
REVIEWER REPORTS:

Referee: 1

Comments to the Author

D. W. Stephan and co-workers report a reactivity study of simple N-heterocyclic carbens (NHCs) towards phosphalkynes. This work focusses on the classical IMes, SIMes and IPr derivatives. Four new compounds 2-5 have been isolated, which contain a triphosphetene (cpd.s 2 and 3), a triphosphole (cpd. 4) and a 1,2-dihydro-1,2-diphosphete-substituted diphosphene framework (cpd. 6). The general structural frameworks of cpd.s 2-4 are well-known in the literature. Triphosphetenes and triphospholes were previously prepared by Hahn and co-workers, using the same methodology (ref. 16, *Angew. Chem. Int. Ed.*, 2000, 39, 2307-2310). In my opinion, the authors should point out more clearly that there is such literature precedent. In addition, the crystallographic characterization of a carbene-stabilized hexaphosphene 5 is described. Although this species could not be isolated as a pure substance, it is an interesting and unprecedented compound. Unfortunately, the crystallographic data are quite poor. Thus, the level of characterization of that compound is very weak.

In sum, this contribution is an interesting extension of the reactivity of NHCs and phosphalkynes, but it lacks the level of novelty and urgency to justify publication in *ChemComm*. In addition, the level of characterization of the reported compounds is insufficient (see comments below). For these reasons, I would like to recommend resubmission of this manuscript to a more specialized journal, e.g. *Dalton Transactions*, after the following issues have been resolved:

1) No elemental analyses are presented for cpds. 2-5, although this is required by the author guidelines of *ChemComm*, see <https://www.rsc.org/journals-books-databases/about-journals/chemcomm/#experimental-guidelines>:

"A new chemical substance (molecule or extended solid) should have a homogeneous composition and structure. Where the compound is molecular, authors must provide data to unequivocally establish its homogeneity, purity and identification. In general, this should include elemental analyses that agree to within $\pm 0.4\%$ of the calculated values. In cases where elemental analyses cannot be obtained (for example, for thermally unstable compounds), justification for the omission of this data should be provided. Note that an X-ray crystal structure is not sufficient for the characterisation of a new material, since the crystal used in this analysis does not necessarily represent the bulk sample.

In rare cases, it may be possible to substitute elemental analyses with high-resolution mass spectrometric molecular weights. This is appropriate, for example, with trivial derivatives of

thoroughly characterised substances or routine synthetic intermediates. In all cases, relevant spectroscopic data (NMR, IR, UV-vis, etc) should be provided in tabulated form or as reproduced spectra. These may be relegated to the electronic supplementary information (ESI) to conserve journal space. However, it should be noted that, in general, mass spectrometric and spectroscopic data do not constitute proof of purity, and, in the absence of elemental analyses, additional evidence of purity should be provided (melting points, PXRD data, etc)."

2) The X-Ray data set for compound 5 is insufficient for publication with $R_{int} > 12\%$, $GOOF > 1,3$ and $R_1 > 10\%$... In my opinion, this is particularly unfortunate considering that the compound was not characterized by other techniques. A better data set needs to be obtained.

3) The discussion of the ^{31}P NMR parameters of cpd.s 2 and 3 is quite superficial and the assignment reported in the ESI seem to be erroneous. Chemical shifts and coupling constants should be discussed in more detail.

For 2, that the signals at 264.7, 18.7 and 2.2 ppm are given the same $1J(\text{P-P})$ coupling of 302 Hz? In addition, the authors report $1J(\text{P-P}) = 185$ Hz for the signal at 18.7 ppm, while $2J(\text{P-P}) = 185$ Hz for the signal at 2.2 ppm? Something seems to be wrong here.

For 3, a different assignment is reported: δ (ppm) 252.5 (dd, $1J_{\text{P-P}} = 323$ Hz, $2J_{\text{P-P}} = 102$ Hz, C=P), 36.6 (dd, $1J_{\text{P-P}} = 215$ Hz, $2J_{\text{P-P}} = 102$ Hz, PC=P), 23.3 (dd, $1J_{\text{P-P}} = 323$ Hz, $1J_{\text{P-P}} = 215$ Hz, C=PP).

4) It should be noted that the term "phosphaalkyne oligomer" is used in a slightly inappropriate way here. Compound 5 is not a "newly discovered phosphaalkyne hexamer" (as stated in the abstract), but a carbene-stabilized hexamer. Moreover, contrary to a statement in the introduction, there is no free, non-coordinated phosphaalkyne dimer up to now, but numerous examples of dimers coordinated to metals.

5) References 13 and 15 are cited in the discussion of Figure 1b. However, the cited publications do not cover PCR oligomers, but some other PCR reactivity with Sn compounds to phosphadistannacyclobutene and side-on coordinated PCR complexes with silver. Instead, the seminal work of Regitz, Binger, Nixon and von Schleyer on the free oligomers should be cited in this paragraph.

6) In the discussion, a more detailed comparison of compounds 2 and 3 with the analogous compounds reported by Hahn is desirable.

7) Citation of the German and international editions of *Angewandte Chemie* is inconsistent.

Referee: 2

Comments to the Author

see attached review

Referee: 3

Comments to the Author

In this work, Prof. Stephan reported some of bulky NHCs reacted with $RC\equiv P$, which provide access to a series of novel vinyl-substituted phosphorus framework. Since the pioneering work of Gier in 1961, the compounds containing a $C\equiv P$ triple bond have been extensively explored as building blocks in organophosphorus chemistry. Although some reactions and computational investigations have been conducted in this manuscript, and some new compounds were synthesized and characterized, even the oligomerizations, the novelty and generality of current work is not obvious to the chemical community. And publication in more special journal is recommend.
