

p_{π} -Double bonds between phosphorus and carbon—a challenge

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Abstract - A survey is given on the field of organophosphorus compounds concerning PC-double bonds, which after isolated observations has developed vividly in the last decade and which in the meantime yielded the synthesis of hundreds of at room temperature stable acyclic compounds. Maintopics of this paper are proofs for the assumption of real p_{π} -bonds and the unexpected affinities between phosphaaalkenes and alkenes, which can be proved by theoretically interesting pericyclic reactions and by their coordination chemistry.

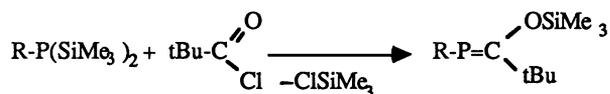
INTRODUCTION

The study of chemistry at its very beginning is like no other subject stimulated by analogous thinking. Reflecting considerations within the periodic system and doctrines as the principle of the electronic octet as well as the rule of double bonds make it possible to classify the immense abundance of compounds and to recognize interrelations when compounds are formed. Thereby it is and was neglected that the periodic system is developed from a law of nature, while the two other doctrines are only rules, the severe interpretations of which may hinder further research and the invention of entire new classes of compounds. Only fortuitous observations frequently set new impulses to research. Examples are the late exploration of the noble gas compounds and the discovery of compounds of the heavier none metallic elements phosphorus, silicon, arsen exhibiting true p_{π} -multiple bonds.

At the beginning of this was the discovery of the phosphaaetylene HCP by Gier (ref. 1), indeed stable only below -120°C . Due to the classical concept of bonding, phosphorus is linked to the carbon via three bonds, one with σ - and two with π -interactions, therewith proving the basic capability of phosphorus in forming p_{π} -bonds, though primarily restricted to low temperatures.

The synthesis of the phosphaa-methincyanine compounds as well as the different phosphabenzenes by Dimroth (ref. 2), Märkl (ref. 3), and Ashe (ref. 4) showed for the first time that these substances can exist under normal laboratory conditions via resonance stabilization of the PC-double bond.

The kinetic stabilization of the PC-double bond by means of protecting the reactive PC-bond using bulky substituents, dates back to Becker (ref. 5), who in 1976 observed the formation of a PC-double bond during the reaction of disilylphosphanes with pivaloylchloride followed by a silatropic migration from the phosphorus to the oxygen.



This report stimulated scientists in numerous countries with the consequence, that today various processes are available to introduce the PC-double bond and in the meantime hundreds of acyclic alkylidenephosphanes or - as these compounds are better termed - phosphalkenes were produced.

The most important methods include the 1,2 elimination of suitable substituted organylphosphanes, condensation reactions, and carbene additions, which are only generally mentioned since they are well known and transmitted in review articles (ref. 6 & 7).

PRESENT SURVEY

This report focusses on two aspects in detail.

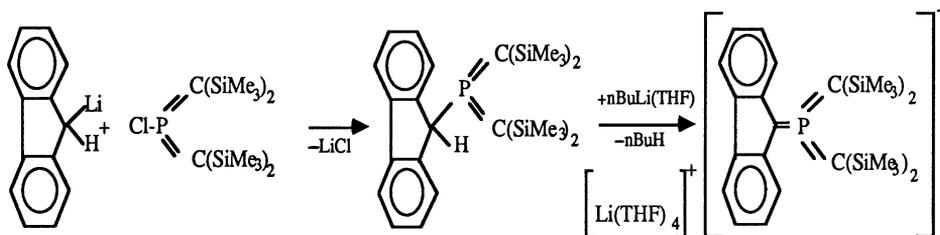
1. Proofs, which justify the assumption of true p_{π} - p_{π} -double bonds within these compounds.
2. The reactivity of the PC-double bond, which shows an amazing affinity to the CC-double bond, an additional support for a real p_{π} - p_{π} -alternating effect.

Besides parameters due to structural chemistry there are after all findings of reaction mechanisms which forces one to the assumption of true π -bondings.

X-ray investigations at about fifty compounds show PC-double bond distances between 161 and 171 pm -an average of about 167 pm- compared to the single bond distance of 185 pm. Bond distances provide no full proof in favour of true double bonds. Moreover one needs a sufficient high barrier for the energy of activation of the rotation process round the PC-axis and of the in plane vibration at the phosphorus which in case of a unequally substituted carbon of the phosphalkenes causes the existence of stable cis/trans (E/Z) isomers. Reliable evidence of E/Z isomers was given by the separation and isolation of the 2,4,6-tritert.-butylphenyl-phenylmethylene-phosphanes (ref. 8 & 9). The more stable stereoisomer melting at 148 °C shows with respect to the X-ray analysis the E-configuration, the equally analysed cis-isomer melts at 84 °C. As distinguished from other investigated phosphalkenes the two stereoisomers are stable in solution with respect to their configurations even upon warming. Only when exposed to radiation they can be interconverted and the equilibrium shows 40 % E versus 60 % Z isomer. Just so as the X-ray parameters -distances and angles- the ^{13}C -nmr spectroscopic facts support the p_{π} -bonds within the phosphalkenes. The sp^2 hybridization at the carbon atom gives characteristic δ -values about 170 ppm.

The PC-double bond has two reactive centres, the P-atom and the π -bonding. Reactions at the phosphorus centre with ozone, sulfur, selenium or selected carbens causes an oxidative increase of the coordination number maintaining the double bond. Here methyleneoxo-, methylenethiooxo-, methyleneselenooxo and bismethylenephosphoranes are formed, which exhibit a trigonal planar geometry due to X-ray investigations.

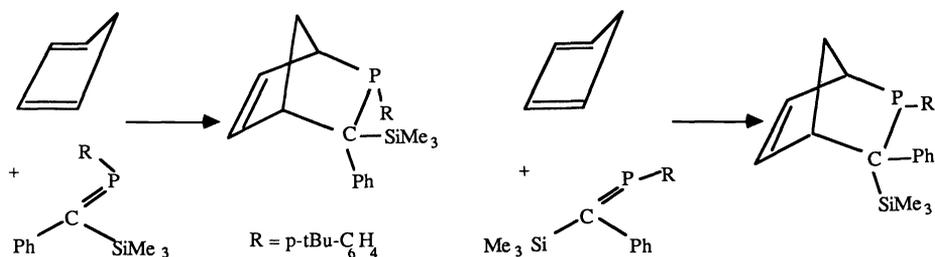
Especially attractive are the bismethylenephosphoranes since they have two carbon atoms doubly linked to the phosphorus and due to a propeller-screw like orientation of the attached silylgroups the molecule shows chirality in the solid state. The P-fluorenyl substituted molecule can be deprotonated using butyllithium to form the trimethylenephosphate anion now exhibiting three double bonds to the carbon atoms (ref. 10).



It is characteristic for the π -bond of phosphalkenes not to undergo a Wittig-reaction and in addition due to low polarity there is no significant tendency for a dimerisation. Some derivatives of the phosphalkenes undergo a [2+2]-cycloaddition forming diphosphethanes, preferably 1,3-diphosphethanes and in some cases 1,2-diphosphethanes are formed. The addition of proton active reagents always shows the proton at the carbon, the anionic part at the phosphorus atom.

Much more similarity to olefins is noticed with respect to quite a number of [2+n] cycloadditions to phosphalkenes. The Diels-Alder reaction was investigated extensively, since the stereochemical control of educts and products gives evidence for a certain reaction mechanism.

For example, cyclobutadiene reacts with *p*-tert.butylphenyl(trimethylsilyl)-phenylphosphalkene forming only the *exo*-product, indicating a stereochemical clean [2+4] cycloaddition. The cycloaddition product maintains the original configurations of the educts. This important test supports a synchronous reaction mechanism preserving the orbital symmetry (ref. 11).



Particularly impressive is the analogy between PC- and CC-double bonds within compounds which contain several PC- and partly in addition CC-double bonds in the same molecule. With respect to the butadiene it could be demonstrated that up to three carbon atoms in different positions can be substituted by phosphorus and that reactivity as well as stereochemistry of these phosphabutadienes are very similar to the pure carbon compounds (ref. 12, 13, 14, & 15).

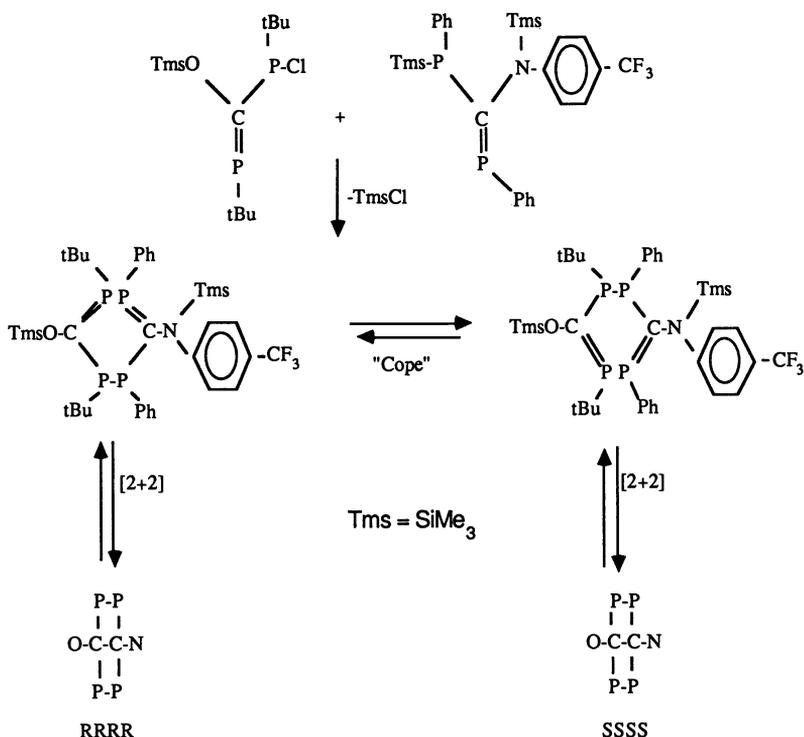
Even more in line with carbon chemistry are a number of phosphahexadienes showing the theoretically interesting phenomenon of a valence isomerisation. Compounds exhibiting the 1,3,4,6-tetra-phosphahexadiene structure can be synthesized in a reaction of organyl-bis(trimethylsilyl)-phosphanes with phosgene or isocyanide-dichlorides differing in a characteristic way.

The compound oxygen substituted at the bridging C-atom immediately cycles forming a tetraphosphabicyclo-[2,2,0]-hexane structure while the N-substituted compound synthesized with isocyanide-dichloride shows due to ^{31}P -nmr spectroscopic investigations the phenomenon of a fluctuating bond system (ref. 16 & 17).

The significant difference between the oxygen and nitrogen substituted compounds caused the synthesis of a mixed substituted compound containing in one half oxygen in the other nitrogen bonded substituents to the bridging C-atoms. As a result there are both structures, the bicyclic and the open tetraphosphahexadiene molecule in solution linked via a cycloaddition and cycloreversion equilibrium. Supplementary the hexadiene molecule shows the phenomenon of a Cope-rearrangement. It was possible to isolate the two compounds and to elucidate the structures by X-ray proving the results of the spectroscopic investigations.

The intensive study of the stereochemistry, the thermodynamic and kinetic parameters of the two components within that system indicate the following:

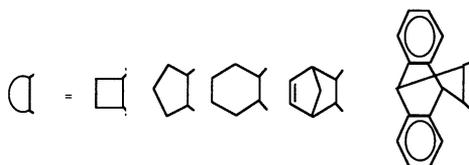
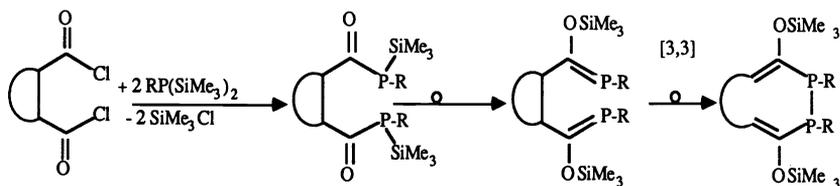
The tetraphospha-Cope-rearrangement totally respond to the Woodward-Hoffmann rules for orbital controlled synchronous processes. The energy diagram points out that the rearrangement via a quasi aromatic transition state does not include the bicyclohexane structure. The valence isomerisation -tetraphosphahexadiene/bicyclohexane- is governed by an independent equilibrium showing a different activation energy (ref. 17).



The first discovered Cope-rearrangement which takes place with the tetraphosphahexadiene is no typical case, as can be seen from the following examples:

1,6-diphosphahexadiene synthesized from succinic acid dichloride using silylphosphanes rearranges under mild conditions displaying a [3,3] sigmatropic shift in opening a CC-bond in favour of a PP-bond ending up as divinyl-diphenyl-diphosphane (ref. 18).

A number of cyclic 1,2-dicarboxylic acid dichlorides follow the same line when reacted with silylphosphanes. The corresponding acid chlorides of cyclohexane, cyclobutane and other ring compounds react quantitatively under ring opening which means CC-bond splitting in favour of the corresponding enlarged cyclic diphosphanes, the structures of which could be confirmed by X-ray (ref. 17&19).

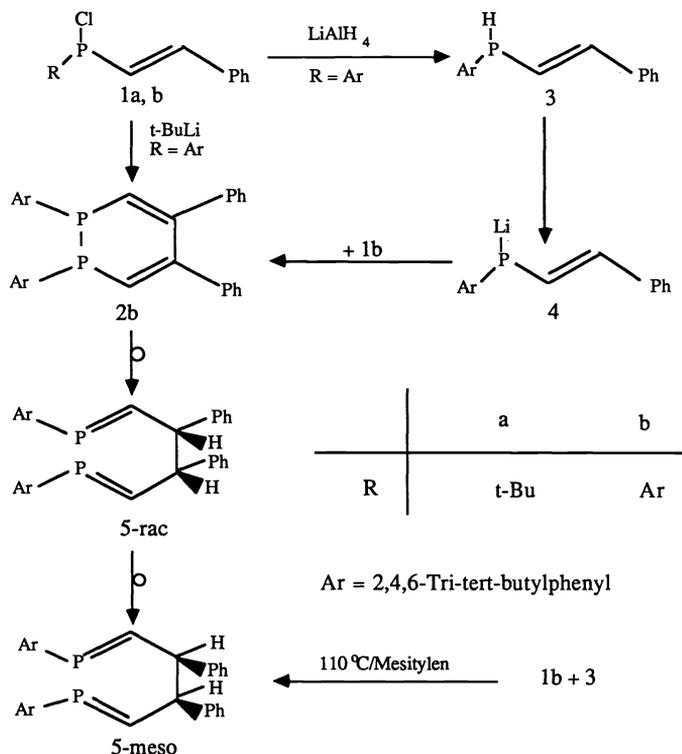


R = as one chooses: phenyl, c-hexyl, t-butyl or silyl

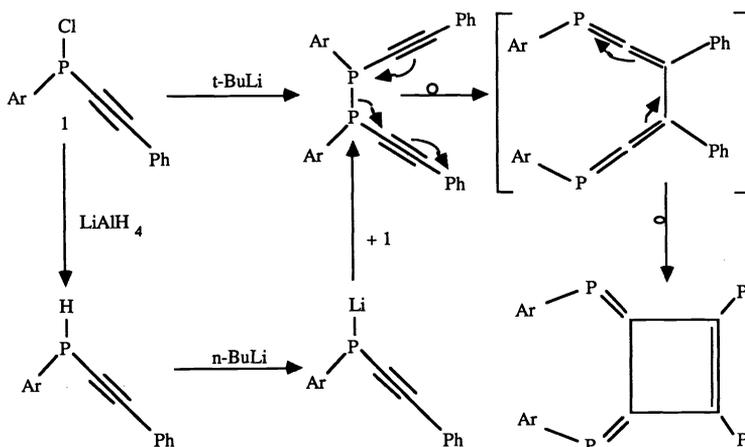
Cope-rearrangements could be discovered so far with compounds exhibiting phosphahexadiene structures, precisely with 1,3,4,6-tetraphospha- and diphospha-hexadienes with phosphorus atoms in positions 1,6 (ref. 17) -1,3 (ref. 20) and 3,4 (ref. 21).

These pericyclic reactions always followed the track of a change from the double coordinated to the more stable triple coordinated species.

Evidence for an inverse Cope rearrangement in which diphosphanes can be transformed into phosphaaalkenes was given for the first time during the synthesis of 1,2-distyryl-1,2-bis-(2,4,6-tri-tert.-butylphenyl)diphosphane, which can be easily converted to the phosphaaalkene even at 40 °C (ref. 21).



Another example of an inverse phospho-Cope-rearrangement was discovered recently as a valence isomerisation of a 3,4-diphospho-1,5-hexadiene which was converted to 3,4-bis(phosphamethylene)-cyclobutene from a 1,5-hexadiene by thermal isomerisation (ref. 22).



This extraordinary analogy to the carbon chemistry can finally be proved by the existence of cumulated bond systems including PC-double bonds.

Mono- (ref.23,24) and diphosphaaallenes (ref.25,26,27) could be synthesized as well as monophosphacarbadiimides (ref.23,28,29,30) and phosphaketenes (ref. 31), which like phosphaaalkenes proved to be exceptionally valuable ligands for transition metal complexes (for example:ref.32,33,34,35,36). These ligands can be coordinated via the free electron pair at the phosphorus or via the π -system itself. With bimetallic complexes both types of coordination are possible.

The results of these investigations can be summarized as follows: With respect to the dogma in chemistry the exceptions from the classical rule of double bonds have become so numerous in the meantime that it can no longer be maintained.

With respect to preparative chemistry of the main group elements one may ascertain, that phosphalkenes have become valuable new supplies for quite a selection of new compounds for instance via cycloadditions. Additionally the coordination chemistry gained a lot of unusual promising ligands.

There still remains a challenge for applied chemistry, to investigate if and where the results of this basic research can be used technically.

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