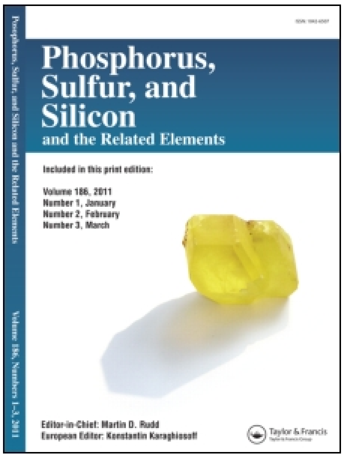

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Cyclic and Acyclic Phospha-phosphocyanines

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Cyclic and Acyclic Phospha-phosphocyanines

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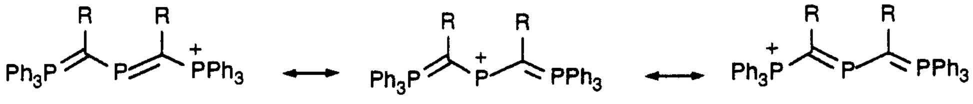
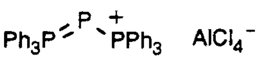
By reaction with a phosphonium silylylid one or two ylid substituents can be introduced in phosphorus trichloride or tribromide (Tetrahedron Lett. 33, 1992, 471). From the second step ionic products are obtained. The cations may be regarded as phospha derivatives of phosphocyanines (G. Märkl, 1964).



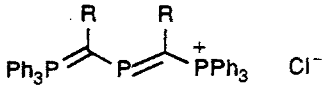
They constitute the second member (n = 1) in the series $P[(CR)_nPR_3]_2^+$ and their ^{31}P-NMR signals are found at a much lower field than those of the first members (Angew. Chem. Int. Ed. Engl. 21, 1982, 63). The opposite applies for the first two members of the phosphacyanines $P[(CR)_nNR_2]_2^+$ (Angew. Chem. Int. Ed. Engl. 24, 1985, 764).

phospha-
phosphocyanines

Schmidpeter,
Lochschmidt 1983



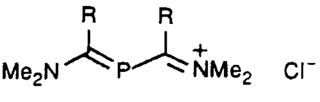
$\delta^{31}P = -174$



$\delta^{31}P =$ 304 (R = Me)
291 (R = Ph)

$\delta^{31}P =$ 264

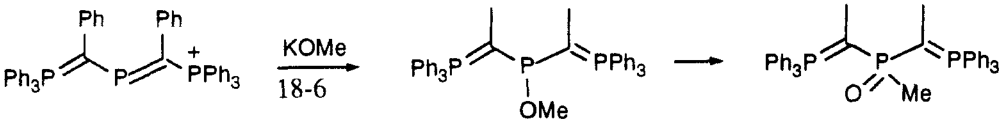
aminophosphenium



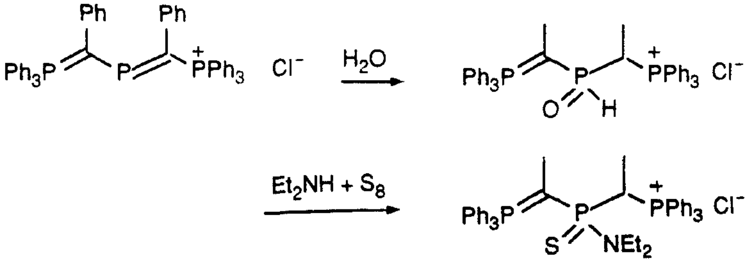
$\delta^{31}P =$ 34 (R = tBu)
116 (R = Ph)

phosphaallylic cations
Schmidpeter, Willhalm
1983

For the bisylidylphosphenium cations in accordance with the suggested bonding system cis/trans isomers are observed in solution and the two PCP-units of the E,E-isomer are almost coplanar in the crystal. The central phosphorus has phosphenium character, with a rather low Lewis acidity, however. While it does not add halide ions, it adds carbanions, hydride ions and hydroxide ions. The addition of methoxide is followed by a noncatalytic Michaelis-Arbusov rearrangement, which demonstrates the high nucleophilicity of the phosphorus.

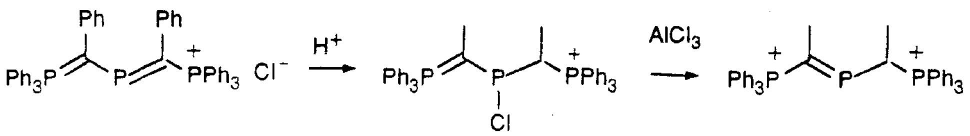


Water adds to give a cationic secondary phosphine oxide. In a similar manner the combination of a secondary amine and sulfur is added, while the amine alone is unreactive.

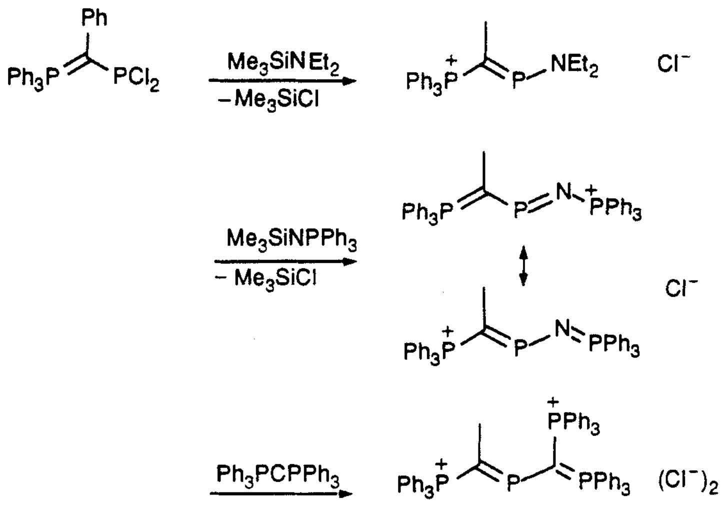


With selenium in place of sulfur the central phosphorus just becomes oxidized (Poster contribution, XIIth ICPC). The product is the first known ionic phosphinoyl halide.

When the cation is protonated (at carbon) it adds at the same time the chloride counter ion which can be abstracted again by aluminum chloride.

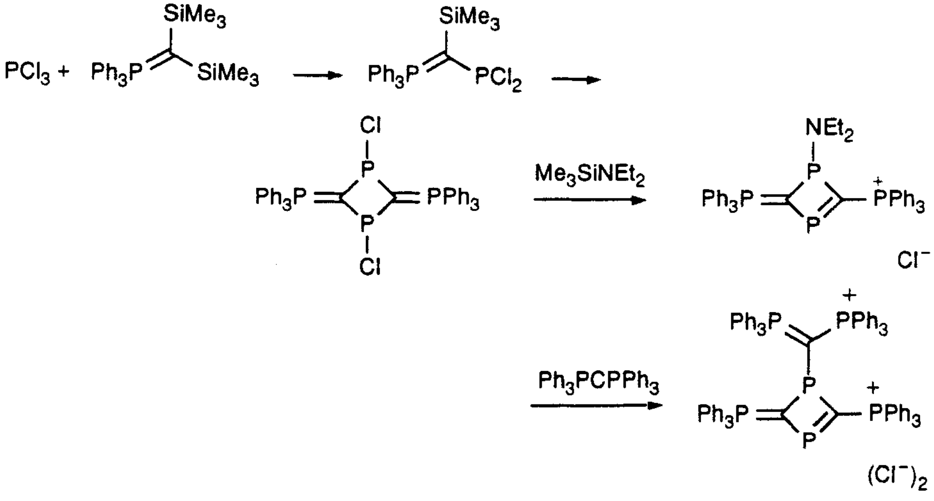


When one chlorine of the ylidylphosphorus dichloride is substituted by a secondary amine (Tetrahedron Lett. 33, 1992, 471) or a phosphine imine the product becomes ionic again. Reaction with a carbodiphosphorane results in a dication.



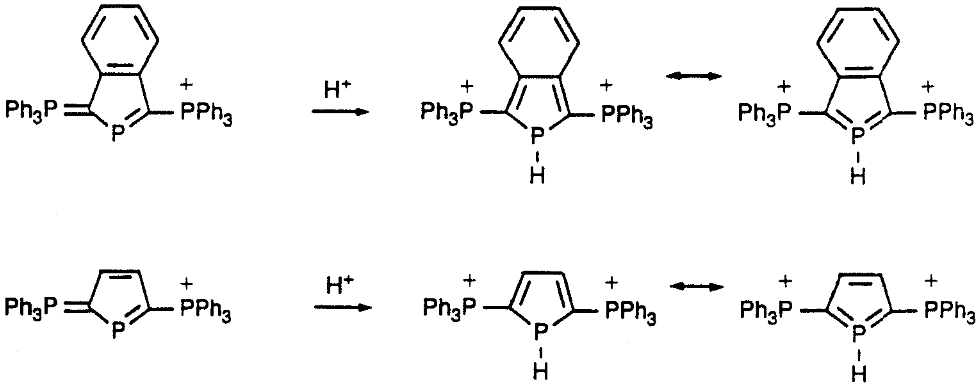
The reaction with sodium disulfide or diselenide ends up in monomeric dichalcogenides with trigonal planar phosphorus (Poster, XIIth ICPC).

Equimolar condensation of a bissilylylid with PCl_3 yields a four-membered ring, the two PCl units of which are covalent. One of them becomes ionic, however, as the other is substituted by an amine or reacted with a carbodiphosphorane.



In the latter case the CP_2 group seems fixed perpendicular to the ring, as is indicated by the nonequivalence of its phosphorus atoms.

Other cyclic versions of phospha-phosphocyanines result when the two ylid substituents are connected by an ortho-phenylene or an ethylene unit. They may also be regarded as bisphosphonio-substituted phospholide and its benzo deriative. (Angew. Chem. Int. Ed. Engl. 30, 1991, 308). In contrast to the open chain compounds above they are not sensitive to hydrolysis and they are protonated (and alkylated) not at carbon but at phosphorus.



The dications formed on protonation represent the first stable P-unsubstituted phospholes. Their ring phosphorus is planar and can thus participate in the cyclic delocalization.