

## CLOSING REPORT

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The aim of the project was to produce phosphorus based radicals in a controllable and easily tunable way, using the ferrocenophane structural motif, which would allow for easy redox or optical switching of the phosphorus center incorporated in the ansa bridge with further phosphino or amino moieties. To have a detailed understanding on the system, we have also investigated related systems with related low valent units, such as carbenes, silylenes and their heavier analogues, as well as the iso  $\pi$ -electronic phosphonium cations. The investigation was based on a cooperation with the Gudat and the Pietschnig groups (Stuttgart and Kassel, respectively), and during the work it was further extended with cooperations in Bonn, Berlin and Rennes to include also further low valent phosphorus and silicon compounds. Originally, in the cooperation we carried out the computational work, while the synthetic work was divided to the nitrogen- and phosphorus- containing ansa linkers in Stuttgart, and Kassel, respectively. In an attempt to extend the ferrocene chemistry toward the analogous silaferrocenes as well, we have attempted the synthesis of such compounds, in our group. Although silaferrocenes themselves could not be synthesized, in the chemistry of silole precursors significant new results were achieved.

During the project we faced several delays. The public procurement process for the purchase of the planned computers lasted for more than two years, and also the postdoc originally employed has left the research group, and we needed to find a substitute. Also during the synthetic work at our cooperation partners some difficulties have slowed down the progress (in particular related to the nitrogen containing ansa bridges). Nevertheless, finally we carried out the originally planned research, and even extended the original plans in some respects. Altogether we published 24 research papers with the sum of the impact factors well above 100, and some further works are under publication.

The most important achievements are the following:

- 1.) We have investigated computationally the stability of the different ferrocenophanes, having different low valent heteroatoms in the central position, and nitrogen, phosphorus and sulfur in the substituent position of the ansa bridge of the ferrocenophane. Apart from the structural investigations we studied the stabilization by isodesmic reactions, and have also investigated the frontier orbitals of the system. Comparisons were made with respect to five and six membered rings, for the latter one including also aromaticity stabilized systems. The results from these calculations have shown that the stability of the ferrocene based systems is close to the six-membered rings, due to their similar steric need, while the five membered rings usually exhibit somewhat more stabilization. While we could not find a direct interaction between the iron center and the low valent unit in the ground state, the presence of the ferrocene unit clearly affects the excited state properties and the reactivity of the system. These results were preliminarily published at a conference, and were incorporated in several papers on the particular compounds, and now are being summarized in a comprehensive computational paper which will be published later. We have further tested the behaviour of the ferrocenophane based N-substituted carbenes in two aspects, and compared them to related carbenes. First we considered the organocatalytic effect in the benzoin condensation (D. Buzsáki et al *Structural Chemistry* 2016) and also the bond formation with different phosphanes, where a large diversity was observed depending on the stability of the reactant carbene (D. Buzsáki et al *J. Phys Chem A*, 2020). In both cases it was found again, that the ferrocenophane based carbene has a similar behaviour to the six-membered ring diaminocarbene, in agreement with the general conclusion that there is no significant interaction in the ground state between the carbene center and iron.

2.) We expected that silaferrocene should be an even more active and attempted the synthesis of this compound. Unfortunately, the silaferrocene synthesis did not work, but we were able to synthesize the precursor silolide with trimethylsilyl substituents at 2,5-positions, and its  $\eta$ -1 iron complex instead of the planned  $\eta$ -5 complex. (Fekete et al. *J. Organomet. Chem.* 2015). Nevertheless, the silyl substitution on the five membered ring turned out to be unique, and we were also able to synthesize the first planar and aromatic silolide anion with this substituent. More interestingly, in this compound the dominant resonance structure is non-classical, with a significant Si=C bonding character (C. Fekete et al. *Chem. Commun.* 2017). Also siloles bearing phosphino side groups were synthesized, but this substituent pattern turned out to be less favourable on the photophysical properties (Mokrai et al. *Eur. J. Inorg. Chem.* 2020 accepted for publication – not listed among the 24 papers without DOI).

3.) Together with the Gudat group we have made preliminary work to study the stability and reactivity of the 3H-1,3,2-diazaphosphole, which contains the N-PH-N fragment present also in the ferrocenophanes, and have noticed an unexpected photochemical dehydrocoupling reaction. By the help of our computations we have revealed the properties of the excited state, and offered a mechanism for the photochemical reaction via formation of an excited state dimer. The resulting paper has been published in the *Angewandte Chemie* in 2015. This result was encouraging, implicating that with the NPN-bridged ferrocenophanes photochemical activation can be achieved even more easily. Unfortunately, however, the synthesis of the analogous ferrocenophane could not be achieved. The only stable NPN based structure obtained was the phosphonium cation, which - according to our computational studies exhibits a closed-shell electronic structure with a formal Fe(II) oxidation state and is thus a true analogue to ferrocenophane-based diaminotetrylenes. The observation of short intermolecular contacts in the crystalline phosphonium salt and its chemical behavior toward donor solvents attest to the cation having an unusually high degree of Lewis acidity, which was confirmed by DFT studies and was related to the presence of a rather large N-P-N angle (Weller et al. *Organometallics*, 2019). It seems that although the ground state of the NPN ferrocenophanes is stable, presumably due to the close lying ferrocene-based states this class of compounds becomes highly susceptible, and the planned controlled reactivity could not be achieved.

While the synthesis of the 2H-1,3-diaza-2-phospha[3]ferrocenophanes was not successful, 2Cl-1,3-diaza-2-phospha[3]ferrocenophanes and 2Br-1,3-diaza-2-phospha[3]ferrocenophanes could be synthesized. Nevertheless, depending on the substituents of the nitrogens the outcome of the base mediated ring closure of diaminoferrocenes with phosphorus halides resulted either in the ring closed ferrocenophanes, or in bis phosphination on the two amino functions. Our DFT calculations have shown the effect of the steric bulk of the N-substituents (Weller et al. *Dalton Transactions* 2019), which influences subtly the thermodynamical stabilization of the products and also the reaction barriers. Thus, the outcome of the reactions cannot be easily predicted by simple considerations. From the open ferrocene bis-phosphines cyclic tetracosphanes could be made, in different conformations. The different conformers have shown different behaviour in cyclic voltammetry, and this behaviour was explained by the formation of a ferrocene-based or the P<sub>4</sub> ring located radical.

4.) While the NPN ansa bridges turned out to be too susceptible, the originally targeted non planar phosphorus heteroatoms in the ansa bridge seemed to be less stabilizing, but due to the high inversion barrier at phosphorus several stable conformers were expected for the precursor saturated compounds. This has turned out to be indeed the case, and before starting the investigation of the possible low valent compounds, we explored the behaviour of the precursors. Triphospha- ferrocenophanes could be synthesized with various substituent at 2P yielding in different stereochemical alignment depending on the substituent effects. In a noteworthy way our DFT studies showed that the HOMO is ferrocene based in one conformer, while phosphorus based on the other one. In fact the inversion of the central

phosphorus center, P2, affects the interaction  $\sigma_{P-X^*}$  ( $X = Cl, Br$ ) LUMO with the neighboring phosphorus lone pairs, stabilizing the occupied and destabilizing the unoccupied orbitals, changing the HOMO from an iron centered (in the cis isomer) to a phosphorus centered orbital (in the trans isomer). These theoretical findings were supported by electrochemical investigations which revealed irreversible processes for the diastereomeric mixtures, however, are well resolved for compounds occurring as single isomers such as the one bearing a bulky tBu substituent at the central phosphorus (Borucki et al Chem. Eur. J. 2017). Further investigations on PPP bridged ferrocenophanes were also carried out on PP-bridged bis[3]PPP-ferrocenophanes, which exhibit a bonding motif known from Hittorf's phosphorus. These compounds show a temperature dependent behaviour, resulting in the reversible formation of a pair of PP(rad)P-ferrocenophane radical, which has two conformers of comparable energy according to our DFT calculations. In agreement with our other observations on the NPN-ferrocenophanes, a PP-bridged compound from the PPP and PNP ferrocenophane showed irreversible behaviour at increased temperature, yielding upon cooling the bis[3]PPP-ferrocenophane, and a reaction product, which could be derived from the NPN-ferrocenophane radical (*Chem. Open* 2019). This finding was again in clear agreement with the high chemical reactivity of the NPN-bridged ferrocenophane systems.

Apart from the PPP-bridged ferrocenophanes, PE:P-bridged systems (E: Si, Ge, Sn, Pb) were also targeted from the beginning of the project aiming to get isolable tetrylenes. The precursors of these compounds were also more straightforward to access, than the elusive NPN-bridged systems. As precursors of the PE:P-bridged systems, PE(XY)P-systems (X,Y: Cl, H) could be synthesized in Kassel revealing two conformers as supported by our DFT calculations, showing a small energy difference between these structures. In spite of significant efforts to remove the X,Y substituent pair (in different combinations, and using different chemistries) the targeted tetrylenes could not be obtained, but in some cases dimers with an E-P-E-P cyclic system could be obtained. Indeed, our calculations revealed that this dimeric form is more stable than the monomers, in accordance with the fact that the highly non-planar phosphorus bridging units are not able to stabilize the tetrylenes (Kargin et al, Dalton Transactions 2016). While none of the tetrylenes (including even the stannylene) could be synthesized with the protecting groups applied, bearing in mind the calculated dissociation energies of the dimers we anticipated that the tetrylenes may be trapped by NHC. This assumption was indeed correct, and from the dimer of the stannylene and the plumbylene the NHC adducts could be obtained in a straightforward manner. The silylene adduct was not available this way, in accordance with the calculated large dissociation energy of the dimer, but reacting the NHC with the precursor (X:H, Y:Cl) with excess NHC yielded finally the NHC adduct. This compound turned out to be highly nucleophilic at the Si center as shown by its high energy HOMO, and accordingly a borane adduct could also be made (Kargin, Chemistry – Eur. J. 2018).

5.) Observing the synthetic difficulties related to the NPN-bridged systems, we were looking for other systems apart from the ferrocenophanes, where low valent phosphorus can be activated in unusual bonding environment. A particularly interesting molecular platform was the tricyclic 1,4-diphosphinine based system synthesized in the Streubel group in Bonn. Diphosphinines are much less studied than phosphinines, and according to our previous results must have very low lying LUMO-s facilitating an interesting redox chemistry, and also high reactivity against nucleophiles. With the synthesis of the tricyclic 1,4diphosphinine (Koner et al, Angew. Chem 2017) the first studies revealed the easy reduction of the system, resulting an immediate dianion formation as observed by cyclic voltammetry. Interestingly, the aromaticities of the constituting 1,4diphosphinine, and imidazol-thione rings does not alter significantly compared to the isolated rings according to our NICS studies. The high electrophilicity of the compound renders its highly reactive, and indeed, among 4+2 cycloaddition reactions apart from the usual pi-bond activating reactions even sulfur-sulfur sigma bond activation

was observed (Koner et al, Chem. Commun. 2018). In a noteworthy manner in the product molecule an unusually low energy barrier for the phosphorus inversion was found by our DFT calculations, accounting for the unexpected formation of the trans product. Apart from the 4+2 cycloaddition products 4+1 cycloaddition with monovalent group13NacNac complex was also realized (Koner et al. Dalton Transactions 2019). A further important modification of the tricyclic compound was the removal of the substituent groups at the 2-positions from the imidazole rings, resulting in a bis-carbene, connected by phosphorus. This could be achieved with saturated P(III) and P(V) units, and using the imidazole-selenone, instead of the imidazole thion (Rauf Naz et al. Chem. Commun 2020). The replacement of the flanking imidazole-thion units of the first synthesized tricycle to thiazole-thion units has further lowered the LUMO level (accordingly, also the reduction potential), and with this tricycle even a stable anion could be synthesized (Begum et al. Chem. Commun 2018).

A further related ring structure which is described as a phosphonium cationic structure was a triazaphospholenium cationic ring system, which is also highly electrophilic, and can alternatively be described as a phosphorus analogue of an abnormal carbene. This stable structure was found to be an aromatic compound (Papke et al. Angew. Chem. 2017).

6.) The behaviour of low valent phosphorus, which is a central issue in the present project was also investigated in relation to conjugated pi-systems, which might have applications in optoelectronics. Among others highly extended pi-system composed of different polycyclic aromatic hydrocarbons (PAH) were investigated. From theoretical studies we could conclude that variation of the aromatic character in one ring of a PAH affects diversly the different rings, this effect might be related to the Clar aromaticity pattern of the PAH (Szűcs et al. Struct. Chem 2015). The interaction of P and Si incorporated at different position by five membered ring formation with the highly emissive pyrene system was also studied, revealing some highly emissive materials (Mocanu et al. J. Org. Chem 2109). Apart from introducing the heteroatom phosphorus in five membered rings the much less investigated seven-membered ring systems incorporated into PAH framework were also studied. Although the seven-membered rings themselves are non-planar, this molecular structure still rigidifies the system providing highly emissive molecules (Delouche et al. Org. Lett 2019, and Delouche et al Chem. Eur. J 2020). While the conjugated pi-systems with incorporated low coordinate phosphorus in six-membered rings show usually low fluorescence, we could show that the oxydation of these phosphorus results in significantly enhanced fluorescence intensities, furthermore, the fluorescence intensity can be related to the increase of the calculated rotational barriers of the ring substituent aryl groups. (Pfeifer et al. Chem. Eur. J. 2020), resulting most importantly in an OLED, with the most efficient luminescent phosphabenzene derivative.

7.) For two other, less project related works in silicon and phosphorus chemistry, we have used resources from this project, and this was mentioned in the acknowledgements (Z. Naturforsch. B 2017, and Szűcs et al. Eur. J. Inorg. Chem. 2020).