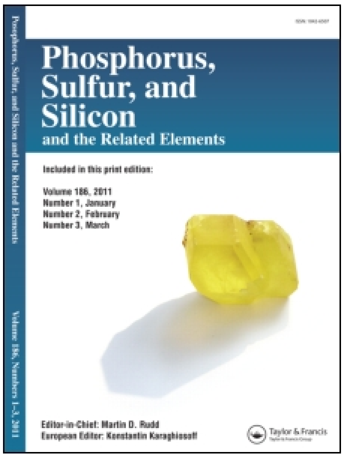

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Synthesis and Reactivity of the First Stable λ^5-Phosphaacetylene

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SYNTHESIS AND REACTIVITY OF THE FIRST STABLE λ^5-PHOSPHAACETYLENE

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Abstract The synthesis and reactivity of the P-bis(diisopropylamino) C-trimethysilylphosphaacetylene (bp 75-80°C/10^{-2}) is reported. Addition of trimethylsilyltriflate to this compound leads to a stable methylenephosphonium salt which has been characterized by an X-ray diffraction study.

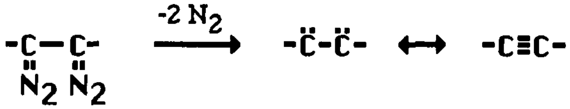
In the course of the tempestuous development of the chemistry of unusually hybridized species, although several stable molecules possessing a tricoordinated-pentavalent phosphorus atom of type **A**[1] or a monocoordinated triple-bonded phosphorus atom of type **B**[2], are known, no examples of stable derivatives of type **C** featuring a triple-bonded quintevalent phosphorus having coordination number 3 were reported before this work[3].


A


B


C

Our approach to the synthesis of compounds such as **C** is based on a very well-known reaction described, one hundred years ago, by Curtius et al[4]. They have shown that α,α'-bis- diazoderivatives spontaneously lost two molecules of nitrogen giving the corresponding alkynes. Since diazo compounds are precursors of carbenes, this result clearly states that an α,α'-bis-carbene is an alkyne.

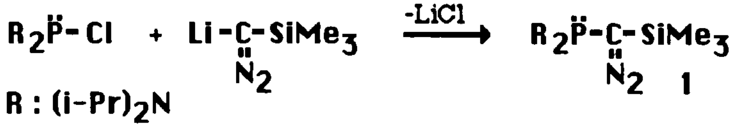


$$\underset{N_2}{\overset{\|}{-C}}-\underset{N_2}{\overset{\|}{C-}} \xrightarrow{-2\,N_2} -\ddot{C}-\ddot{C}- \longleftrightarrow -C\equiv C-$$

Like carbenes, a tricoordinated-trivalent phosphorus atom possesses a lone pair of electrons and an accessible vacant orbital and thus it was reasonable to think that an α-phosphinocarbene would be a λ5-phosphaacetylene.

$$>\ddot{P}-\ddot{C}- \longleftrightarrow >P\equiv C-$$

α-diazophosphanes seemed to be the ideal precursor and in the hope of stabilizing the desired product we chose bulky substituents at phosphorus and carbon, namely diisopropylamino groups and a trimethylsilyl group, respectively. The diazophosphane **1**[5] is easily available in one step by treatment of the lithium salt of (trimethylsilyl)diazomethane with a stoichiometric amount of bis(diisopropylamino)chlorophosphane.

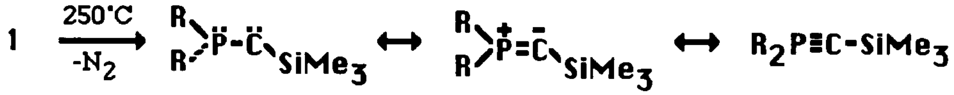


$$R_2\ddot{P}-Cl + Li-\underset{N_2}{\underset{\|}{C}}-SiMe_3 \xrightarrow{-LiCl} R_2\ddot{P}-\underset{N_2}{\underset{\|}{C}}-SiMe_3 \quad \mathbf{1}$$

$$R : (i\text{-}Pr)_2N$$

We first studied the photochemical behavior of diazo **1** in the presence of a variety of trapping agents. This allowed us to demonstrate that the corresponding phosphinocarbene **2** behaves as a phosphorus-carbon multiply-bonded species[5a]. These first results were corroborated by Regitz et al[6] and by ourselves[5b] starting from other α-diazophosphanes. However all attempts to isolate the postulated, photochemically generated, λ5-phosphaacetylenes failed.

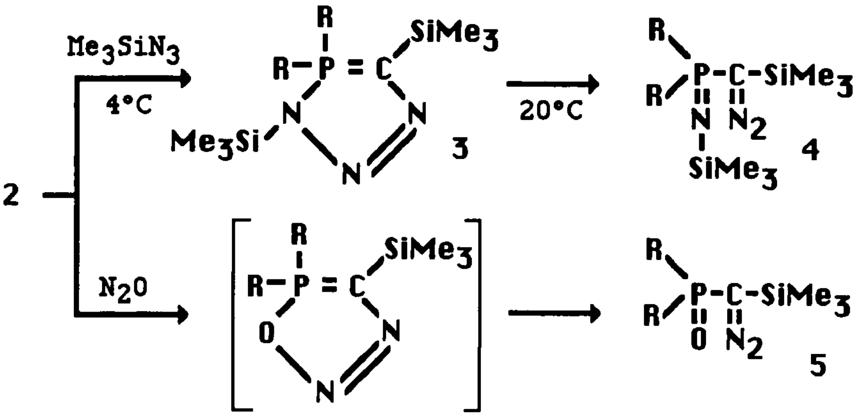
In marked contrast, we have been able to isolate the desired compound **2** using flash thermolysis technique ($250°C/10^{-2}$ mmHg)[3].



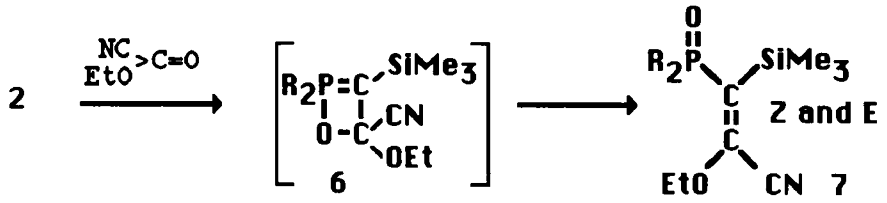
2a **2b** **2c**

2 is a red oily material (bp $75-80°C/10^{-2}$ mm Hg) which is stable for several weeks at room temperature, in benzene solution. Theoretical calculations performed on H_2PCH predicted[7] that, in **2a** the phosphorus atom would be pyramidal, **2b** would be a planar molecule but bent at the carbon, while **2c** would be planar and linear. Based on NMR spectroscopy, **2** possesses a multiple-bond character and is best represented as λ5-phosphaacetylene **2c**.

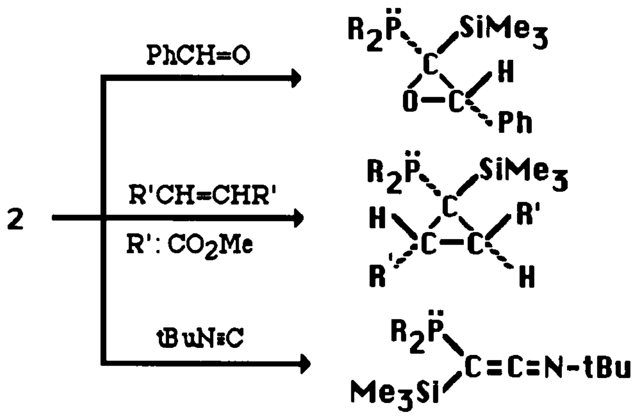
Although **2** is thermally stable, it is quite reactive. Its λ^5-phosphaacetylene-like behavior was definitively demonstrated by its reactivity with trimethylsilyl azide and nitrous oxide. Diazo derivatives **4** and **5** were isolated in 92 and 84%, respectively, and the first formed [2+3] cycloadduct **3** was even characterized by NMR spectroscopy, at 4°C.



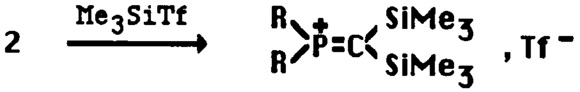
Further proof for the phosphorus-carbon multiply-bonded character of **2** was found in its reaction with ethylcyanoformate. The obtention, in high yield of phosphorylalkene (Z and E) **7** can be rationalized by a [2+2] cycloaddition, followed by ring opening of **6**. This reaction can be considered as a Wittig reaction where the phosphorus ylide ($R_3P{=}CR_2$) would be replaced by a phosphorus vinyl ylide $R_2P{\equiv}CR$



At that point, it seemed clear that a λ^3-phosphinocarbene was a λ^5-phosphaacetylene. However, in contrast with the α,α'-bis-carbenes which always behave as alkynes, compound **2** can also react as a "simple" carbene as illustrated by its reactivity with benzaldehyde, dimethylfumarate or tert-butyl- isocyanide.



Note that species **2** is also a very good precursor for new unusually hybridized phosphorus species. For example, treatment of **2** with a stoichiometric amount of trimethylsilyltriflate affords the stable methylenephosphonium **8** in quantitative yield. Its structure has been proved by an X-ray diffraction study.



Tf: CF_3SO_3

8

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