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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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Guy Bertrand^a; Antoine Brceiredo^a; Ghislaine Sicard^a; Michel Granier^a

^a Laboratoire des Organométalliques, U.A. 477, Université Paul Sabatier, Toulouse cedex, France

To cite this Article Bertrand, Guy , Brceiredo, Antoine , Sicard, Ghislaine and Granier, Michel(1987) 'Triple-Bonded-Like Tricoordinated Phosphorus Species P=', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 30: 1, 353 — 356

To link to this Article: DOI: 10.1080/03086648708080593

URL: <http://dx.doi.org/10.1080/03086648708080593>

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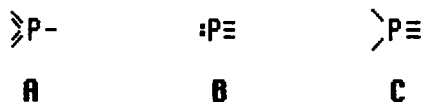
TRIPLE-BONDED-LIKE TRICOORDINATED PHOSPHORUS SPECIES $\text{>P}\equiv$

GUY BERTRAND, ANTOINE BACEIREDO, GHISLAINE SICARD and
MICHEL GRANIER

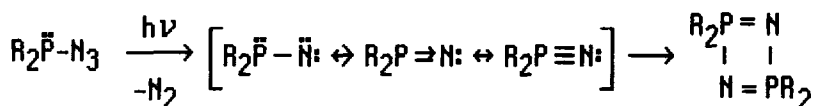
Laboratoire des Organométalliques, U.R. 477, Université
Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex,
France

Abstract Depending on the nature of the diazo-carbon substituent, the intermediates generated by photolysis or thermolysis of various α -diazophosphines behave either as "true" carbenes or as phosphorus-carbon multiple-bonded species.

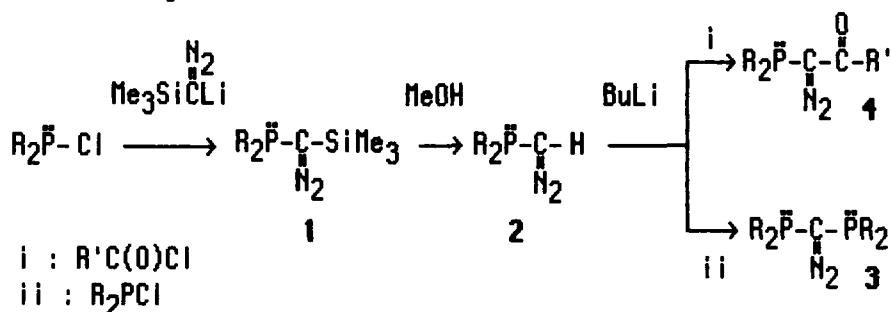
In the course of the tempestuous development of the chemistry of unusually hybridized species, although tricoordinated-pentavalent phosphorus derivatives of type A^1 and triple bonded σ^1 , λ^3 -phosphorus compounds (B)² are well documented, interest has only recently been focused on triple-bonded quinquivalent phosphorus having coordination number 3 (C).³



We have recently demonstrated that λ^3 -phosphinonitrenes, generated by photolysis of phosphine azides, can be regarded as λ^5 -phosphonitriles⁴ which dimerize giving the corresponding cyclodiphosphazenes.⁵



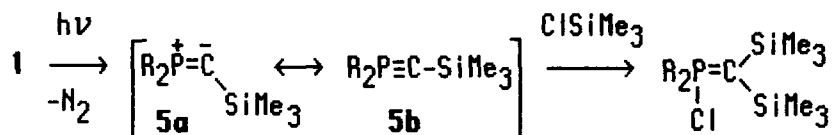
We wanted to find out if the generation of a carbenoid species next to a heteroatom bearing both a lone pair and a vacant p or d orbital is a general method for obtaining "triple-bonded-like" derivatives. Here we wish to report our results concerning the λ^3 -phosphinocarbene λ^5 -phosphaacetylene analogy. Diazo compounds are classical precursors of carbenes. However, although diazo λ^5 -phosphorus derivatives are well known,¹ no examples of molecules possessing a diazo group bonded to a λ^3 -phosphorus atom were reported before this work.⁶ At first sight, these molecules should be unstable due to possible intermolecular reactions of the diazo moiety with the phosphorus lone pair. Surprisingly, we have been able to synthesize a variety of diazophosphines, some of them being stable enough to be purified by distillation.



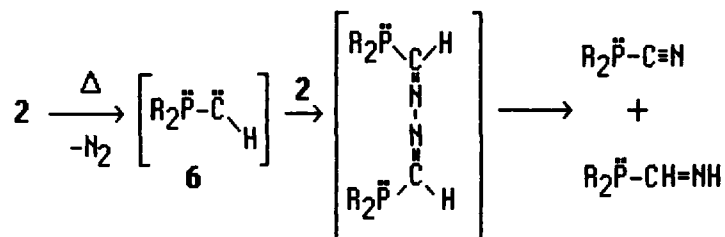
The structures have been clearly established by NMR, IR and mass spectroscopy as well as by a single X-ray diffraction study in the case of 3. Of particular interest, the N-N bond length (1.146 Å) is slightly longer and the C-N bond distance (1.278 Å) a little shorter than those observed in the diazoalkanes examined to date. The lower bond order of the nitrogen-nitrogen bond is confirmed by a low IR frequency ($\nu_{\text{NN}} = 2010 \text{ cm}^{-1}$).

The photochemical or thermal behavior of diazophosphines appears to be strongly dependent on the nature of the phosphorus and carbon substituents.

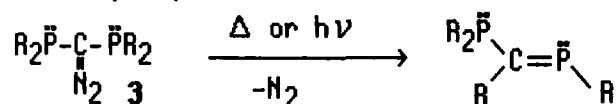
The products obtained in the photolysis of **1** in the presence or in the absence of trapping agents strongly suggest the transient formation of a multiple-bonded intermediate **5a** or **5b**. For example :



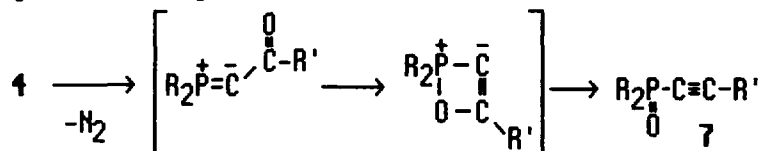
In marked contrast, a phosphinocarbene **6** is certainly involved during the thermolysis of **2**



In the case of the bis(phosphino)diazomethane **3**, a 1-2 migration leading to the corresponding phosphalkene is observed. This is the first example of a Wolff type rearrangement in the λ^3 -phosphorus series.



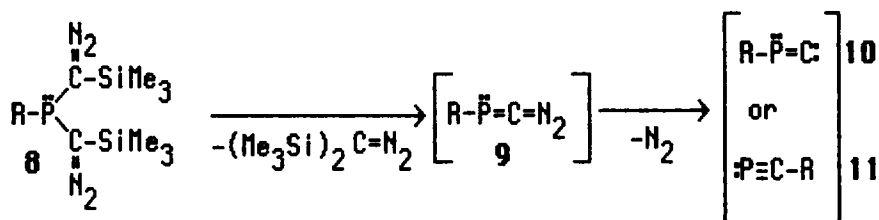
Starting from **4**, the formation of acetylenic derivative **7** strongly suggests the intramolecular addition of the carboxy group to the phosphorus-carbon multiple-bond. This would be a new type of Wittig reaction.



Thus, although an α -dicarbene is an acetylenic derivative, a λ^3 -phosphinocarbene can react either as a true carbene or as a multiple-bonded phosphorus species. Obviously as a "normal"

phosphorus ylide, the double or triple-bonded character of the P-C bond will depend on the back-bonding of the carbon electrons into the phosphorus d orbitals.

We have also been able to prepare a bis-diazophosphine **8** and surprisingly, according to mass spectroscopy, the major decomposition pathway involves the loss of bis(trimethylsilyl) diazomethane with primary formation of the 'dicoordinated phosphorus species **9**, followed by subsequent loss of nitrogen leading to a phosphalkyne **11** or isophosphalkyne **10**. The characterization and/or the trapping of these exciting species are under active investigation.



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