Summary of research

In the following we present our results based on the publications. Here we denote the reactivity classes as:

1) nucleophilic substitution

2) cycloaddition

3) P transfer.

The following studies involve parts a) and c) in Work plan.

A. NaOCP and acyl chlorides: 1) and 2) and 3)

The reaction mechanism of the reaction of 2 eq of NaOCP with 2 eq mesitoyl chloride resulting in the formation of a 1,2,4-oxadiphosphole, 2 NaCl and CO was investigated in detail by low temperature NMR measurements and calculations at the CCSD(T) level, and from the combination of these studies a possible mechanism was suggested. The electronic structure and aromaticity of the oxadiphosphole was also studied (NICS values, AIM analysis), and a secondary interaction was found between a P of the ring and the mesitoyl substituent. This was also a case study for the reactivity of the OCP ion which involves all the three classes shown above.

We published the results in the following paper, with the PI as a corresponding author:

Heift, D ; Benko, Z ; Suter, R ; Verel, R ; Grutzmacher, H The reactivity of acyl chlorides towards sodium phosphaethynolate, Na(OCP): a mechanistic case study CHEMICAL SCIENCE 7 : 9 pp. 6125-6131. , 7 p. (2016)

B. NaOCP + imidoyl chlorides: 1) and 2) and 3)

The reaction above was extended to imidoyl chlorides and in this case not only neutral but also anionic species were isolated. Based on ab initio calculations we were able to explain why different isomers are obtained in these reactions depending on the substituent of the imidoly group (steric effect and delocalization). These species gave access to highly functionalized species for materials. The electronic structure of the new anions and molecules was also studied by DFT calculations.

We published the results in the following paper, with the PI as a corresponding author:

Suter, R ; Benkő, Z ; Grützmacher, HA Convenient Synthesis of 1,2,4- and 1,3,4-Azadiphospholes

CHEMISTRY-A EUROPEAN JOURNAL 22 : 42 pp. 14979-14987. , 9 p. (2016)

C. NaOCP and pyiridyl chlorides: 1) and 2) and 3)

The azadiphospholide anion can be part of a more delocalized system via annulation forming anion An- in the Research plan. These species have been accessed and isolated in Zurich and show very unusual optical properties (intense deep color). The silylation of these anions results in a strong bathochromic shift, which can be reversed by fluoride ions, underpinning a possible application as fluoride sensor. The effect of silylation on the molecular orbitals and the optical properies was also analyzed in detail.

The following studies have been performed in Budapest besides the experimental collaboration at ETH Zurich, where all the syntetic work was executed:

- In order to understand the colours of these species and colour changes upon silyation, TD-DFT and MO studies were carried out with different functionals and basis sets on a family of selected compounds. These results show that the first excitation is the HOMO->LUMO with significant charge transfer character in the anions, while the charge transfer is much smaller for the neutral species.

- The formation of the anion was studied computationally and a feasible reaction mechanism was suggested.

- The ground state electronic structure of these systems (both anions and neutral analogues) was investigated: delocalization and aromaticity parameters were analysed. Despite the exocyclic =O function the P2C2N rings are aromatic in the anions, but the annulated rings are non-aromatic.

These results were published in Angew. Chem. and highlighted in C and EN News of ACS.

Suter, R ; Benko, Z ; Bispinghoff, M ; Grutzmacher, H Annulated 1,3,4-Azadiphospholides: Heterocycles with Widely Tunable Optical Properties ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 56 : 37 pp. 11226-11231. ,6 p. (2017)

Ambident anions: In the proposal we intended to study the possible formation of RPCO and ROCP isomers. This is denoted as b) in the Work plan.

D. Boryl species: 1) and 2)

The reaction of R2B-Cl and NaOCP at low temperature results in the formation of both isomers phosphaethynolate and oxyphosphaalkyne. We performed calculations on the relative stability of these isomers with different substituents and at different levels of theory, and these results nicely agree with the experimental finding. These species are precursors for P3C3(OH)3, a heavier analogue of cyanuric acid, whose electronic structure was also studied by the PI.

These results were published in Angew. Chem. and highlights in C and EN News and Helv. Chim, Acta.

Suter, R ; Mei, YB ; Baker, M ; Benko, Z ; Li, ZS ; Grutzmacher, H 2,4,6-Tri(hydroxy)-1,3,5-triphosphinine, P3C3(OH)(3): The Phosphorus Analogue of Cyanuric AcidANGEWANDTE CHEMIE-INTERNATIONAL EDITION 56 : 5 pp. 1356-1360. , 5p. (2017)

E. New OCP salts: 1)

The structure and electronic structure of compounds with a formula of Mg(OCP)2(THF)4 and the analogous Na-species with 5 THF molecules were studied. Besides the optimised geometrical parameters, WBI (Wiberg bond indices) and NPA charges were obtained. These results show that the O-Mg and O-Na bonding is rather of ionic nature, which fits nicely to experimental data. These results were published in Dalton Trans.

Gilliard, RJ ; Heift, D ; Benko, Z ; Keiser, JM ; Rheingold, AL ; Grutzmacher, H ; Protasiewicz, JD An isolable magnesium diphosphaethynolate complex DALTON TRANSACTIONS 47 : 3 pp. 666-669. , 4 p. (2018)

F. OPC and OCP isomers: 1) and 2) and 3)

The electronic structure of the O-P-C anion was studied. This anion was accessed as a carbene - phosphonium adduct and the formed carbene supported species were also studied by DFT calculations. This is an unusual example of constitutional isomerisms. From this OPC isomer new singlet biradicals were accessed as dimers whose structures were studied by DFT calculations.

Li, Z ; Chen, X ; Andrada, DM ; Frenking, G ; Benkö, Z ; Li, Y ; Harmer, JR ; Su, C-Y ; Grützmacher, H (L)2C2P2: Dicarbondiphosphide Stabilized by N-Heterocyclic Carbenes or Cyclic Diamido Carbenes ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 56 : 21 pp. 5744-5749. , 6p. (2017)

and

Dr. Zhongshu, Li ; Dr. Xiaodan, Chen ; Dr. Zoltán, Benkő ; Liu, Liu ; Dr. David, ARuiz ; Jesse, L Peltier ; Prof, Dr. Guy Bertrand ; Prof, Dr. Chen-Yong Su ; Prof, Dr.Hansjörg GrützmacherN-Heterocyclic Carbenes as Promotors for the Rearrangement of Phosphaketenes to Phosphaheteroallenes: A Case Study for OCP to OPC Constitutional Isomerism ANGEWANDTE CHEMIE-INTERNATIONAL EDITION 55 : 20 pp. 6018-6022. , 5p. (2016)

G. Possibility of ROCP and RPCO isomers: 1)

As reported before, in the case of R = SiMe3both isomers have been detected, we aimed to stabilize the elusive ROCP. First we considered several R substituents to design new ROCP species. We determined the relative energies of the R3SiOCP and R3SiPCO isomers with different substituents on the Si atom (R: alkyl, aryl, OR', NR'2, COR', R'. alkyl, aryl, etc.) using DFT and ab initio methods. We also studied the mechanism of the interconversion of the two isomers with computations on a prototype system, with R = Me (monomolecular, bimolecular, dissociative mechanisms).

As these studies did not deliver the expected results, that is the Si atom is not oxophilic enough to stabilize the ROCP isomer, we conducted investigations on systems with a different heteroatom (instead of Si): BR'2, AlR'2, NR'2, PR'2, PR'2=O, PR'2=S units with substituents R' = H, Me, Ph. The best result was obtained with boryl and alyl units.

These results are not yet published but the draft is under way.

H. Ambidency of XCP anions. Marcus theory: 1)

Detailed studies were performed on the structure of XCP anions where X is O, S, RN, or RP. This involved NBO, NRT and AIM calculations at various levels of theory and obtaining MEP.

The relative energies of the RXCP and RPCX isomers were also obtained with R = Me. This can be used to predict which coordination can be more stable.

We also computed the intrinsic activation barriers for the identity reaction of these P anions. Based on our results it is clear that the X = O and NR show close similarity (reacting on the P centre in SN2 reactions both themodynamically and kinetically). In contrast, the X = S and PR are also similar, in these cases both X and P heteroatoms can react in similar way.

These results are not yet published but the draft is under way.

Overlap of Work plan and the actual timing

All the tasks outlined in the Work plan have been achieved except for one in part c): due to synthetic difficulty the products were not realized (complexes of the anionic P rings). Thus, the description of these species is not meaningful as we still do not know the composition of the products. We hope that this issue will also be solved.

Otherwise we have addressed all subprojects.

Publications

We published 15 original papers in high impact journals. The PI is corresponding author in several of them.

The PI presented several invited lectures at universities and conferences.

Spending costs

We tried to follow the plan, but there were 2 changes: we could not purchase computers due to limitations at our university and at end the of the project we obtained consumables for model experiments which will be connected to this purely theory oriented project. The costs for the latter are only minor.