
REVIEWER REPORT

EVALUATION:

Reviewer's Responses to Questions

1. Please rate the importance of the reported results

Reviewer #1: Highly important (top 20%)

Reviewer #2: Highly important (top 20%)

2. Please rate the citation of previous publications

Reviewer #1: Appropriate

Reviewer #2: Insufficient

3. Please rate the length of the manuscript

Reviewer #1: Concise

Reviewer #2: Concise

4. Please rate the verification of hypotheses and conclusions by the presented data

Reviewer #1: Fully consistent

Reviewer #2: Major inconsistencies

5. Please indicate which other journal you consider more appropriate

Reviewer #1: (No Response)

Reviewer #2: (No Response)

COMMENTS TO AUTHOR:

Reviewer 1: The authors of manuscript anie.201812529 describe some interesting chemistry observed with vinyl-substituted diphosphenes. They have reacted CAAC 1 with two different phosphalkynes at ambient temperature obtaining the diphosphenes 2 and 3 in good yields. If the reaction is performed at low temperature (-20 °C), the monophosphorus phosphirene intermediates 4 and 5 were obtained which dimerize rapidly upon heating giving 2 and 3. In addition, the unsymmetrical divinyl diphosphene 6 was obtained from equimolar amounts of 1 and two different phosphalkynes while the symmetrical divinyl diphosphene derivatives 2 and 3 do not rearrange into the unsymmetrical derivative 6. The bonding situation in divinyl diphosphene 3 was also investigated with DFT methods.

The divinyl diphosphene 3 was also reacted with elemental sulfur to give the unique dithiophosphorane 7 via cleavage of the P=P double bond. Diphosphene 3 also reacts with [AuCl(tht)] to give (most likely via cleavage of the P=P double bond and formation of a phosphinidene intermediate) the product of insertion of the phosphinidene into the Dipp substituent followed by coordination of the phosphorous atom to gold. The same insertion into the Dipp substituent was observed upon treatment of 2 and 3 with HOTf giving a seven-membered C₆P ring which can be considered a phosphorus-containing analog of the tropylium ion. The majority of the reactions described above have not been observed with the adducts obtained from NHCs and phosphalkynes.

The manuscript discloses novel and interesting diphosphene reactivity which clearly advances the state of the art and is perfectly suitable for publication in Angew. Chem. New compounds

have been fully characterized and the conclusions drawn are supported experimentally.

The manuscript could be further improved by some editorial changes such as

- (tbt)AuCl should be [AuCl(tbt)] in accord with IUPAC regulations
- not everybody might be familiar with the term DAC and the authors might want to name the specific NHC used
- is the terminus dithioxophosphorane correct? I would use dithiophosphorane
- the cleavage of the P=P double bond could proceed similarly to the cleavage of dicarbenes (tetraazafulvalenes) as described in *Angew. Chem. Int. Ed.* 2000, 39, 541-544 and the authors might wish to reference this publication.

Reviewer 2: This paper from Stephan group reports a rearrangement reactions of phosphirenes to form vinyl-substituted diphosphene derivatives. These diphosphenes further underwent P=P bond cleavage by a treatment with elemental sulfur, gold chloride, and methyl triflate. As a result, dithioxophosphorane, phosphepin-gold complex, and methylphosphepinium salt formed. All of these reactivity are new and should be described in ACIE. Because the discussion should be improved and some of data should be added to know the property of the compounds, the reviewer recommends major revision before the acceptance. Please find the comments before the revision.

1) In the second paragraph in the introduction should have structural information about the previously reported compounds being capable for P=P cleavage in Figure 1.

2) page 2, left, Figure 2 should have metrical parameters, especially for P-C, C=C, and C-N bonds, which should have information about conjugation between P=P and C=C bonds if it exists.

3) page 2, left, bottom line, explanation about "vinyl-substituted diphosphene 2" should have information about ^{13}C - ^{31}P coupling on the vinylic carbon atom in ^{13}C NMR spectrum. Same to 3.

4) page 2, right, 2nd column, the authors used "trans-" and "cis-". Are they correct in IUPAC nomenclature to describe the relationship between two alkyl groups?

5) page 2, right, last paragraph, the authors stated "while the HOMO (-5.88 eV) corresponds to the non-bonding lone pairs on P and the π orbitals of the vinyl substituents (Figure 3b), indicating the π -donating ability of vinyl substituents." What is the acceptor of vinylic π -

electrons? If the authors would like to claim it, molecular orbitals having π -type interaction between π orbitals of C=C and P=P double bonds should be found and illustrated here. Is there any shortening of P-C bond in 3 compared with those of aryl-substituted diphosphene? Twisted structure with a large dihedral angles between C=C and P=P planes in its X-ray structure would also be against to this conclusion for π -type interaction from vinylic π -electron. Can NBO analysis help to understand how this type of π -donation from vinylic group is important?

6) page 3, left, line 26, "addition" should be "additional"

7) page 3, right, line 43, Because the authors pointed out ^1H -non-decoupled ^{31}P NMR spectrum, please insert it into SI. Also, $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum should also be measured to confirm JPH coupling constants in ^{31}P and ^1H NMR spectra are same.

8) page 3, right, last 3 lines, the authors stated as "This was evidenced by an unresolved broad multiple resonance at 38.7 ppm and a doublet of pseudo- quintets at 38.7, respectively". Did the authors try VT NMR experiments or use more polar solvent to sharpen the signals? Because the reviewer guesses that the compound 9 would have a slightly stronger interaction between cationic part and triflate anion as confirmed with the X-ray analysis of compound 10.

9) page 4, second paragraph, Although the authors stated 9 and 10 could be considered as P-analog of tropylium ions and claimed their homoaromaticity, homoaromaticity and tropylium ion itself do not have relationship as the cited references 29 did not point out it. The authors should learn about "homoaromaticity" before claiming.

10) For SI, all the coupling constants in ^1H NMR spectra should be rounded to integer because some pairs of coupled nuclei do not provide same coupling constants. The reviewer guesses the measurement condition which the authors used would not have sufficiently high digital resolution of NMR spectroscopy. For compounds 8-10, please provide $^1\text{H}\{^{31}\text{P}\}$ NMR spectra to confirm the ^1H - ^{31}P coupling in the ^1H NMR spectra. All the UV-vis spectra should be accompanied with a concentration of the solution having at least three significant figures. Please use molar absorption coefficient for Y-axis of UV-vis spectra.

11) In the combined CIF file, compound numbers are wrong. Please correct them appropriately.