
Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish in JACS after minor revisions.

Comments:
The manuscript of Stephan and coworkers is interesting and of high quality. However, reactions of acetylene and the same aluminum(I) compound have been previously reported and the products structural characterized. Also insertion reactions into the three-membered AlC2 ring have been reported. Moreover, K. B. Dillon, F. Mathey and J.F. Nixon wrote a book with the title: Phosphorus: The Carbon copy. I mention this that the reported results in this manuscript are not surprising. Indeed to report for nearly every new compound theoretical calculations and present these in the main text is an exaggeration of the results. I recommend to place most of the theoretical results in the supporting part.

Additional Questions:
Significance: High (suitable for JACS)

Novelty: High (suitable for JACS)

Broad interest: High (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

Do the contents justify the length of this manuscript?: No

Reviewer: 2

Recommendation: Publish in JACS after minor revisions.

Comments:
In this manuscript, Liu, Stephan et al. present a thorough study of synthesis and characterization of two unprecedented phosphaaluminirenes 2 and 3 and their reactivity towards a series of compounds upon ring enlargement. For the first time a compounds with unsaturated aromatic with AlCP ring is presented. The reactivity of these compounds and theoretical studies are well done. Besides the characterization of the compounds by multinuclear NMR spectroscopy and X-Ray diffraction studies, the thermodynamics as well as the mechanisms of the reported reactions were investigated by means of detailed computational studies. The well-written manuscript shows that 2 and 3 can serve as pecursors for numerous novel heterocycles and I consider it as an extensive contribution to the field of heterocycles containing heavier main group elements. The paper is sound, insightful and well written. This article is of high fundamental interest to the community of molecular chemistry. It is suitable for publication in JACS if the following issues listed below are addressed properly:

(1) The authors state that resonances for the P-bound carbons could not be observed in the 13C NMR spectra of 2 and 3. Why weren't the shifts observed? The authors do not offer an explanation. How do the calculated shifts of these carbons compare to the shifts of the carbons in compounds A and B? However, proton-coupled 2D spectra, such as HC-HMBC, of those compounds might provide this missing information, as two and three bond carbon-proton couplings are possible due to the tBu/Ad side groups. Are such spectra available and can the respective information be extracted? If so, it should be compared subsequently to the theoretically calculated values that are presented in the draft on page 2 above Scheme 1.
(2) On page 6, the authors report that, in contrast to the reaction with Se, the reactions with S8 and Te afforded complicated mixtures. Did the authors investigate the possibility to use other sources of S and Te, such as S=PR3 or Te=PR3 ?
(3) While it is acceptable that compounds 4 – 10 (derived from reactivity studies) have only been characterized by X-Ray diffraction studies and by multinuclear NMR, more analytical data should be provided for the starting materials 2 and 3 (CHN analysis and/or high-resolution mass spectra) in order to show the purity of the bulk material.
(4) The reactivity towards isocyanides suggests that 2 and 3 could possibly activate CO. Have any calculations been conducted in this matter or can the authors report on any experimental investigations?
(5) In general, how were the NMR chemical shifts assigned for all of the compounds? No explanation is given and no 2D NMT spectra are presented. Also no MS or EA analysis is provided. The lack of these analytical data is a weak spot of this article.
(6) About aromaticity and NICS calculations:
What are the NICS values for the parent systems, i.e. HAl(HC=P) and HAl(HC=CH) at the same level of theory? These should be given for comparison to understand by which extent the ligand

affects the aromaticity of the AlCP ring. Also for the saturated systems HAl(H2C-PH) and HAl(H2C-CH2) the values should be given.

(7) What is the singlet-triplet energy gap for the AlCP aromatic system?

(8) Figure 7. What is the barrier for rotation to form 4 from IN1a?

(9) Scheme 2. Please number the reactions in scheme 2 and refer to them by their number in the text. It will make the article much easier to read.

(10) Datablock: 9 in checkcif file has an Alert level B. Please fix or explain.

Additional Questions:

Significance: High (suitable for JACS)

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

Broad interest: Highest (top 5%, suitable for JACS)

Scholarly presentation: High (suitable for JACS)

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

Are the literature references appropriate and correct?: Yes

Do the contents justify the length of this manuscript?: Yes
