

**THE ROLE OF DELOCALISATION IN
STABILITY AND REACTIVITY OF
PHOSPHORUS COMPOUNDS**

PhD theses

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1. Introduction

During the last decades the chemistry of the main group elements (for example phosphorus) has become an intensively developing area of the chemical research. Consequently a plethora of compounds with unusual structure and unique chemical behaviour could be synthesised and characterised with experimental techniques. Besides these experiments the theoretical studies allows deeper understanding the electronic structure and thus the physical and chemical characteristics of these molecules.

During the three years of my PhD studies I have dealt with several phosphorus containing compounds whose common characteristic is the delocalised electronic structure. In the first part of my research I carried out investigations on stabilisation of highly reactive and unstable phosphinidenes, subsequently I suggested computationally a new synthetic way for phosphinidene generation. The starting materials of this method are annelated 1,3,2-diazaphospholenes. A further topic of my studies was the structure and aromaticity of the recently synthesised 1,3,2-diazaphospholenes and some of their monoannelated analogues. In order to better understanding the structure and reactivity of heteropentadienes, I performed quantum chemical calculations on these compounds.

- ^{E10} **Benkő Z.**, Nyulászi L.: Tírány és szelenírány gyűrík szerkezete és stabilitása, *MTA Szervetlen és Fémorganikus Kémiai Munkabizottsági ülés*, 2007. május 10. Budapest
- ^{E11} **Benkő Z.**, Nyulászi L.: Foszfínidének „komplexei”: új lehetőség foszfínidén előállítására, *XXX. Kémiai Előadói Napok*, 2007. október 29-31. Szeged
- ^{E12} **Benkő Z.**, Nyulászi L.: Különleges vegyületek és reakció-mechanizmusok a foszfórkémiában, *BME Oláh György Doktori Iskola 5. Doktoránskonferenciája*, 2008. február 2. Budapest
- ^{E13} **Benkő Z.**, Új vegyületek, érdekes reakciómechanizmusok a foszfórkémiában, *KeMoMo-QSAR tudományos ülés*, 2008. május 8-9. Szeged

Poster presentations

- ^{P1} **Z. Benkő**, R. Streubel, L. Nyulászi: Stability of Phosphinidenes – Is Any of Them Synthetically Accessible? *3rd Humboldt Conference on Computational Chemistry*, 2006. június 24-28. Várna
- ^{P2} **Z. Benkő**, R. Streubel, L. Nyulászi, Stability of phosphinidenes – Are they synthetically accessible? *1st European Chemistry Congress*, 2006. augusztus 27-31. Budapest
- ^{P3} **Z. Benkő**, L. Nyulászi, Structure and stability of thiirane and selenirane rings, *5th European Charge Density Meeting*, 2008. június 6-11. Gravedona

Presentations

In English

- E1 **Z. Benkő**, R. Schmutzler, L. Nyulászi: Quantum chemical investigations on dimerisation of fluorinated phosphorus ylides, *2nd PhD Seminar on Phosphorus Chemistry*, 2005. március 14-15. Bonn
- E2 **Z. Benkő**, R. Streubel, L. Nyulászi: Stability of phosphinidenes – Is any of them synthetically accessible? *3rd PhD Workshop on Phosphorus Chemistry*, 2006. március 13-14. Lipcse
- E3 **Z. Benkő**, L. Nyulászi: Structure and stability of thiirane and selenirane rings, *4th PhD Workshop on Phosphorus Chemistry*, 2007. március 19-20. Amszterdam

In Hungarian

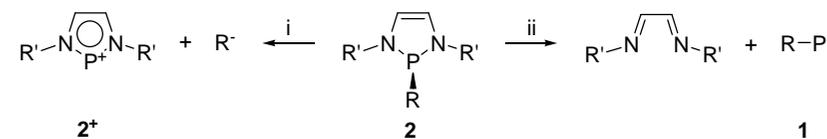
- E4 **Benkő Z.**, R. Streubel, Nyulászi L.: Flurozott foszforilidek stabilitása, *XXVIII. Kémiai Előadói Napok*, 2005. október 24-26. Szeged
- E5 **Benkő Z.**, R. Streubel, Nyulászi L.: Foszforilidek és foszforiminek stabilitása, *XI. Nemzetközi Vegyészkonferencia*, 2005. november 11-13. Kolozsvár
- E6 **Benkő Z.**, Nyulászi L.: Vannak stabil foszfinidének? *BME Oláh György Doktori Iskola 3. Doktoránskonferenciája*, 2006. február 7. Budapest
- E7 **Benkő Z.**, R. Streubel, Nyulászi L.: Foszfinidének stabilitása, *KeMoMo-QSAR miniszimpózium*, 2006. április 27-28. Szeged
- E8 **Benkő Z.**, R. Streubel, Nyulászi L.: Foszfinidének stabilitása, *XII. Nemzetközi Vegyészkonferencia*, 2006. október 3-8. Csíkszereda
- E9 **Benkő Z.**, D. Gudat, Nyulászi L.: A foszfinidének „komplexei”: új lehetőség foszfinidének előállítására, *BME Oláh György Doktori Iskola 4. Doktoránskonferenciája*, 2007. február 7. Budapest

2. Literature survey

Phosphinidenes (R–P, **1**) are hypovalent, σ^1, λ^1 -P containing compounds, analogues of carbenes (RR'C:), nitrenes (R–N) and silylenes (RR'Si:). Due to their extraordinary reactivity, no free phosphinidenes have been isolated so far.¹ The ground state of phosphinidenes is usually triplet; however, it is apparent that they can only be stabilized in the singlet state. The aim of my work was to find the most appropriate stabilising groups for phosphinidenes.

There are a few methods in the literature for *in situ* phosphinidene generation and for the synthesis of their transition metal complexes, however, most of the starting materials can only be synthesised very circuitously.

The 1,3,2-diazaphospholenes (**2**) are a unique class of the nonaromatic σ^3, λ^3 -P-compounds. Via heterolytic dissociation (i) they yield diazaphospholenium cations (**2⁺**, the P-analogues of the Arduengo carbene), which have remarkable aromatic character.

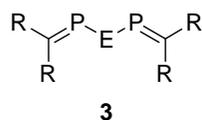


A hitherto unexplored method for the generation of phosphinidenes is the decomposition of a five-membered diazaphospholene ring **2** by means of formation of a diazabutadiene as a byproduct (ii). It can be conceived that by varying the substituent pattern of the complexing diazabutadiene moiety, appropriately substituted 1,3,2-

¹ (a) K. Lammertsma, *Top. Curr. Chem.* **2003**, 229, 95. (b) F. Mathey, *Angew. Chem.* **2003**, 115, 1616; *Angew. Chem. Int. Ed.* **2003**, 42, 1578. Similarly to carbenes, the transition metal complexes of phosphinidenes are often applied for synthesis of P-heterocycles.

diazaphospholenes might be utilised as phosphinidene sources. A further aim of my studies was to analyse the dissociation behaviour of annelated 1,3,2-diazaphospholenes and suggest new phosphinidene precursors for the synthetic work.

The unsaturated phosphorus compound with conjugated electronic structure may provide several interesting applications (OLED, OFET, solar cell)². Since the unsaturated phosphorus compounds are highly reactive (e.g. they are prone to polymerisation), only a few examples are known in the literature. Very recently, compounds sharing the C=P–E–P=C (E: S, Se) moiety (**3**, R: SiMe₃) have been synthesised and characterised experimentally.



As these compounds presumably have delocalised electronic structures, the π communication through the heteroatoms influences the reactivity of these bifunctional phosphalkenes: the addition of chalcogen yields unusual heteronorboranes.

List of publications

- ^{S1} **Z. Benkő**, R. Streubel, L. Nyulászi: Stability of phosphinidenes – Are they synthetically accessible?, *Dalton Trans.* **2006**, 4321. (IF: 3,005 C: 3)
- ^{S2} W.-W. du Mont, T. Gust, J. Mahnke, R. M. Birzoi, L. Barra, D. Bugnariu, F. Ruthe, C. Wismach, P. G. Jones, K. Karaghiosoff, L. Nyulászi, **Z. Benkő**: From 2,4-diphospha-3-thia- and 3-selenapentadienes [(Me₃Si)₂C=P]₂E (E = S, Se) to heteronorbornane cage compounds, *Angew. Chem. Int. Ed.* **2007**, *46*, 8682; *Angew. Chem.* **2007**, *119*, 8836. (IF: 10,232)
- ^{S3} **Z. Benkő**, D. Gudat, L. Nyulászi: A promising way for phosphinidene generation: Complexes of phosphinidenes with N-donor ligands, *Chem. Eur. J.* **2008**, *14*, 902. (IF: 5,015 C: 1)
- ^{S4} **Z. Benkő**, S. Burck, D. Gudat, M. Nieger, L. Nyulászi, N. Shore: Pyrido-annelated diazaphospholenes and phospholenium ions, *Dalton Trans.* **2008**, DOI: 10.1039/b804621b (IF: 3,212)
- ^{S5} S. Burck, D. Gudat, M. Nieger, **Z. Benkő**, L. Nyulászi, D. Szieberth, Spontaneous phosphorus-halogen bond cleavage in N-heterocyclic halogenophosphanes revisited: The case of P-Br and P-I bonds, *Z. anorg. allg. Chem.* – submitted for publication

Further publications

- ^{S6} **Z. Benkő**, L. Nyulászi: Three-membered Rings with Two Heteroatoms including Selenium or Tellurium; Three-membered Rings with Three Heteroatoms, in *Comprehensive Heterocyclic Chemistry III*, A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor (Eds), Elsevier: Oxford, **2008**, *Vol. 1*, p 679–694. (book chapter)
- ^{S7} L. Nyulászi, **Z. Benkő**: Aromatic phosphorus heterocycles, in *Top. Heterocycl. Chem.* (book chapter) – in press

² T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681.

7. The neutral pirido-annellated 1,3,2-diazaphospholenes are nonaromatic, however, the five membered C₂N₂P rings in the corresponding cations possess remarkable aromaticity, whilst the C₅N fragment is only slightly aromatic.^{S3}
8. In the case of the disilylamino-substituted pirido-annellated 1,3,2-diazaphospholene the aromaticity of the ring correlates with the conformation of the disilylamino group.^{S3}
9. On the basis of Bader analysis, partial charges and aromaticity indices, the spontaneous bond dissociation of 2-iodo-1,3,2-diazaphospholene is due to a combination of intramolecular stabilisation (aromatisation of the phosphonium cation formed) and intermolecular Lewis-acid/base interactions, which are present only in the crystal.^{S4}
10. In the case of 2,4-diphospha-3-thio- and 2,4-diphospha-3-selenapenta-1,4-diene remarkable conjugation was established using isodesmic reactions, NBO analysis and molecular orbitals.^{S5}
11. A mechanism being in fully accordance with the experimental observations was suggested for the formation of unusual heteronorboranes.^{S5}

3. Computational methods

For my PhD studies I applied quantum chemical modelling. The computations have been performed with the GAUSSIAN 98, GAUSSIAN 03 and ACES II suits of programmes. The geometries were usually optimised using DFT (density functional theory) techniques (often with the B3LYP functional). For each structure analytic second derivatives were calculated to characterise the optimised stationary points on the PES (potential energy surface). The suitability of the methods was tested using higher level calculations [e.g. MPn, CCSD(T), CBS-QB3]. The topological analysis of the electron density was performed using the AIM 2000 code, the natural orbitals were analysed with the NBO 5.0 programme. The following aromaticity criteria were applied to study the aromatic delocalisation: Bird index, bond shortening index (geometric criteria), NICS (nucleus independent chemical shift; magnetic criterion), and diverse isodesmic reaction (energetic criteria).

4. Results

4.1. Stability of phosphinidenes

The relative stability of phosphinidenes containing different R substituents was estimated by the (hypothetic) isodesmic reaction below (at the B3LYP/6-311+G** level of theory).



Linear relationship was found between the isodesmic reaction energy above and the singlet-triplet gap of the phosphinidenes.

Among several substituents, the best stabilisation was achieved in the case of the (yet not studied) methyleneamino (R: -N=CH₂) substituent. The stabilisation of the singlet H₂C=N-P (**4**) can be understood applying the MO theory. The

stabilising donation-backdonation interactions are shown in Figure 1.

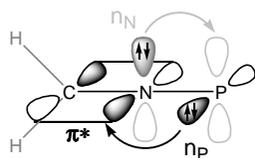


Figure 1.

Henceforth the stability and reactivity of **4** was estimated in real chemical reactions (*e.g.* dimerisation, oligomerisation). The dimerisation reactions of $\text{H}_2\text{C}=\text{N}-\text{P}$ are both thermodynamically and kinetically feasible, thus the methyleneamino-phosphinidene seems not stable enough for isolation.

As it is possible to further tune the stability of **4** by varying the R' substituents of the $\text{R}'_2\text{C}=\text{N}$ moiety, the stability of further phosphinidenes was estimated using reaction (1). Then these phosphinidenes were also tested computationally in “real” chemical reaction. The best stabilisation was gained in the case of $(\text{R}_3\text{Si})_2\text{C}=\text{N}-\text{P}$. The calculated reaction Gibbs free energies and activation barriers show that these compounds (R: H, Me) can be considered both thermodynamically and kinetically stable compounds in these reactions, allowing to conclude computationally that $(\text{R}_3\text{Si})_2\text{C}=\text{N}-\text{P}$ is a promising synthetic target.

4.2. Generation of phosphinidenes from annellated 1,3,2-diazaphospholenes

The dissociation of 1,3,2-diazaphospholenes (as “complexes” of phosphinidenes with N-donor ligands) may yield phosphinidenes (see above). The diazaphospholene ring can be tuned by benzo- or pirido-annellation. The dissociation of these annellated compounds is accompanied with the formation of

5. Theses

1. The relative stability of different phosphinidenes can be given by using an appropriate isodesmic reaction. The energy of this isodesmic reaction is in linear correlation with the singlet-triplet splitting of the phosphinidene.^{S1}
2. Using isodesmic reaction (1) $\text{R}_2\text{C}=\text{N}-\text{P}$ was found to be the most stable among the phosphinidenes studied. The stabilisation is due to the delocalisation (donating-backdonating interactions) which was also supported by the delocalised MO-s and Bader analysis.^{S1}
3. On the basis of isodesmic reaction (1), I stated that the π -donating R substituents (R: halogen, cyano, triafulvene) destabilise the $\text{R}_2\text{C}=\text{N}-\text{P}$ phosphinidene, whilst the π -withdrawing substituents (SiH_3 , SiMe_3 , pentafulvenes) stabilise the phosphinidene. All these stabilising substituents strengthen the NP bond.^{S1}
4. Investigating the thermodynamics and kinetics of dimerisation, oligomerisation, rearrangement reactions of $\text{R}_2\text{C}=\text{N}-\text{P}$ it has been turned out that $\text{H}_2\text{C}=\text{N}-\text{P}$ is not stable enough for isolation, however, $(\text{Me}_3\text{Si})_2\text{C}=\text{N}-\text{P}$ is a promising synthetic target.^{S1}
5. Anellated 1,3,2-diazaphospholenes have different dissociation Gibbs free energies (to phosphinidene and N-donor ligand) – depending on the nature of the ligand and the phosphinidene.^{S2}
6. The two most important factors in the dissociation of annellated 1,3,2-diazaphospholenes are (i) the stability of the phosphinidene and (ii) the aromaticity of the remaining ligand.^{S2} The phosphinidene complexes with negative dissociation Gibbs free energies seem to be promising precursors for experimental studies directed to the generation of stable free phosphinidenes.^{S2}

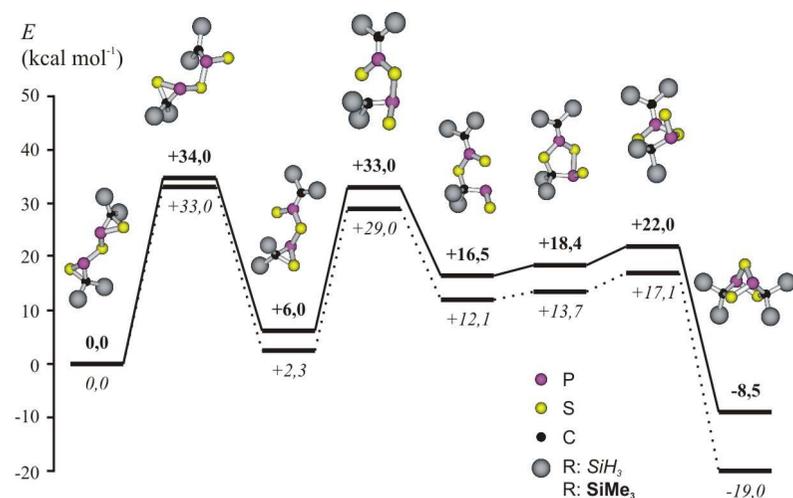
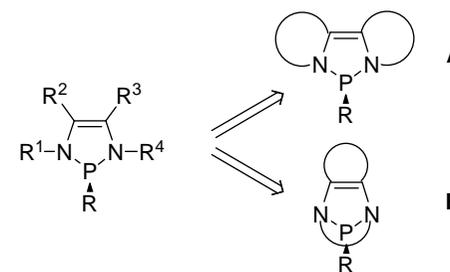


Figure 3. Calculated pathway for the isomerization of a bis(thiaphosphiranyl) sulfide to the heteronorbornane; R=SiH₃ (italics) and R=SiMe₃ (bold).

aromatically stabilised systems (e.g. 1,1'-bipyridine, pyrazine, etc.).



The dissociation energy and Gibbs free energy of these complexes were computed at the B3LPY/6-311+G** level of theory with different R substituents [R: H, NH₂, NCH₂, NC(SiH₃)₂] and annulations (Figure 2).

On the basis of the calculated energies, two different tendencies can be observed (Figure 2). The more stable the (singlet) phosphinidene is, the less stable the reactant complex and the more negative the dissociation Gibbs free energy. On the other hand, the aromaticity of heterocycles and the bare ligands (type **A** and **B**) has an influence on the thermodynamics of the dissociation.

The mechanism of the dissociation was also studied. On the basis of the activation barriers, all the thermodynamically feasible reactions are also kinetically possible. Hence a wide range of phosphinidene precursors seem to be suitable for experimental studies aimed for the generation of stable free phosphinidene.

Based on the promising results of the computations, Gudat *et al.* have synthesised a pirido-annellated derivative [R: N(SiMe₃)₂]. The preliminary thermoanalytical studies attest that this compound has an unusually low thermal stability; however, more comprehensive investigations of this matter are necessary to prove that these reactions lead indeed to transient phosphinidenes.

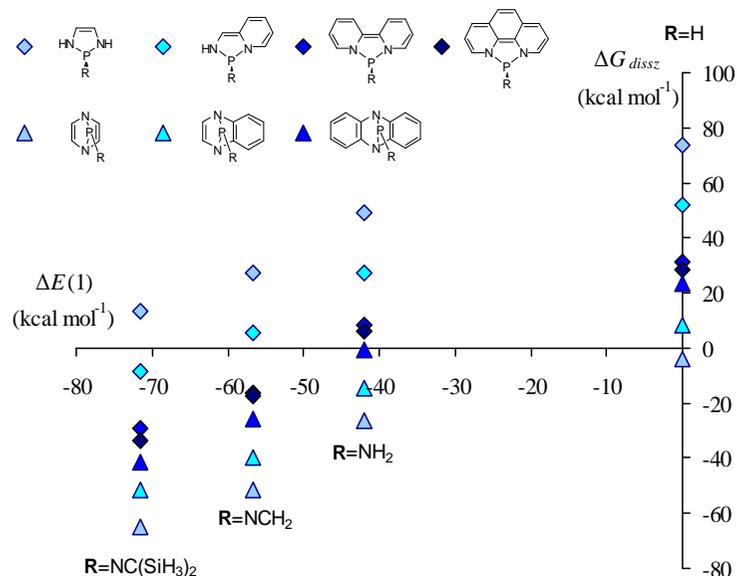
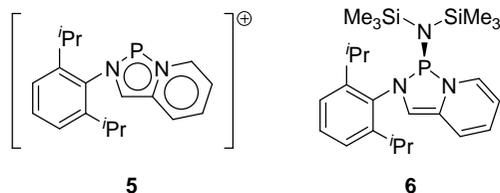


Figure 2. Relationship between the dissociation Gibbs free energies (ΔG_{dissz}) and the energies of the isodesmic reaction [$\Delta E(1)$] at the B3LYP/6-311+G** level.

4.3. Aromaticity of annellated 1,3,2-diazaphospholenes

The aromaticity of cation **5** and molecule **6** (and their smaller analogues) was estimated using Bird and bond shortening indices, NICS values and isodesmic reactions.



The neutral pirido-annellated 1,3,2-diazaphospholenes (**6**) are nonaromatic, however, the five membered C_2N_2P rings in the cations possess remarkable aromaticity, whilst the C_5N fragment is slightly aromatic.

4.4. Structure of 2-iodo-1,3,2-diazaphospholene

Spontaneous heterolytic dissociation was suggested for 2-iodo-1,3,2-diazaphospholene (**2**, R: I) on the basis of the elongated P–I bond distances in its crystalline structure. To study this phenomenon, gaseous phase calculation were carried out and the aromaticity of this compound was also investigated. These studies indicated that the bond dissociation is due to a combination of intramolecular stabilisation (aromatisation of the phosphonium cation 2^+ formed) and intermolecular Lewis-acid/base interactions, which are present only in the crystal.

4.5. Structure and reactivity of heterodiphosphapentadienes

The conjugation in the recently synthesised 2,4-diphospha-3-thio- and 2,4-diphospha-3-selenapenta-1,4-diene (**3**, E: S, Se) was studied computationally. Within the C=P–E–P=C moiety remarkable delocalisation was established on the basis of isodesmic reactions, NBO analysis and molecular orbitals.

The chalcogen addition on these compounds was also studied. I suggested a mechanism being in fully accordance with the experimental observations. The energy profile is shown in Figure 3.