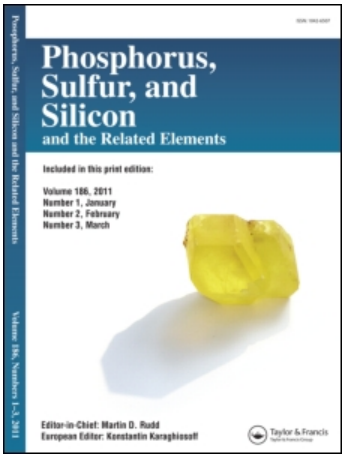


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

1,3,5-Triaza-2-phosphapentalenes

Konstantin Karaghiosoff[a]; William S. Sheldrick[b]; Alfred Schmidpeter[b]
[a] Institut für Anorganische Chemie der Universität München, München [b] Fachbereich Chemie der Universität Kaiserslautern Erwin-Schrödinger-Strasse, Kaiserslautern

To cite this Article Karaghiosoff, Konstantin , Sheldrick, William S. and Schmidpeter, Alfred(1987) '1,3,5-Triaza-2-phosphapentalenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 780
To link to this Article: DOI: 10.1080/03086648708079272
URL: http://dx.doi.org/10.1080/03086648708079272

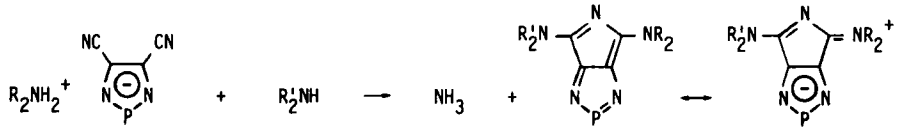
1,3,5-Triaza-2-phosphapentalenes

Konstantin Karaghiosoff*, William S. Sheldrick and Alfred Schmidpeter

Institut für Anorganische Chemie der Universität München
Meiserstrasse 1, D-8000 München 2

Fachbereich Chemie der Universität Kaiserslautern
Erwin-Schrödinger-Strasse, D-6750 Kaiserslautern

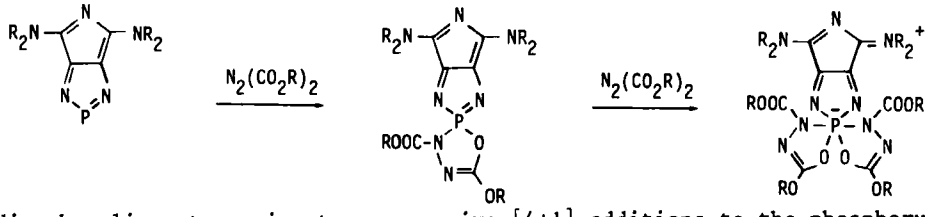
Refluxing a dialkylammonium 4,5-dicyano-1,3,2-diazaphospholate[1] with a dialkylamine in chloroform gives a 4,6-bis(dialkylamino)-1,3,5-triaza-2-phosphapentalene[1] in good yield as the only reaction product. Unsymmetrically substituted representatives are accessible this way too.



R, R' = Me, Et, CH_2Ph, $(CH_2)_5$

The diamino-phosphapentalenes are stable, deep red crystalline solids. They represent the first known $(4n)\pi$ heterophospholes. As in the case of the corresponding carbocyclic pentalenes[2] the 8π system is stabilized by the two amino substituents. According to the second mesomeric formula the diaminopentalenes can be regarded as zwitterions, consisting of an anionic 1,3,2-diazaphospholyl and a cationic 2-azaallyl part. The molecular structure, as obtained from an X-ray analysis, strongly supports this view. The colour of the diamino phosphapentalenes is due to an intramolecular charge transfer. The results are in good agreement with MNDO-calculations.

The chemical reactivity of the phosphapentalenes is also in accord with their zwitterionic character and compares to that of the 1,3,2-diazaphospholate anion. Under simultaneous oxidation by sulfur or selenium alcohols add to the P=N bond yielding deep blue products.



Azodicarboxylic esters give two successive [4+1] additions to the phosphorus yielding purple and colourless products, respectively. The latter provides the first example of a hexacoordinate phosphorus with an N_4O_2 surrounding.

[1] A. Schmidpeter and K. Karaghiosoff, Nachr. Chem. Tech. Lab. 33 (1985) 793 and references cited therein.

[2] K. Hafner, K. F. Bangert and V. Orfanos, Angew. Chem. 79 (1967) 414; Angew. Chem. Int. Ed. Engl. 6 (1967) 451.