

From Nature Chemistry:

(We withdrew this paper in the revision process as we cannot accept the comments given by the reviewer #1)

Reviewer Comments:

Reviewer #1 (Remarks to the Author):

In the Summary the authors state "For a long time compounds containing a low coordinate main group element defying the octet rule were considered only as reactive intermediates, ...". This reviewer takes issue with the implied claim that the current "singlet phosphinidene" is a compound for which the octet rule is defied. A carbene such as the parent, methylene, is indeed a species that does not satisfy the octet rule because it has only six valence electrons. Accordingly, methylene is only a transient species or a reactive intermediate.

In contrast, compounds such as the N-heterocyclic carbenes, or indeed carbon monoxide, it may be argued are isolable precisely because they do not violate the octet rule at carbon. The resonance structures that are the truest representation of their electronic structure are ones in which four pairs of electrons surround the carbon atom as three bond pairs and one lone pair.

The same is certainly the case for the isolable "singlet phosphinidene" reported here. Indeed, the authors with their own calculations understand that the best resonance structure for the title compound is one in which the octet rule is not violated; they draw in Figure 4g a resonance structure with two bond pairs and two lone pairs at the 1-coordinate phosphorus atom.

Given this understanding, the title compounds should not be drawn in Figure 1 as if they only have three pairs of electrons at the low-coordinate phosphorus center. Such a resonance form likely contributes very little if at all to the true electronic structure of these systems that have a planar central phosphorus atom and multiple bonding between the two phosphorus atoms.

It is probably wrong or misleading to refer to the present compounds as "phosphinidenes" since they are better contextualized with reference to other types of reactive P-P multiply bonded systems. Similarly these authors have referred to their related compound with strong PN multiple bonding as a "nitrene" whereas it is better viewed as a multiply bonded system obeying the octet rule at nitrogen, rather unlike the case for parent nitrene which is actually electron-deficient. Figure 1 needs to be re-drawn to respect the authors' true view of the electronic structure of these systems.

Given the foregoing discussion, the title compounds can be seen to belong to the rare class of compounds in which a central planar phosphorus atom engages in P-P double bonding and forms two additional single bonds. An example is the cation obtained by methylation of a diphosphene as structurally characterized and reported by Grutzmacher and co-authors in *ACIE*, 1999, 38, 3329. Another is the amazing planar diphosphane dication reported in *JACS*, 2013, 135, 5561. The authors should cite these examples as well as any other relevant ones.

The Introduction, title, and text should be re-written with a focus on planar P-P multiply bonded systems, and with de-emphasis of the less relevant "phosphinidene" theme.

In Fig. 3 the line drawing of A4 should show the P=P double bond and make clear that there are four pairs of electrons around both phosphorus centers (the octet rule is satisfied).

The authors have described the synthesis of the first isolable compound of the sort $(\text{CH}_2\text{NAr}^{**})_2\text{P}=\text{P}$, which has been stabilized by a sterically demanding and pi-donating substituent. This is a very impressive result. The

reactions shown in Fig. 3 are convincing evidence of the illustrated sequence. The logic behind the development of the diazaphospholidine derivative with bulky "Ar**" moieties is laid out, and their efforts to use more typical Dipp moieties are chronicled. The NMR spectra, frontier orbitals, and further reactivity of phosphinidene A4 are discussed.

If the authors insist on referring to their compound as a phosphinidene, then the Introduction should be re-written to include discussion of relevant precedent. The introduction does not mention that there has been experimental work done on singlet phosphinidenes in the past. In particular, the work of François Mathey has elucidated the behavior of transient singlet phosphinidenes chaperoned by group six pentacarbonyl Lewis acids, which can sometimes even be removed following transfer. Beyond that, usage of cyclo-oligophosphanes as phosphinidene synthons has been documented. There is also a large chemistry of transition metal phosphinidene coordination complexes. References to such works on singlet phosphinidenes are important to contextualize the synthesis of singlet A4, and would strengthen the introduction.

Carbon monoxide extrusion from a phosphoethynolate derivative is a clever way to access a low-valent phosphorus center, and raises a few questions. Is this precedented? It seems likely that this has been tried before; if so, were the same photolytic conditions necessary? Can A2 or A4 be accessed thermally, and if not why not? Is there no change or do they decompose? Are there side reactions, and if so can any products be identified/characterized?

In fact, Grutzmacher et al. have prepared and reported recently on the chemistry of the closely related phosphanyl phosphaketene, (HCN[Dipp]₂)P-PCO, and has illustrated several of its thermal reactions: *Dalton Trans.*, 2015, 44, 6431-6438. The chemistry in this paper needs to be discussed in relation to the present work. In their concluding remarks, these authors state "A phosphanyl phosphinidene as an intermediate in the reaction reported here is highly unlikely and it remains elusive."

On page 4, the authors write "...we first prepared the phosphaketene 2a by reacting the chlorodiazaphospholidine 1a... with the 2-phosphoethynolate anion" but "react" is not a transitive verb.

The phosphinidene A4 seems to be stable to dimerization at room temperature, and the commentary on its thermal stability seems to imply that high temperature dimerization is not seen either; however, dimerization could be an entropically controlled process. In this case, it would be interesting to know if any (A4)₂ forms at low temperature and if this is reversible. A VT NMR study would be very interesting. Because diphosphenes are often red-purple (just as 3a is reported to be here), it might even be possible to take a low temperature UV/Vis spectrum. To establish that A4 is a monomer in solution, it is recommended to carry out DOSY NMR experiments.

Most NMR spectra in the SI show impurities in the isolated products. The authors acknowledge most of the impurities, but do not comment on what they think these impurities might be. Have they tried to remove them? If so, how and why might it have failed? This is not just limited to the incredibly greasy Ar**-containing derivatives, but also the Dipp compounds (2a and 4a).

A major drawback to this manuscript is the lack of X-ray crystallographic characterization of A4. In the absence of a structure, the characterization of A4's geometry seems to be lacking both computationally and experimentally. A structure would answer many questions about the geometry of this species, but as written, this manuscript seems to leave them almost entirely unaddressed. A few things that come to mind:

It may not be highly likely, but the ¹H/³¹P NMR data don't necessarily conclude a planar endocyclic phosphine within A4 if phosphine inversion is facile. Phosphine inversion is generally slow enough not to be a concern in NMR, but the activation barrier to inversion is known to be lowered by steric bulk and electron

donating groups. This environment was finely tuned to provide both criteria in spades, so if there were ever a time to consider phosphine inversion it would be here. What is the energy difference computationally between a pyramidalized and a planar endocyclic phosphine? Do predictive NMR calculations (likely on smaller model compounds) agree better with experiment when using a pyramidalized or planar phosphorus center?

To further connect the computed structure of A4 with the available spectroscopic data, the authors should use computational methods to predict the ^{31}P NMR shifts and the P-P coupling constant and compare the values predicted by computational chemistry to those obtained by experiment. Note that the def2-SVP basis set mentioned as being used for the calculations is a small basis set and probably a larger one is needed to give believable results.

The sentence beginning "Natural bond orbital (NBO) calculations ... give a large Wiberg bond index" is incorrect. Wiberg bond indices do not come from NBO.

On the experimental side of characterization, is there any broadening of the endocyclic phosphine ^{31}P NMR resonance at low temperature? This could imply that a fluxional process (phosphine inversion) is in play. Have any attempts been made to experimentally probe the geometry by IR/Raman spectroscopy? Could a powder pattern be solved to elucidate the structure?

Only impure NMR spectra are provided to substantiate the identity of A4. Expanding the characterization to include at least HRMS would be beneficial to demonstrating its identity, especially in the face of the impurities. HRMS might even give clues to the identities of the impurities. (As an aside, in the HRMS of 3a, is anything assignable to A2 observed?)

The further reactivity of A4 with isocyanides and alkenes is a good hint at its identity, but more direct characterization would strengthen this work tremendously.

My recommendation is in favor of publication after major revision. This is a very nice contribution but it falls short in its present form both in the completeness of characterization of the title compound, and in establishing purity. Some key references were not cited, and the electronic structure description should be consistent throughout with P=P double bonding and no violation of the octet rule.

Reviewer #2 (Remarks to the Author):

The authors report a seminal preparation (via irradiation of precursor) of a singlet phosphinidene. While the nature of the compound prevented its experimental isolation, the authors leave little doubt that they did, indeed, prepare this remarkable compound by studying its reactivity with electron poor alkenes and isonitriles. The experimental, computational, and crystallographic work is of high quality and the manuscript is written in concise, yet pleasing, fashion. Moreover, the authors seem to have cited the appropriate existing prior work. This is a remarkable achievement that fully warrants publication in Nature Chemistry.

Reviewer #3 (Remarks to the Author):

Although much information is available on transition metal complexes and Lewis base-adducts of phosphinidenes and phosphino-phosphinidene derivatives, this paper affords the first experimental data on a free, stable phosphino-phosphinidene. For this reason, I can recommend publication of this paper.

On a conceptual point of view, this paper does not afford unexpected breakthroughs. The spectroscopic data and calculations mainly confirm the previous hypothesis about the electronic structure, the multiple bond character of the P-P bond and the expected stabilization of the singlet state by the phosphino and amino-phosphino substituents (see for instance JOC 1996; Appl. Organomet. Chem. 2003 and references therein).

It shows, nevertheless, that the (extreme) steric hindrance of the N-substituents can overcome the inherent instability of the phosphinidene.

It might be interesting to comment the divergent behavior of these diazaphospholane-based phosphino-phosphinidenes, with respect to the closely analogue phosphino-phosphinidenes bearing diazaphosphetidine units (Chem. Eur. J. 2015, 4596) which tend to convert into tetraphosphetes, instead of diphosphenes.

In the last paragraph, the sentence "... after the isolation of diphosphenes by Yoshifuji et al., this work demonstrates that the corresponding monomers can be stable enough..." is not fully correct, as far as Yoshifuji's diphosphenes are dimers of aryl-substituted phosphinidenes, while Bertrand's work relates to phosphino-phosphinidene, i.e. to phosphinidenes with a totally different electronic structure.

Additional supporting information is required:

For most compounds, the ^{13}C NMR signals should be assigned more carefully, especially JC-P couplings should be given for signals at 55-20 ppm.

Mass spectra should be given for all compounds and especially for A4 (if possible).

Compounds 4b and 4c contain high amounts of impurities (see ^{31}P NMR data). A suitable purification procedure should be established

From Chem:

Reviewers' Comments:

Reviewer #1: An excellent piece of work. Crystallography is well performed, but just requires moderate technical additions in the supplementary information. The supplementary information could be structured better - perhaps with a contents page. The General section should include a little more detail as to how the crystal structure data collection and analyses were performed (software used etc), and in particular it is necessary to provide a brief description as to how the disorder was modeled in each case.

Reviewer #2: This paper describes a stable phosphinidene of interest in every respect; synthesis, structure, physicochemical character, chemical reactivity, theoretical calculation, and so on.

As for the title of this paper, however, the term "singlet phosphinidene" is a little too general or universal; "singlet phosphinophosphinidene" is more specific, because the described compound is not a little stabilized due to electronic or resonance effect, in addition to the steric effect. As is shown by theoretical calculation, A' appears to be a major contribution, which cannot formally be classified phosphinidene, without

mentioning the strict definition of phosphinidene. However, the reviewer is pleased to know that a GIAO calculation of P-31 NMR chemical shift and coupling constant for a model compound has been carried out to confirm the proposed structure. The drawing of A' in Figure S30 (right) in SI with bonding and charges should appear in the main text.

Although by putting the additional word "phosphino" to "phosphinidene," the title will limit the phosphinidene but the title will not reduce the interest and importance of the paper. It is a pity that the authors failed so far to get a suitable crystal for X-ray analysis of the phosphinophosphinidene. The picture of graphical abstract is misleading because "room temperature stable" is included in the title and the substituent used is sophisticated. Thus the readers will believe at a glance that the structure has been unambiguously confirmed by X-ray. The authors are fair if they mention that the figure shows a computed optimized structure of a model compound.

Discussions and reference citations are almost appropriate. The paper should be published with minor revision.

On introducing substituents Ar* and Ar**, papers by Protasiewicz should be referred in addition to that of Power.

Ref. 17: 1,2-dibromethane should read 1,2-Dibromethane.

Reviewer #3: The authors present the synthesis of an isolable singlet phosphinidene. Phosphinidene chemistry has been a highly active area for decades, and this is a substantial development in the field. What is particularly attractive about this preparation is its simplicity; this is a compound that other researchers may prepare. The authors show that steric effects are essential for this system where the smaller 'dipp' derivative failed to produce a phosphinidene. I support publication in Chem with minor revision.

The products are well characterized with the exception that analytical characterization is limited. There is a mass spectrometry data for perhaps three of them. Data for all the products is ideal.

The text is well conceived. I take some exception to the last sentence in the eTOC text. This may indeed be a transformative discovery, but it is presumptive for the authors to inform me of that. As a more nuanced point, a very straightforward argument can be made about how phosphinidenes will not have the impact of carbenes. A more guarded statement should be made there.

Reviewer #4: This is beautiful work that is done to a high standard as expected from these authors.

It is certainly of interest to the general chemistry readership and with minor revisions as indicated below it is worthy of publication in a leading, high-impact journal.

Under "Bigger Picture" the authors write:

"For a long time compounds containing a low coordinate main group element defying the octet rule were thought to be only short-lived intermediates, the quest for stable

versions being even unreasonable. This paradigm changed at the end of the 20th century with the isolation of singlet carbenes."

With this, the authors imply that their title compound defies the octet rule. However, because of the multiple PP bond, this is not the case. The authors should revise to make it clear that, when a compound is in fact able to be isolated, it adheres to the octet rule in some manner due to a flexible electronic structure. If on the other hand, a compound cannot find a way to achieve an octet, then it will not be stable and isolable under normal conditions.

The statement "It is likely that these findings will be as transformative as the discovery of stable carbenes." is really too speculative at this point. It is also of dubious veracity, given that ridiculously bulky groups are needed for the present "phosphinidene" to be isolated.

In the Intro, the authors write "Phosphinidenes are compounds containing a monocoordinated phosphorus atom featuring two lone pairs and a vacant orbital." I agree with this. However, their title compound does not fit this definition due to the PP multiple bonding.

It is not clear what is meant by the M06-2X/def2-TZVPP//M06-2X/def2-SVP level of theory. Same functional repeated, two different sized basis sets? Authors, please clarify.

The authors carried out NBO analysis but should really use the natural resonance theory (NRT) algorithm included with NBO in order to get the percentage contribution of the leading resonance structures to the overall density.

Looking at Figure 4, there is likely to be an important resonance structure as well that incorporates a PP triple bond. The relative importance of such a resonance structure as compared with the zwitterionic double-bond resonance structure is important to ascertain. This should be done using NRT and the results should be presented in a revised Figure 4.

It should be noted that in addition to comparing the title compound to stabilized forms of carbenes and nitrenes, sulfur-element multiple bonded systems such as in triple-bonded NS(C₆F₅)₃ are also relevant. Since sulfur is next to P in the periodic table, this would be a relevant comparison.

In the last paragraph the phosphorus is referred to as "monovalent" but this is only true for the resonance structure with two lone pairs. In the triple bonded resonance structures there is one lone pair and phosphorus is "trivalent".

Some of the new compounds are characterized by HRMS, but not the title compound A4. What is the reason for this omission? Especially in view of the lack of a crystal structure this information would be reassuring.