Phosphaalkynes: from monomers to polymers

Thesis

Author: Tibor Hölzl
Supervisor: Dr. Tamás Veszprémi

BME Department of Inorganic and Analytical Chemistry

2010
1. Introduction

Until the last decades it was commonly accepted that the elements with higher atomic number do not form multiple chemical bonds. This was explained by the unfavored overlap of their \( p_z \) orbitals. This rule is now disproved, as during the last two decades several compounds with \( \text{C}=\text{Si}, \text{C}=\text{P}, \text{Si}=\text{Si, Ge}=\text{Ge}, \text{P}=\text{P} \) or other similar double bonds were synthesized. However, these compounds are generally reactive, thus they can be used as precursors in the synthetical chemistry. There are two commonly used methods to stabilize these molecules. First, the double bonds are protected by bulky substituents, such as \( \text{t}-\text{butyl} \) or \( \text{supermethyl} \). Second is the delocalization of the double bond, by e.g. incorporating it in an aromatic framework.

Study of unsaturated compounds has a tradition in the Department of Inorganic and Analytical Chemistry of the Budapest University of Technology and Economics. During my work I have studied the formation, structure and in some cases the reactions of phosphaalkyne dimers, trimers and polymers.

I have joined to the quantum chemistry group of Professor Tamás Veszprémi in 2001, as a first year student. My first work was the study of the structure and aromaticity of 1,4-diphosphatriafulvene. This compound has been assumed by Yoshifuji et al. as an intermediate during the preparation of 1,3,6-triphosphafulvene. 1,4-diphosphatriafulvene can be regarded as a dimer of phosphaethyne, therefore our second goal was the study of the possible dimerization pathways leading to this compound. However, we have realized that only a few dimers and the corresponding dimerization pathways were reported in the literature. The published results could not interpret all the experimental observations, most notably the fact that phosphaethyne polymerizes rapidly, even at low temperatures. We have published the dimerization paths in the *Chemistry-An European Journal*, while the aromaticity of phosphatriafulvenes were reported in the *Journal of Molecular Structure (Theochem)*.

1,3,6-triphosphafulvene, is one of the most interesting phosphaalkyne trimer has been synthesized by Yoshifuji et al. in 2001. We have studied the electronic structure of this compound and the formation reaction paths using quantum chemical computations. We have also studied the synthetically important derivatives. These results were published in the *Organometallics*.

Study of phosphorus ylides derived from 1,3,6-triphosphafulvene were concluded in cooperation with Professor Yoshifuji. The results were published also in the *Chemistry – An European Journal*.

During the last decades several remarkable discoveries were made in the research area of carbon containing polymers. Conductive polymers can be prepared starting from poly-acetylene, while the „preparation” of graphene opened a new, fascinating and rapidly developing research area.
Graphane, the hydrogenated graphene has also been synthesized successfully. Similarly to the poly-acetylene, graphe can also be considered as a polymer of acetylene. On the other hand, it is also well known that phosphaethyne, the basic compound of phosphaalkynes polymerizes easily. However to the best of our knowledge the structure of the polymer has not been investigated previously. Therefore our aim was to investigate phosphaethyne polymers using quantum chemical methods. This work was published in the *Comptes Rendus Chimie*.

2. Literature summary

Phosphaethyne (its formula is HCP), the basic compounds of phosphaalkynes was synthesized first in 1961 in a special reactor. Using infrared spectroscopy it was concluded that there is a real triple bond in this compound. This is one of the first reported case, where a heavier element forms a real multiple bond. Phosphaethyne is a colorless gas, which is pyroforic with water or oxygen. This compound polymerizes slowly at -124 °C, and more rapidly above -80°C. During the polymerization a black product is formed, which is also pyroforic. However after aging the polymer becomes considerably more stable. The element-analysis indicates that this is a real polymer of phosphaethyne.

The detailed study of phosphaethyne showed that the carbon-phosphorus chemical bond is notably short, only 1.542Å, compared to the length of 1.67Å of a typical carbon-phosphorus double bond. Moreover the molecule has a linear shape. These results support the existence of a real triple bond. The dipole moment of phosphaethyne (0.39D) is considerably smaller than that of the hydrogen-cyanide (2.975D). This is explained by the smaller electronegativity of phosphorus atom.

Several new, more feasible synthetic methods were developed instead of the complicated original one. These can also be used to prepare substituted derivatives of phosphaethyne. Among the substituted phosphaalkynes most important compounds are protected kinetically by bulky substituents, such as t-butyl or supermesityl (2,4,6-tri-t-butylphenyl) groups. These can be handled easier than phosphaethyne and can be used to conclude several interesting reactions. Most interesting reactions are the formation of the oligomers, as indicated in Figure 1.
Figure 1. Phosphaalkyne oligomers and their supposed formation pathways.

Only one dimer has been synthesized in its free form: kinetically protected 1,4-diphosphatriene (i) was prepared by Yoshifuji et al. Other dimers are supposed as intermediates in chemical reactions. It is interesting to note that during the polymerization of phosphaethyne no dimer or other oligomer could be detected, even using mass spectrometry. At the same time 1,3- and 1,4-diphosphacyclobutadienes (ii and iv) and their bent isomers have several (mainly transition metal) complexes. Their general preparation method is illustrated in Figure 2.
Figure 2. Preparation of 1,3-diphosphacyclobutadiene complexes.

The reaction pathways leading to the diphosphacyclobutadienes were determined by Dr. Minh Tho Nguyen and his group in the middle of 90's. However the reaction barriers were notably high (more than 200 kJ/mol), hence these results can not interpret the observed high reactivity of phosphaethyne.

Two stable phosphaethyne trimers were prepared with bulky protective groups. 1,3,5-triphosphabenzenes (vi) has been prepared using catalyzed trimerization of t-butyl-phosphaethyne. The relative stability of this compound is explained by the existence of an aromatic ring. 1,3-diphosphacyclobutadiene is expected to be an intermediate during the preapration of this compound. The mechanism of the addition of phosphaethyne to 1,3-diphosphacyclobutadiene has been explored using quantum chemical methods. It is interesting to note that among the compounds with (CH)₃P₃ formula and a six-membered ring most stable is the 1,2,3-triphosphabenzenene, second most stable is the 1,2,4-triphosphabenzenene and than the synthesized 1,3,5-triphosphabenzenene. This seemingly contradiction disappears when the effect of the large substituents is also taken into account, as these prefere the farthest position. Thus with the experimentally applied t-butyl substituents most stable is the 1,3,5 isomer.

Figure 3. Supposed synthetic mechanism of 1,3,6-triphasphafulvene.
1,3,6-triphosphafulvene (vii) has been synthesized by Professor Yoshifuji starting from supermesityl-phosphaethyne and phosphanylidene carbonoid (Figure 3). This compound is a fulvene, and can not be described with the (CH)$_3$P$_3$ formula. It is interesting to note that during the preparation an acetylene byproduct has also been observed. Its appeareance can be interpreted by assuming 1,4-diphosphatetrafulvene as an intermediate.

Several phosphaethyne tetramers were successfully prepared. Among these the most known is the tetraphosphacubane, which was synthesized by tetramerization of t-butyl-phosphaethyne. The reactants were heated without catalyst to proceed this reaction. Byproducts ix, x and xi were observed. The structure of these compounds suggests that 1,2- and 1,3-diphosphacyclobutadienes appear as intermediates in this reaction.

3. Computational methods

Quantum chemical computations were carried out using the Gaussian 03, Turbomole 5.8, Molcas 6.4 and 7.2, and AMICA program packages. Molecules, molecular orbitals and molecular electrostatic potentials were visualized using the Molden, Jmol and gOpenMol programs. Closed-shell compounds were optimized using density functional theory (with B3LYP functional), while accurate thermochemical data were obtained using the CBS-QB3 method. The results were compared to that of other high level quantum chemical methods (CCSD(T)). Multi-reference methods (CASSCF, CASPT2, MR-ACPF-2) were applied in the case of open-shell systems.

Aromaticity was analyzed using different aromaticity indices (based on the bond lengths, isodesmic reactions and also the nucleus-independent chemical shifts). Bonding patterns were analyzed using the Mayer- and Wiberg-bond indices, natural bond orbital analysis as well as the electron localization function.

4. Results

The most important phosphaethyne dimers are depicted in Figure 4. The global minimum on the potential energy surface is 1,2-diphosphatetrahedrane, which is followed by diphosphatetrahedrane. These are similar to the acetylene dimers. Two bond-stretch isomers exist in the case of 1,2-diphosphacyclobutadiene (compounds 6 and 7). There are carbon-carbon and phosphorus-phosphorus double bonds in the more stable isomer, while a pair of carbon-phosphorus double
bonds exist in the less stable one. No transition structure could be located between the two isomers. The E and Z isomers of 1,4-diphosphatriafulvene are both less stable than 1,2-diphosphatriafulvene. The reason of this finding is that in the latter compound both phosphorus atoms are in the three membered ring, and small bonding angles are more preferred around phosphorus than around carbon. A new type of triafulvene was also observed (17). There is a formally trivalent and also a formally pentavalent phosphorus atom in this compound, which are connected by a formal triple bond. The detailed analysis showed however that there is a double bond and a zwitterionic (ylide-like) structure in this molecule.

Aromaticity of triafulvenes was analysed in detail. The different aromaticity indices showed that aromaticity increases when the exo carbon is substituted by phosphorus, while ring phosphorus atom has the opposite effect. All the studied phosphatriafulvenes are partially aromatic compounds, except the new type of triafulvene. The most important feature of this latter compound is that it is a formal adduct of an acetylene and diphosphorus, and is expected to be synthesized in this way. Diphosphorus as a synthetic reagent has been reported recently.

Our multi-configurational computations indicated the existence of open-shell, biradical isomers (Figure 4). The closed shell description is not adequate in this case, and can only be regarded as a hypothetical, model structure. The more stable, biradical isomer of 1,2-diphosphacyclobutadiene contains more balanced bond lengths than the closed-shell model compound. However the bond stretch isomers still exist as separate minima on the potential energy surface. Several closed shell reaction mechanisms were found. Among these 1,4-diphosphatriafulvene is formed by the smallest activation barrier of 145 kJ/mol. However the open-shell reaction paths are more favored kinetically (Figure 5).

Phosphaethyne dimers are relatively small molecules, thus it is expected that all the low energy structures are found. On the other hand it would consume considerably high computational resources to locate all the low energy phosphaethyne trimer. There are 209 minima on the acetylene trimer (benzene) potential energy surface. The number of the possible isomers increases dramatically as three C-H groups are substituted by phosphorus. Previously only phosphaethyne trimers with (HC)₃P₁ formula were studied. Relative Gibbs-free energies of phosphaethyne trimers compared to the global minimum are available in figure 6. As 1,3,6-triphosphafulvene has been synthesized, and can not be described with the previous formula, we have analyzed it and its synthetically interesting derivatives.
Figure 4. the most stable phosphaethyne dimers and their relative energies compared to the separated monomers. Numbering indicates the order of the stability. Compound 1 is the most stable one.
**Figure 5.** Open-shell dimerization reaction paths.

**Figure 6.** Relative Gibbs-free energies of phosphaethyne trimers compared to the most stable 1,2,3-triphosphabenzene. The numbers indicate the positions of the phosphorus atoms.

Reaction paths of 1,3,6-triphosphafulvene formation from 1,4-diphosphatriafulvene and phosphaethyne as well as from phosphanylidene carbenoid and phosphaethyne were also determined.
This latter can be regarded as a formally lithium-bromide catalyzed reaction path. In the case of the non-catalyzed reaction path the effects of the methyl and butyl substituents were also investigated. Reaction activation barriers increase with the size of the substituents, and also the intermediates and the products became less stable, as expected.

It has been shown that in the lithium-bormide catalyzed reaction 1,4-diphosphatriafulvene can also be formed. This compound could not be observed during the preparation of 1,3,6-triphosphafulvene. However using $^{31}$P NMR spectroscopy the signals of an intermediate were observed. These are in good agreement with that of the exo-protonated 1,4-diphosphatriafulvene. This intermediate also explains the existence of the byproduct on Figure 7.

![Diagram](https://via.placeholder.com/150)

Figure 7. Formation of 1,3,6-triphosphafulvene (III) and the byproduct (IV).

Formation of phosphorus ylides from 1,3,6-triphosphafulvene has been studied in cooperation with professor Yoshifuji. This compound is exceptional, as there is a hydrogen substituent on the phosphorus atom and in contrast to similar compounds it does not isomerize. The synthesized compounds were modeled using the molecules on Figure 8. It is interesting that the phosphorus ylide (8) is aromatic to a similar extent as 10. On the other hand, 1,3,6-triphosphafulvene is less aromatic.
Thus the driving force during the preparation is the appearance of the aromaticity. During the isomerization of 8 to 11 or 12 the aromaticity decreases, therefore these are not as favored processes as in other phosphorus ylides.

![Phosphorus ylide structures](image)

**Figure 8.** Phosphorus ylide (8) and other model compounds.

The high spin radical compounds can be important building blocks in organic magnets or in spintronic devices. Several compounds are known with 1,3,5-trimethylenebenzene sub-unit, however the chemical modification of this basic compound by heteroatom substitution has not been studied. Therefore we have studied the nitrogen, phosphorus and arsenic substituted compounds. The 2,4,6-trimethylene-1,3,5-triphosphabenzenes can formally be derived from 1,3,5-triphosphabenzenes.

All the compounds have high spin (quartet) ground state. However the doublet-quartet gap is reduced as heavier substituent atoms are applied. By substitution the position of the unpaired electrons can also be tuned.

Phosphaethyne polymers were studied in the last part of my thesis. The one dimensional phosphaethyne polymer analogous to the cis-polyacetylene and the graphane-like two dimensional polymer has also been investigated. This latter material is also analogous to the black phosphorus. Its energetic stability is similar to that of the analogous acetylene and phosphorus polymers. Therefore it is expected that graphane-like moieties are present in phosphaethyne polymers.
Figure 9 Graphane-like two dimensional polymers of acetylene, phosphaethyne and diphosphorus. The polymerization energies per monomer units are also depicted.
5. Thesis points

1. I have found in total 12 low energy closed-shell and 5 open shell minima on the phosphaethyne dimer potential energy surface. In the case of the latter the closed-shell structure was also computed as a hypothetical, model structure.

2. The computations indicated that the global minimum of the phosphaethyne dimer potential energy surface is 1,2-diphosphatriafulvene. It was pointed out that the two mesomeric 1,2-diphosphacyclobutadienes are separated minima on the potential energy surface, even with high-level ab-initio methods. A new type of triafulvene was found, where phosphorus is attached by a triple bond to an unsaturated ring.

3. Several reaction paths on the potential energy surface were also determined. Two head-to-head, one head-to-tail and three other dimerization reaction paths were found, all with high activation barriers. This suggests that different equilibrium states of C₂P₃H₂ potential energy surface are usually kinetically stable. It has been pointed out that LiBr plays the role of catalyst in the closed-shell reaction path, and the activation energy of the first step is fairly low (only 44.8kJ/mol). All the four possible reaction channels of this reaction yields 1,4-diphosphatriafulvene with a fairly low activation Gibbs-free energy. This result (together with the thermodynamic and kinetic stability of 1,4-diphosphatriafulvene) indicates that reactions from substituted phosphanylidenecarbenoid via 1,4-diphosphatriafulvene are accessible processes. An open-shell head-to-head reaction path has been found with 98.9 kJ/mol activation barrier leading to 1,2- and 1,3-diphosphacyclobutadiene, indicating that in contrast to the previous studies, polymerization of HCP, and tetramerization of t-Bu-phosphaethyne (yielding derivatives of tetraphosphacubane and other tetramers) follows open-shell reaction path. While the dimerization of HCP follows head-to-tail mechanism, bulky substituents causes the enlargement of its activation energy, and both head-to-head and head-to-tail mechanisms are possible.

4. I have investigated several synthetically interesting trimers, most notably the derivatives of the synthesized 1,3,6-triphosphafulvene. Several new trimers were identified, many with synthetic potential.

5. I have identified the molecular mechanisms of the formation reactions. The analysis demonstrated that two independent reaction mechanisms leading to 1,3,6-triphosphafulvene exist, and both can occur during the experiment. The first mechanism starts from the 1,4-diphosphatriafulvene, First step is the rate determining with an energy barrier of \(~100\) kJ/mol, depending on the substituents. Also a slightly more favored biradical reaction pathway was identified, which can be realized physically, while the closed-shell path did not exist.
possibility is a head-to-tail reaction of phosphanylidenecarbene and two phosphaalkyne molecules. Here, the first step is also the rate determining step with a tiny energy barrier of only 4 kJ/mol (virtually a barrier-free reaction). Protonated form of 1,4-diphosphatriafulvene was suggested to play an important role in the synthesis of 1,3,6-triphosphafulvene, and it explains the occurrence of the alkyne byproduct.

6. Formation of ylides from 1,3,6-triphosphafulvene was investigated in cooperation with Professor Yoshifuji. It was demonstrated that 1,3,6-triphosphafulvene is a promising material for preparation of phosphorus ylides bearing a P–H bond. My calculations suggest the ylide properties of experimentally synthesized compounds. The π-electron accepting effect of 1,3-diphosphacyclopentadiene moiety seems to be stabilized effectively the structure of these molecules.

7. I have investigated an interesting, 1,3,5-triphospha benzene based triradical compound. The effect of the substitution of the ring CH groups of 1,3,5-trimethylenebenzene is studied using quantum chemical methods. The CASPT2/CASSCF(9,9)/ANO-RCC method is used to determine the energetic parameters and also to probe the wavefunctions. The ground state of these compounds is consistently a quartet, which can be well described using single determinantal methods. Therefore the electronic structure of the quartet states is analyzed using the B3LYP functional in conjunction with the electron localization function, natural charges and Wiberg-indices. Substitution of the ring CH groups of 1,3,5-TMB by nitrogen, phosphorus or arsenic invariably reduces the quartet-doublet energy gap in this order. Accordingly, this provides us a possibility to tune the band gap in triradicals by chemical modifications. Also, the phosphorus and arsenic atoms tend to localize the unpaired electrons on the ring, while the nitrogen atoms tend to form electron pairs. Therefore the position of the unpaired electrons in these triradicals can also be modified chemically by substitution.

8. The thermodynamic stability, electronic and structural properties of cis-polyacetylene and graphane-like phosphaethyne polymers were studied using density functional theory methods. Their properties were compared to oligomers and polymers of acetylene and diphenanthrene. These compounds are thermodynamically stable, however, especially the one dimensional cis-polyphosphaethyne needs also kinetic stabilization by bulkier groups to be synthesized. Phosphaethyne-graphane may present in the originally prepared polymer of phosphaethyne. Its promising properties (e.g. layered structure, large surface area, large band gap, chemically tunable properties by changing the acetylene: phosphaethyne ratio in copolymers) imply a wide range of applications.
6. Possible applications

These results interpret several experimental findings. Moreover they help to optimize the reaction conditions to obtain a given phosphaalkyne dimer or trimer. Several, synthetically interesting molecules were identified. We hope that these will be synthesized in the close future. Phosphaalkyne polymers can be used in material science as an organic semiconductor or as a two dimensional substrate. The nitrogen, phosphorus and arsenic analogue of 1,3,5-trimethylenebenzene can be important building blocks in organic magnets and spintronic devices.
7. Publications underlying the thesis

1.) S. Ito, H. Miyake, M. Yoshifuji, T. Höltzl, T. Veszprémi: 


**Other publications**


5.) T. Höltzl, E. Janssens, N. Veldeman, T. Veszprémi, P. Lievens, M.T. Nguyen: The Cu_{2}Sc Cluster is a Stable $\sigma$-Aromatic Seven-Member Ring Chem. Phys. Chem. 9, 833 (2008)


Presentations


2.) Foszfaetin dimerek képződése, XI. MTA Anyagtudományi Munkabizottsági Ülés (2006. June)

3.) Foszfaetin dimerek és trimerek képződési, MKE Szerves- és Gyógyszerkémiai Szakosztályának QSAR és Modellezési Szakcsoportja és az MTA Szegedi Akadémiai Bizottságának Kemometria és Molekulamodellezés Munkabizottsága által szervezett tudományos ülés (KEMOMO konferencia
Szeged, 2008. május 8.)

4.) Foszfaalkinek kémiája, Oláh György Doktori Iskola 2009. évi konferenciája előadás (Budapest, 2009. február 4.)

5.) Phosphaalkynes: from monomers to polymers, 7th European Workshop of Phosphorus Chemistry (Budapest, 2010. március 25, 26.)

Posters


2.) Foszfaetin dimerek és trimerek képződése – mechanizmus és elektronszerkezet Oláh György Doktori Iskola 2009. évi konferenciája (Budapest 2008. február)