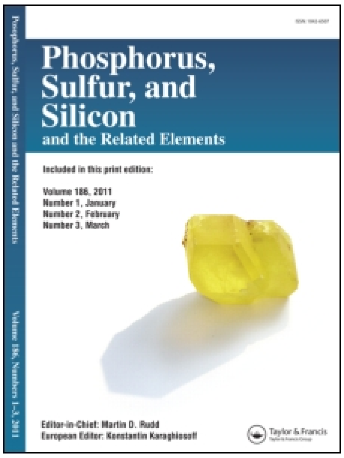

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

2-Phospha-Allylic Systems

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To cite this Article Schmidpeter, Alfred , Willhalm, Angela , Kroner, Jürgen , Day, Roberta O. , Holmes, Joan M. and Holmes, Robert R.(1987) '2-Phospha-Allylic Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 495 — 498

To link to this Article: DOI: 10.1080/03086648708080628

URL: http://dx.doi.org/10.1080/03086648708080628

Phosphorus and Sulfur, 1987, Vol. 30, pp. 495–498
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2-PHOSPHA-ALLYLIC SYSTEMS

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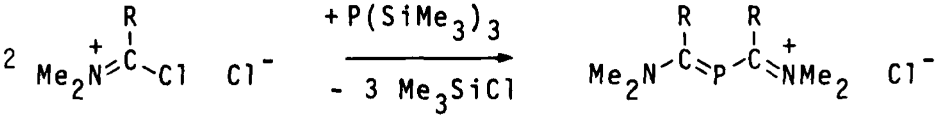
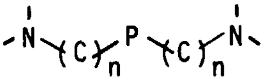
Phosphamethincyanines prepared in 1964 by Dimroth and Hoffmann were among the first compounds with two-coordinate phosphorus. They are special cases of 2-phospha-allylic cations. Simple representatives of this type become available from the reaction of imidoyl chlorides with tris(trimethylsilyl)phosphane.



$$2\ Me_2\overset{+}{N}{=}C(R){-}Cl\ \ Cl^- \xrightarrow[-\ 3\ Me_3SiCl]{+P(SiMe_3)_3} Me_2N{-}C(R){=}P{-}C(R){=}\overset{+}{N}Me_2\ \ Cl^-$$

They even form with white phosphorus; due to side- and secondary reactions this route is, however, not preparatively useful.

As the π-charge alternates along a polymethincyanine chain, the phosphorus in a symmetric phospha-methincyanine

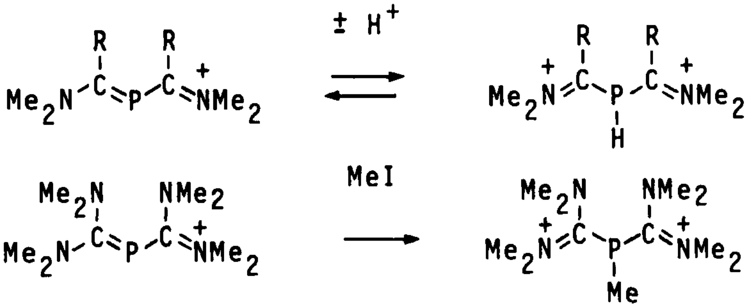


is expected to differ in character for even and odd numbers of n. In contrast to phosphenium ions (n = 0) phospha-allylic cations (n = 1) thus are little electrophilic, they are stable as ionic chlorides and not sensitive to hydrolysis. They are colourless to deep red, depending on the substituents at carbon and nitrogen. Their ^{31}P-NMR shifts extend over a remarkably large range from -112 to +172.

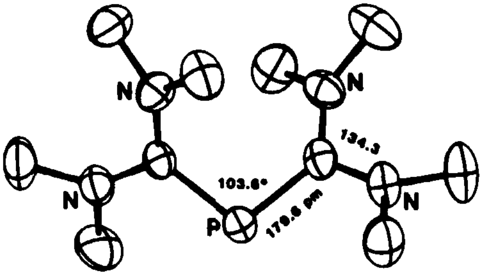
STO-3G calculations show the bent coplanar form of the tetra-amino 2-phospha-allylic cation to be favored by 100 kcal mol^{-1}

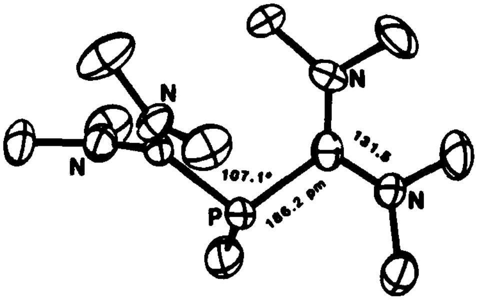
over the straight allene form. The phosphorus carries a π-charge of -0.5.

In highly acidic media 2-phospha-allylic cations are protonated reversibly at the phosphorus as detected by (extremely high) $^1J_{PH}$. Depending on the nature of R they are more or less easily alkylated to dications.



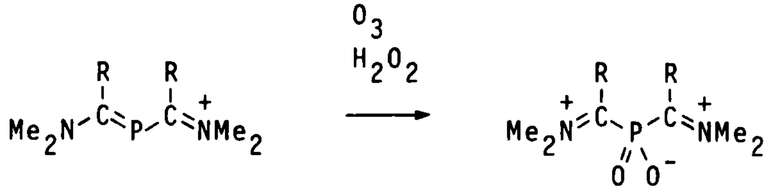
As indicated by the formulas used, allylic delocalization is completely destroyed with the phosphorus becoming three-coordinate. This is clearly shown by a comparison of the two structures of the tetrakis(dimethylamino) 2-phospha-allylic cation and its P-methyl derivative.

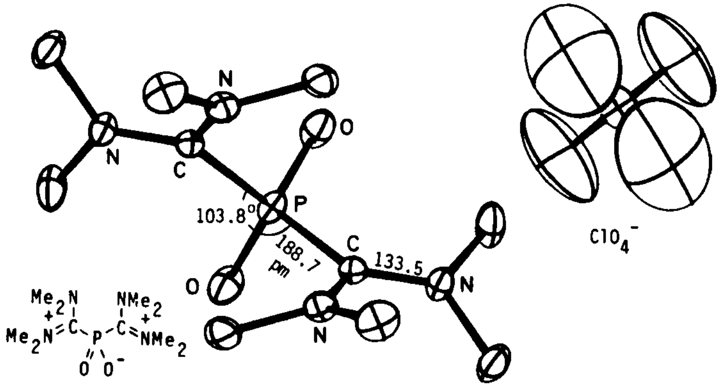




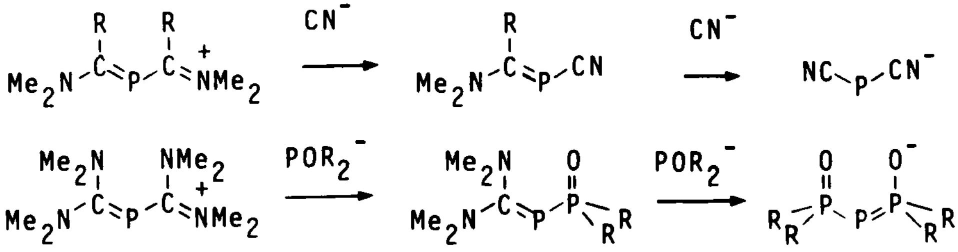
Ab initio calculations result in a good agreement with the observed structures. Furthermore, MNDO calculations indicate the electrophile to approach the phosphorus in the above reaction not in the allylic CPC plane, but rather almost perpendicular to it, with the lone pair remaining stereochemically active all the time.

Ozone or hydrogen peroxide convert the 2-phospha-allylic cations into their dioxides, which must be understood as zwitterionic amidinio-phosphinates.



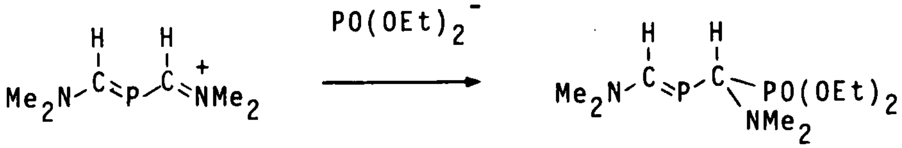


As mentioned above, the phosphorus in 2-phospha-allylic cations does not associate with the anion. Strong nucleophiles, however, give rise to a substitution reaction leading to donor/acceptor-substituted phosphaalkenes in the first, and to acceptor-substituted phosphides in the second stage.

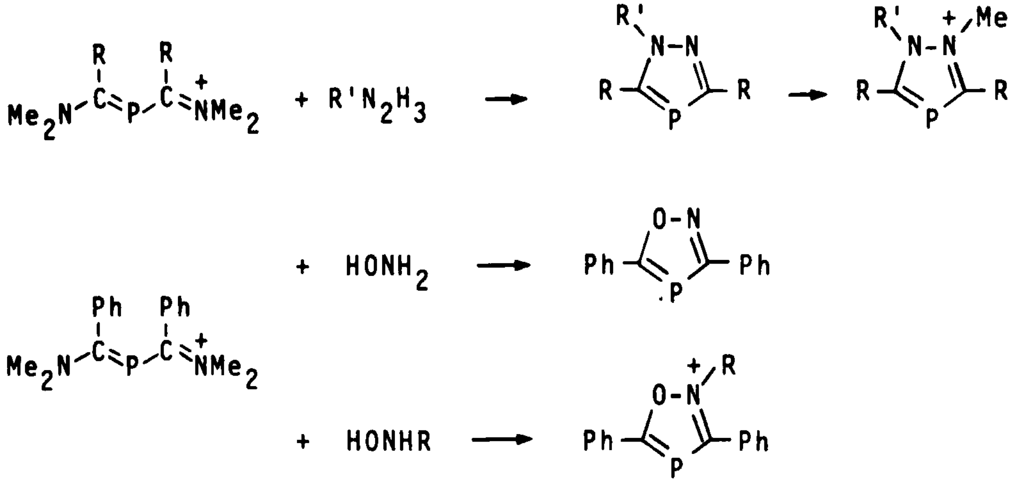


This transformation can be reverted by reacting the phosphide with imidoylchloride again.

In other cases C-addition of the anion is detected.



Of special preparative importance are nucleophilic substitution reactions at the carbon. With hydrazines and hydroxylamines they give rise to 1,2,4-diazaphospholes and -oxazaphospholes, respectively.



Although a 2-phospha-allylic system is formally still present in the heterocycles, the ring closure causes an essential change: the colour fades and the influence of R on $\delta^{31}P$ decreases. For R = H the transition from *cis,cis* to the *trans,trans* position is reflected by the sharp increase of $^{2}J_{PH}$. In the 1,2,4-diazaphospholes the phosphorus can no longer be alkylated or oxidized. The representatives with $R = H$, $R' \neq H$ are deprotonated by strong bases in 5-position. In basic media they undergo a H/D-exchange, fast in 5- and slow in 3-position. In general the 1,2,4-diazaphospholes resemble the pyrazoles or 1,2,4-triazoles in behaviour and chemistry.