawings for structures coming from X-ray crystallography. Thermal ellipsoid plots are preferred because they can convey information about the quality of the structure determination. In addition, to be fair to Regitz, his was also structurally characterized, just as its tungsten pentacarbonyl adduct. The authors should take this opportunity to make a comparison between the molecular structure of the free versus the complexed 2H-phosphirene, and give Regitz due credit for having found a way to crystallize his using tungsten pentacarbonyl.

The authors mention that the ortho-quinone is a well-known trapping agent for phosphinidenes. Actually, this type of reagent is capable of forming bonds to phosphorus without a phosphinidene needing to be formed in the reaction at all. Note that the rearrangement of Figure 3 required heating in toluene at 110

C for 12 hours, while the quinone reactions take place rapidly at room temperature. This disparity in reaction conditions strongly suggests that a free phosphinidene is not an intermediate in the case of the quinone reactions. The authors should rewrite the quinone section with due acknowledgement to the likelihood that free phosphinidenes need not be invoked for this aggressive class of reaction partner. The statement in the conclusion that "The intermediacy of the vinylphosphinidene is supported computationally and by the isolation of phosphinidene oxidation products 3 and 4" needs to be modified accordingly because the phosphinidene is not a required intermediate in the formation of 3 and 4.

There are two relevant papers by Mathey on vinylphosphinidene complexes that ought to be cited: Access to New Phosphorus Structures by the Way of the Transient Terminal Phosphinidene Complexes (<https://doi.org/10.1080/10426509308045621>), and Molecular Orbital Study of the Vinylphosphinidene to Phosphapropyne Rearrangement (10.1021/om00014a040).

It has been reported that vinylphosphinidene is generated during the pyrolysis of vinylphosphirane. The authors should consult the paper "Computational View of the Mechanism of Vinylphosphirane Pyrolysis and a New Route to Phosphaalkynes" (10.1021/om960696y) and references therein as this literature suggests that vinylphosphinidene is generated as a transient species during this pyrolysis. In Figure 1(e) the authors highlight two things that are the important key advances in the present work: (i) the first crystalline phosphirene, and (ii) the first transient vinylphosphinidene. Clearly, the second claim is not correct because there is good evidence in the literature that pyrolysis of vinylphosphirane generates vinylphosphinidene.

On balance, this is nice work overall but I don't think the bar was met for publication in JACS. The synthetic method of reacting tBuCP with a carbene was known, the ensuing reactions are not really surprising, and in the case of the quinone reactions probably mis-interpreted as to their mechanistic significance.

page 2, line 3: we report the preparation [of] a

bottom of page 3, the formula is missing a)

Additional Questions:

Significance: Moderate (not suitable for JACS)

Novelty: Moderate (not suitable for JACS) Broad interest: Moderate (not suitable for JACS) Scholarly

presentation: Moderate (not suitable for JACS) Are the conclusions adequately supported by the data?: In

Part Are the literature references appropriate and correct?: In Part

Reviewer: 3

Recommendation: Publish in JACS after minor revisions.

Comments:

Stephan and coworkers have done a sublime job in the experimental and theoretical mapping of a phosphirene-phosphinidene rearrangement. The well-written, crisp study is amply supported by X-ray structures and suited for a communication in JACS.

My comments are minor:

- 1) First line below Figure 1 ending with "...cyclopropylidenes." This sentence deserves some references as there are many. The topic was hot for several decades even though it is already some time ago.
- 2) Figure 1e is somewhat of a misnomer. The two illustrations are certainly not the first crystalline and first transient species. Leave it out or do something more substantial.
- 3) In connection the phrasing of "...this strained ring system" on page 2, line 7, is not appropriate as it is not identified what structure is talked about.
- 4) I would suggest that the authors reexamine the HOMO of 1 (Figure 2c). I believe that it doesn't reflect a C(1)-P sigma-bond but rather one of the 'degenerate' ring CCP bonding orbitals.

Additional Questions:

Significance: High (suitable for JACS)

Novelty: Highest (top 5%, suitable for JACS) Broad interest: High (suitable for JACS) Scholarly presentation:

Highest (top 5%, suitable for JACS) Are the conclusions adequately supported by the data?: Yes Are the literature references appropriate and correct?: Yes
