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Cyclic and Bicyclic (Ph_3PCPX) Oligomers

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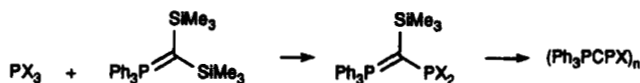
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Cyclic and Bicyclic (Ph₃PCPX) Oligomers

Alfred Schmidpeter, Hans-Peter Schrödel and Georg Jochem

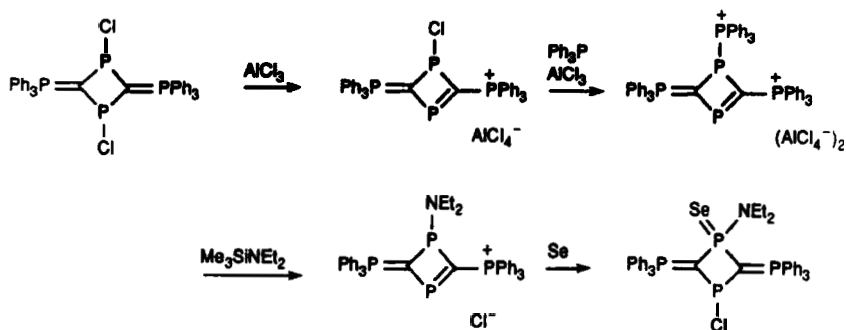
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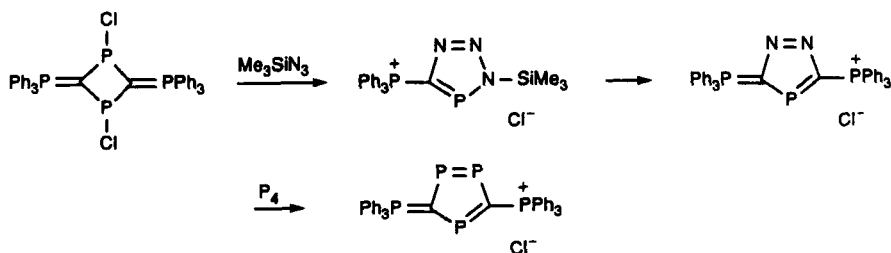
The title compounds (Ph₃PCPX)_n, X = Cl, Br and n = 2, 3, 4 are obtained from the condensation of a disilylylide and phosphorus trichloride or tribromide ¹⁻³.



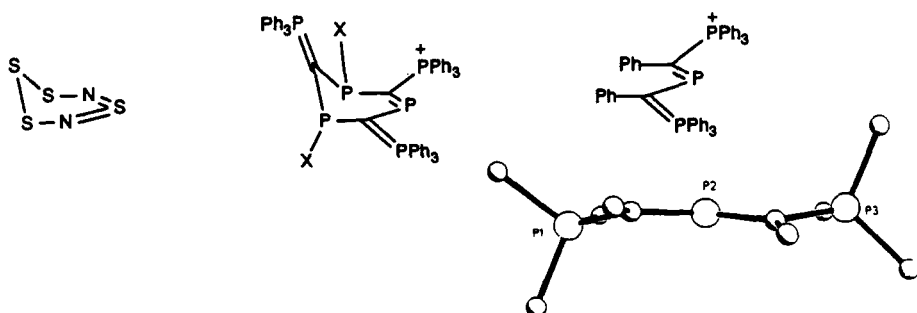
They are analogues in composition to the cyclophosphazanes (RNPX)_n with the imino groups RN exchanged for the isoelectronic triphenylphosphonium ylide groups Ph₃PC. The ylide moieties exert, however, a definitely stronger electronic effect and are thus expected to shift the systems more towards dissociation of the PX bonds. This must necessarily have its structural consequences.

According to their A₂B₂ type ³¹P-NMR spectra and also to an X-ray investigation ⁴ the dimers (Ph₃PCPX)₂ have the expected 1,3-diphosphetane structure. The PCl bonds are extremely long (220 and 225 pm) because of the strong negative hyperconjugation in the present conformation. Chloride abstraction, nucleophilic substitution, 1,3-dipolar cycloaddition and reductive ring enlargement reactions give rise to new cationic four- and five-membered heterocycles of two-coordinate phosphorus.

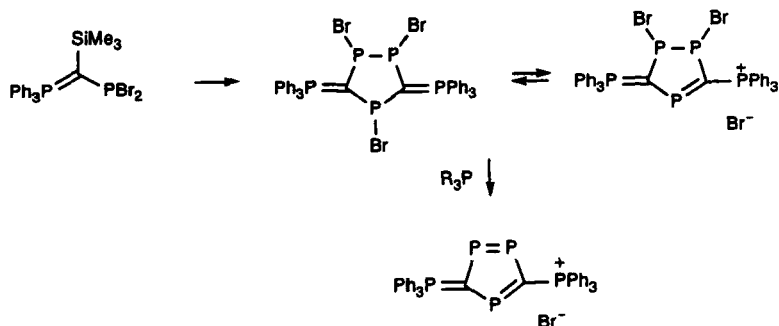




The ^{31}P -NMR spectra of the trimers $(\text{Ph}_3\text{PCPX})_3$ also at first seem to indicate a symmetric structure. They turn out, however, to result from a rapid exchange of ionic and covalent PX bonds. At lower temperatures or when the ionic halide is replaced by tosylate the spectra show all six phosphorus atoms to be nonequivalent. This suggests a structure of the cation as for the isoelectronic S_4N_2 molecule ⁵, with the two-coordinate phosphorus atom bonded like in the acyclic prototype ¹ and with the remaining two PX bonds in equatorial and axial orientation.

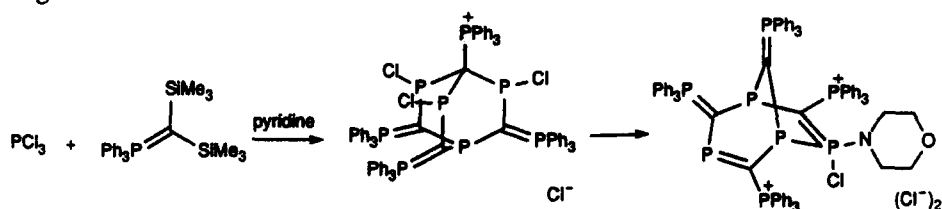


If the preparation of the bromide is performed under a little different conditions instead of the trimer $(\text{Ph}_3\text{PCPBr})_3$ a product with one ylide moiety less $(\text{Ph}_3\text{PC})_2(\text{PBr})_3$ is obtained.



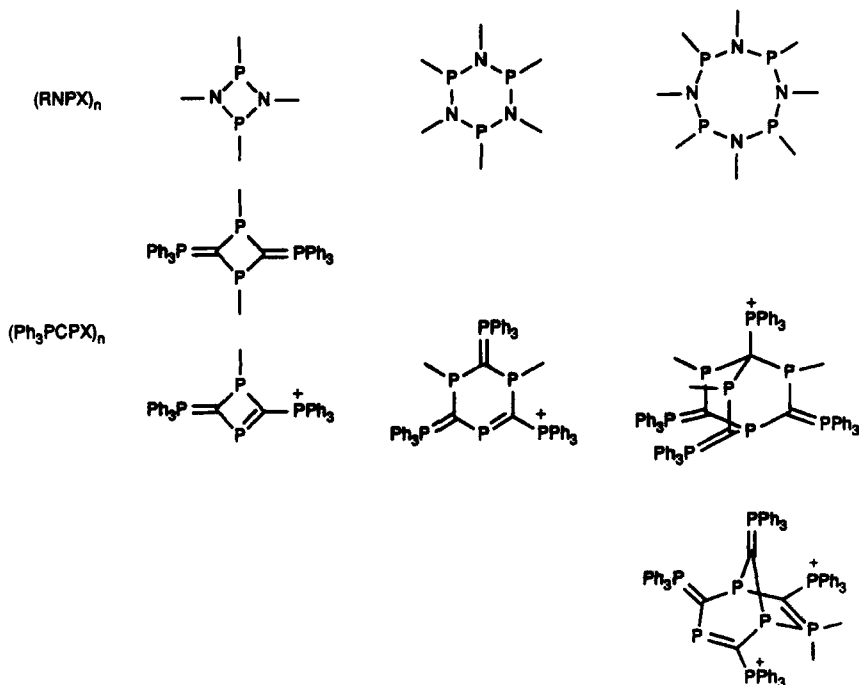
By ^{31}P -NMR spectra and X-ray investigation ⁴ it is identified as a 1,2,4-triphospholane derivative. Of the three PBr bonds that at P-4 is longest (247 pm) and is dissociated in solution. Reduction leads to the 1,2,4-triphosphole cation mentioned above.

In the chloride series we could also obtain the tetramer (Ph₃PCPCl)₄ which, however, has not the expected eight-membered ring structure. It is ionic both in the crystal and in solution, the cation in contrast to all the other cations mentioned before does not contain a two-coordinate phosphorus. As seen from the ³¹P-NMR spectra and from an X-ray investigation ⁴ it has a threefold symmetry. The remaining PCl bonds (235 pm) are still longer than in the dimer.



If one chlorine substituent in the cation is replaced for an amino group, a second dissociation takes place, the cation rearranges as to provide the new two-coordinate phosphorus the same stabilisation as in the trimer.

Summary: The isoelectronic RN/Ph₃PC exchange leads from the cyclophosphazanes to a novel series of phosphorus heterocycles (Ph₃PCPX)_n which are analogous in composition but mostly different in structure.



The tendency for dissociation is higher and increases with n . In the cation of the trimer three ylide moieties share the positive charge in a dynamic mode, in the cation of the tetramer they form bicyclic structures in which the additional bond compensates the loss of electrons and eventually allows a second dissociation.

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