From Editor:

Thank you for submitting your Communication for publication in the Journal of the American Chemical Society. Your manuscript has been examined by three independent referees whose reviews are attached. While the work is recognized as technically sound and novel, two of the reviewers believe the work may be too highly specialized for the JACS audience. This diminishes the case for rapid communication in JACS.

However, in reading the manuscript, I think that the rationale for the construction of this specific precursor and its successful formation of the 4+2 product is very educational, and allows predictions for other E=C additions. Therefore, I am recommending publication pending consideration of the comments made by the reviewers.

Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish elsewhere.

Comments:
Although this paper reports a very novel rearrangement, it is too specialized for the broad audience of JACS. This reviewer does not see how these results could be used for future developments, except as mentioned in the conclusion for other main group elements. Having said that, the chemistry has been done very professionally as usual for the Stephan group. To publish this paper in a more specialized journal, it would be good to shorten it. The discussion concerning the NMR and X-ray characterization would be better in the supplementary information.

Additional Questions:
Significance: Moderate (not suitable for JACS)

Novelty: Highest (top 5%, 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?: Yes

Are the literature references appropriate and correct?: Yes

Reviewer: 2

Recommendation: Publish in JACS after minor revisions.

Comments:
This is a very nice work by Stephan and co-workers establishing a reversible cycloaddition between phosphaalkene and an aryl ring.

Deprotonation of phosphenium cations (1) and (3) with KHMDS furnishes phsophaalekens, that undergo intramolecular [4+2] cycloaddition with the diisopropylphenyl ring on the N atom to afford 2-phosphabicyclo[2.2.2] molecules (2) and (5). While compound (2) is stable, a chlorobenzene solution of compound (5) leads to an equilibrium mixture with 2-phospha-butadiene (4). Computational studies propose that phosphabicyclo[2.2.2] molecules are thermodynamically more stable than the corresponding phosphaalkenes, and the [4+2]cycloaddition reaction proceeds in a concerted manner. In addition, it turns out that the linkages in compounds (4) and (5) appear to play a significant role to establish the equilibrium. Products are nicely characterized, compounds (2) and (5) represent the first examples of structurally characterized 2-phosphabicyclo[2.2.2]octa-5,7-dienes, and those raw spectral data are given in the Supporting Information.

While it has been reported that hetero aromatic main group molecules undergo the reversible [4+2] cycloaddition reactions with alkenes (for instance, Chem Sci 2015, 6, 7150), which is the contrary combination to the present study, the result in this manuscript represents the first reversible cycloaddition between a main group multiply bonded species and an aromatic ring. It is remarkable that the equilibrium is reached under ambient condition or even lower temperature (-5 oC) and without irradiation.

Overall, the present work is highly original and fundamentally significant. I believe that the present result will be of broad interest to main group community, and will allow for designing not only the system involving other main group multiply bonded species, but also an intermolecular version of such system. Hence, I recommend the acceptance of the present manuscript for publication in JACS. A minor point shown below can be considered in the revised manuscript.

(i) Abstract: As a general structure involving “R” substituent is not given for compounds (1) and (3) in the main text, I feel that the description as “R = adamantly, Ad” “R = tBu” seem inadequate here.

(ii) The yields for the formation (6) and (7) could be given in the main text.

(iii) By methylation of (2) with MeOTf, the authors obtained (7), which is stable and no retro-cycloaddition (to release [-MeP=CH2]+) was observed, according to the Supporting Info. I am curious about the similar reaction of MeOTf with the mixture of (4) and (5), have the authors tried this reaction? I was wondering if the corresponding methylated molecules are still in equilibrium or not. I assume that a phosphonium species like (7) is more stable than a phosphenium (P-methylated species of (4)) and thus, methylation of the mixture of (4) and (5) might give only the methylated product of (5). If such case, the intermolecular version can be considered with a phosphenium, it is beyond the scope of the current study and can be their future work though.

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

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

Broad interest: Highest (top 5%, 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

Reviewer: 3

Recommendation: Other Reconsider after revisions

Comments:
The manuscript by Stephan Douglas and co-authors describes a reversible intramolecular cycloaddition of a phosphaalkene mojety to an arene ring. The products of the cycloaddition

reaction were characterized crystallographically and the authors have undertaken theoretical calculations in order to get insight into the mechanism of this process.
In this particular reaction, the phosphaalkene was generated by reaction of a phosphepinium cation with KHMDS and reacted in an intramolecular fashion with the remaining N-bound benzene derivative. In case of a less bulky phosphepinium cation, the cycloaddition reaction turned out to be reversible. The products are the first examples of crystallographically characterized 2-phosphabicyclo[2.2.2.]octa-5,7-dienes.
[4+2] cycloaddition reactions of phosphaalkynes and phosphaalkenes with heteroaromatic rings and dienes (e.g. under formation of phosphinines, diphosphinines, 1-chloro-phosphacyclohexenes, etc.; the authors should also cite some of those papers, particularly by F. Mathey and P. Le Floch) are well established in the literature. However, I am indeed not aware of any reversible cycloaddition reaction of a phosphaalkene to a benzene (-derivative). In my opinion, I find the here described results rather spectacular, even though the reversible reaction seems to be limited to very particular substrates/substitution pattern and is not a general phenomenon. The scope of this reaction might therefore be very limited. The part of the manuscript about the reversibility of the reaction (page 2, right side, last paragraph) is a bit confusing. It seems that the equilibrium is far on the product side (5:95), but what happens after even longer time? What happens, if the crystals of the cycloaddition product 5 are dissolved again in a solvent? Can the authors comment in more detail about the scope of their findings.
In view of the very interesting results, the manuscript might become suitable for publication in J. Am. Chem. Soc., after the above-mentioned issues have been addressed. It should, however, be noted that the results are mainly suitable for a more specialized readership.

Additional Questions:
Significance: High (suitable for JACS)

Novelty: High (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

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