

PBSi 2019

International Conference On
Phosphorus, Boron and Silicon

Dec 2-4, 2019

Rome

BOOK OF ABSTRACTS

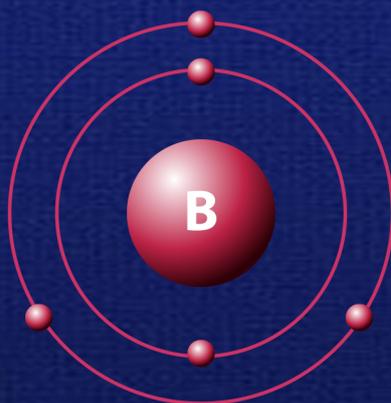
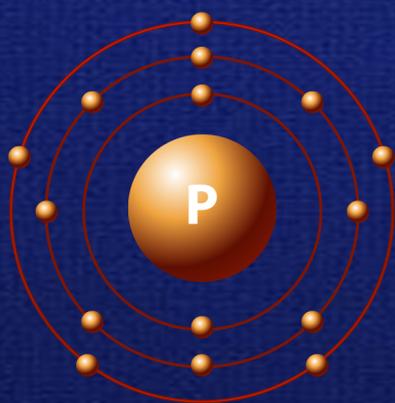


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STABLE CARBENES, PHOSPHINIDENES AND BORYLENES

Monday, 2nd December - 09:05: Plenary speech (Auditorium) - Oral - Abstract ID: 261

Prof. Guy Bertrand¹

1. UCSD

In the last few years, thanks to very bulky substituents featuring peculiar electronic properties, we have been able to isolate a variety of highly reactive species. In 2016, this was the first room temperature stable phosphinidene **A** (Figure 1),¹ and we will discuss its reactivity. More recently, we have prepared and fully characterized, including by single crystal X-ray diffraction study, a monosubstituted carbene **B**.² The isolation of the latter prompted us to use similar substituents to isolate novel types of carbenes, phosphinidenes and even borylenes.³ These recent results will be discussed.

Figure 1. The first stable phosphinidene **A** (blue: N; orange: P; red: tert-butyl group) and mono-substituted carbene **B** (blue: N; green, F)

References

1. Liu, L.; Ruiz, D. A.; Bertrand, G. **Chem.** **2016**,*1*, 147-153.
2. Nakano, R.; Jazzar, R.; Bertrand, G. **Nature Chem.** **2018**,*10*, 1196-1200.
3. Vermersch, F.; Nakano, R.; Junor, G.; Jazzar, R.; Bertrand, G. **2019**, *Unpublished work*.

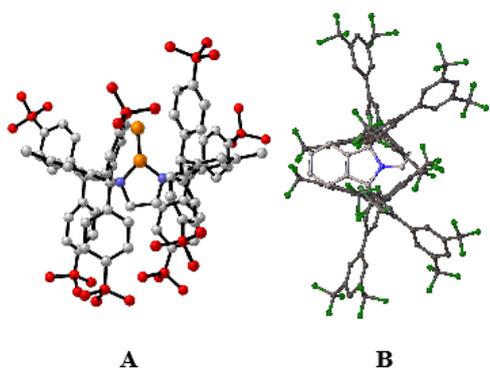


Figure 1 gb.png

Phosphines and phosphinosilanes together with metal hydrides

Monday, 2nd December - 09:45: Plenary speech (Auditorium) - Oral - Abstract ID: 251

Dr. Sylviane Sabo-Etienne¹

1. Laboratoire de Chimie de Coordination du CNRS ; Université Toulouse III Paul Sabatier

Phosphine ligands are widely used to stabilize transition metal complexes. They are often spectator ligands but they can also be active participants for a variety of reactions. During this lecture, we will look at two different systems involving groups 8-10 metals. The first one is dealing with metal hydrides, and the role they might play in the field of energy with respect to hydrogen storage. One can achieve a reversible hydrogen uptake at room temperature and low pressure when starting from dihydrogen phosphine ruthenium complexes or lower significantly the desorption temperature of material hydrides such as MgH₂. Improvement has been achieved when switching to nickel hydride precursors. The second system concerns phosphines bearing additional functional groups such as silanes. Most of the time, catalytic transformations require access to one or two vacant sites around the metal center. Labile or hemilabile ligands are thus interesting bricks to produce unsaturated species keeping in mind stability factors with respect to activity. A few examples will show that the coordination chemistry of phosphinosilanes might be quite versatile, and that Si-H bond activation might induce many different pathways depending on the metal center and on the substituents at P and Si sites.

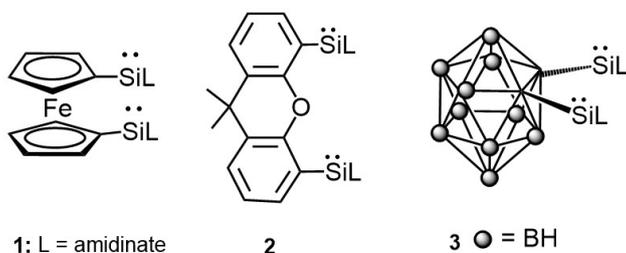
The rise of silylenes for cooperative chemical transformations

Monday, 2nd December - 10:45: Plenary speech (Auditorium) - Oral - Abstract ID: 10

Prof. Matthias Driess¹

1. Technische Universität Berlin

Selective activation of small molecules by using non- and semi-metals instead of expensive and toxic precious metals is a contemporary challenge in molecular chemistry and catalysis in particular. Recently, a variety of isolable N-heterocyclic silylenes were realized, which show versatile reactivity pattern with respect to selective carbon-heteroatom bond activation of organic substrates based on divalent silicon. Now we learned that the reactivity of silylenes can be boosted if two silylene moieties are placed in close proximity, giving rise to cooperative bond activation. This new features will be demonstrated with the bis(silylene)-based compounds **1-3** which enable cooperative and selective coupling reactions, including the deoxygenative homocoupling of CO to give C=C=O (ketene) and related heterocoupling of CO with isocyanide to ketenimines (C=C=NR).



Md 1.jpg

Hydrophosphination: new twists in an old reaction

Monday, 2nd December - 11:25: Plenary speech (Auditorium) - Oral - Abstract ID: 254

Prof. Paul Pringle¹

1. University of Bristol

Consultation of any textbook on organometallic chemistry or homogeneous catalysis would reveal how important tertiary phosphine ligands have been to the development of both of these fields over that last half century. The enormous variety of tertiary phosphines that are accessible means that the properties of the metal complexes and catalysts that they form can be controlled and finessed to an unparalleled degree. The synthesis of tertiary phosphines typically involves the use of highly reactive phosphorus nucleophiles or electrophiles (pathways (a) and (b) in Scheme 1) in reactions that are stoichiometric, produce salt waste and are not amenable to the incorporation of reactive functionalities in the product ligands. Hydrophosphination of alkenes (pathway (c) in Scheme 1) is an attractive alternative since it is 100% atom efficient and, when Pt(0)-catalysed, is tolerant of many functional groups [1].

Here we show how Pt(0)-catalysed hydrophosphination of activated alkenes gives access to phosphine ligands that contain ester, nitrile or amide groups. Surprisingly, this catalysis is also applicable to the synthesis of diphosphines (Eq 1) despite the potential for catalyst inhibition by the powerfully chelating products. The diphos product is the ligand on the Pt(0)-complex that is the catalyst for its production; so this is an example of an unusual catalytic, self-replication process [2] illustrated schematically in Figure 1. The mechanism of the reaction to give ligand **1** (Eq 1) and the elaboration of ligand **1** to a bioconjugated ^{99m}Tc-radioimaging agent will be discussed.

[1] Bange, C. A.; Waterman, R., *Chem. Eur. J.***2016**, *22*, 12598-12605

[2] Chadwick, A. C.; Heckenast, M. A.; Race, J. J.; Pringle, P. G.; Sparkes, H. A. *Organometallics***2019**, *38*, 3871-3879.

Synthesis of alkenyl-functionalized silsesquioxanes and spherosilicates via hydrosilylation of alkynes

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 189

Ms. Kinga Stefanowska¹, Dr. Adrian Franczyk², Dr. Jakub Szyling², Dr. Jędrzej Walkowiak²

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Polyhedral oligomeric silsesquioxanes (POSS) are among the most intriguing examples of well-defined, nanostructured, functionalized building blocks, which find applications in academia and industry.[1,2] They have been used in the synthesis of an enormous number of hybrid (co)polymers and nanocomposites characterized by complex composition, different functionalization, and architecture. Recently, much interest has arisen in silsesquioxanes bearing conjugated groups which are often called alkenyl-silsesquioxanes.[3]

One of the most versatile synthetic methods for the preparation of such systems is the hydrosilylation reaction. The process gives the possibility for selective formation of specific isomer during the Si-H addition. Moreover, the hydrosilylation can be performed in the wide range of temperatures, in different types of solvents, under air atmosphere, using easily available reagents, in the presence of stable and tolerable for many reactive functionalities or impurities catalysts. All of that makes it a powerful tool which appropriately used can easily provide a wide spectrum of silsesquioxanes bearing various types of functionalities.

In the communication we report studies on the hydrosilylation of a wide spectrum of the terminal and internal alkynes with monofunctional silsesquioxane (HSiMe₂O)(i-Bu)₇Si₈O₁₂) as well as octafunctional spherosilicate ((HSiMe₂O)₈Si₈O₁₂).[4-6] This method permitted to obtain a series of new alkenyl-substituted silsesquioxanes and spherosilicates in high yields and selectivity. The products were characterized by ¹H, ¹³C, ²⁹Si NMR, FT-IR spectroscopy, ESI HR-MS spectrometry, and X-ray crystallography. The influence of the reaction conditions (alkyne structure, type of the catalyst, solvent, temperature) on the process rate, its efficiency and selectivity will be presented.

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Acknowledgments: The authors acknowledge the financial support of the National Centre for Research and Development in Poland – grant LIDER/26/527/L-5/13/NCBR/2014, grant no. POWR.03.02.00-00-I023/17 co-financed by the European Social Fund under the Operational Program Knowledge Education Development and National Science Centre in Poland by grant PRELUDIUM UMO-2017/27/N/ST5/00224.

Formation of tin(II) amidinates from carbonitriles via migration of SiMe₃ group from Lappert's stannylene

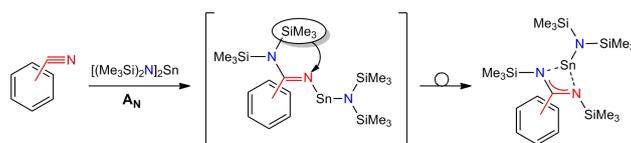
Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 175

Dr. Tomas Chlupaty¹, **Ms. Kristyna Brichova**¹, **Dr. Zdenka Ruzickova**¹, **Prof. Ales Ruzicka**¹

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The chemistry of complex and organometallic compounds of main group elements underwent rapid development in the past two decades. This development and obviously a bright future of that field are interconnected to the employment of a high number of new electronically and/or sterically stabilizing ligands. A higher electron density NCN chelated compounds as for example amidinates and guanidates[1] are the modern members. A new class of tin(II) *N,N'*-disubstituted amidinates prepared via an addition reaction of Lappert stannylene ($[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$), with subsequent migration of trimethylsilyl fragment, to polarized triple C≡N bond(s) of cyanobenzene, 1,2-dicyanobenzene, 1,3-dicyanobenzene, 1,4-dicyanobenzene a 1,3,5-tricyanobenzene in various stoichiometric ratios and reaction conditions will be discussed. Moreover, selective thermodynamic versus kinetic reaction control depending on the time, temperature as well as concentration of starting compounds of an interaction of Lappert stannylene with the excess of cyanobenzene will be also demonstrated.

Acknowledgements: For financial support from the Czech Science Foundation (grant nr. 17-10377S).



Formation of tin ii amidinates from carbonitriles via migration of sime3 group.jpg

Reactivity study of a new germaphosphaalkenyl derivative

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 187

Dr. Gabriela Nemes¹, **Ms. Lavinia Buta**¹, **Mr. Ionut-Tudor Moraru**¹, **Dr. Raluca Septelean**¹

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The study of unsaturated derivatives of group 14 and 15 elements, containing a phosphalkenyl unit (P=C), are an interesting topic due to their possible use as building blocks to organometallic or coordination compounds.¹ This work focuses on the synthesis and investigation of new stable compounds containing the P=C-Ge unit, having the germanium atom included into a fluorenyl cycle. We have reported a new air stable germaphosphaalkenyl derivative (9-chloro-9-phosphaalkenylchloro-9-germafluorene) which was fully characterized in solution by NMR spectroscopy and mass spectrometry methods and in solid state by single crystal X-ray diffraction.²

We present here the reactivity of 9-chloro-9-phosphaalkenylchloro-9-germafluorene towards organolithium derivatives. For example, by reaction with *n*-butyllithium, instead of the expected lithiation at the central carbon atom of the P=C-Ge unit³, a substitution of the chlorine atom on the germanium atom with the alkyl chain occurred. The reaction with *t*-butyllithium led to the formation of a digermane derivative, as presented in Figure 1.

Figure 1. Molecular structure of digermane compound determined by X-Ray diffraction (hydrogen atoms were omitted for clarity)

Aiming to understand whether the inclusion of the Ge atom within the fluorenyl unit influences the stability of these compounds, calculations were carried out at the DFT level of theory (B3LYP/Def2-TZVP). NBO and NICS analyses were alongside performed, as secondary electronic effects may play important roles in the investigated species.

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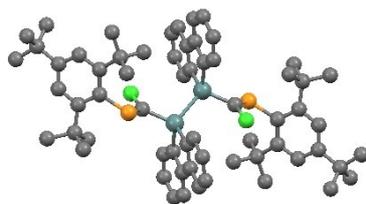


Figure 1.jpg

Surface molecularly imprinted solid phase extraction of griseofulvin from pharmaceutical preparations

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 109

***Mr. Kamran Bashir*¹, *Prof. Qiang Fu*¹, *Mr. Guoning Chen*¹, *Dr. Pengqi Guo*¹, *Mr. Yunzhe Li*¹**

1. Xian Jiaotong University

Introduction

Substandard and counterfeit medicines directly influence the health and impose a great danger to individual patients and to public health. There are a large number of sub-standard medicines flooded in markets which affect human health directly and indirectly. Therefore, some novel analytical techniques are necessary to be established for detecting these sub-standard drugs.

Methods

Griseofulvin is the first oral antifungal drug and is a drug of choice for the treatment of *Tinea capitis*. In this study, the griseofulvin surface molecularly imprinted polymers (SMIPs) were grafted on the amino-modified silica particles and were applied as a Solid-phase extraction sorbent. The factors affecting the extraction process such as sample pH, ionic strength, and elution solvents were optimized. The application of SMIPs as a sorbent was exhibited by packing it in solid-phase extraction cartridge and coupled it with HPLC to extract and analyze griseofulvin from tablet formulation through an offline analytical procedure.

Results and Discussion

The method is linear over the range of 0.1-500 µg/mL. The method detection limit and quantification were 0.02 and 0.05 µg/ml respectively. Good recovery of 98.69-101.47 % was achieved after surface molecularly imprinted solid-phase extraction. The within-day and between-day relative standard deviations (n=3) were 4.3 and 7.1% respectively. The proposed method was applied for the determination of griseofulvin in three commercial pharmaceutical formulations. Moreover, the reuse-ability of SMIPs was also evaluated. The results assured that the prepared polymer particles had good durability and can be reused many times with relatively low-performance loss. This simple, specific, selective and cost-effective method can be applied for the routine quality control analysis of griseofulvin.

Nucleophilic alkaline earth boryls: from conception and theory to application

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 113

Mr. Henry Shere¹, **Dr. Anne-Frédérique Pécharman**¹, **Dr. Mary Mahon**¹, **Prof. Michael Hill**¹

¹. University of Bath

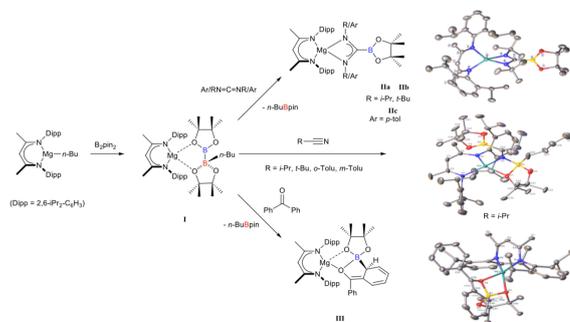
Contemporary advances in main group chemistry have shown that boron compounds can be used as electron donors, in contrast to their conventional Lewis acidic nature. As a result, there is a burgeoning interest in the use of convenient nucleophilic boron reagents for the direct construction of B-C bonds. Perhaps the most promising route to these valuable compounds is through the use of sp^2 - sp^3 diboranes, where one boron atom in conventional, commercially available diboranes can be quaternised by either a neutral or anionic nucleophile. Hill *et al.*¹ recently reported the synthesis of a nucleophilic boryl via the generation of a sp^2 - sp^3 diboronate, **I**. Both the terminal boryl and **I** were shown by the group to act as an apparent source of an anionic boryl nucleophile, synthesised in mild and facile conditions.¹⁻³

Accordingly, this research aims to further investigate the chemistry behind these findings; primarily through reacting the activated magnesium diboronate, **I**, with different unsaturated electrophiles. With its reactivity towards imines (R_2 -C=N-R) evaluated within the last year,² this work focuses on the possible nucleophilic behaviour of **I** towards the similar functional group of nitriles (R-CN).

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Nucleophilic boron scheme.png

Struvite as an alternative phosphorus fertilizer for horticultural crops

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 98

Dr. Carolina Mancho ¹, Dr. Mar Gil-Diaz ¹, Mr. Juan Alonso ¹, Mr. Sergio Diez-Pascual ¹, Dr. Pilar García-Gonzalo ¹, Dr. M.Carmen Lobo Bedmar ¹

1. IMIDRA

The global increase in population makes clear the need for an adequate production of quality food, which in turn can be met through the intensification of the agricultural sector. The role of fertilizers is crucial to ensure production being phosphorus (P), whose world reserves are decreasing, one of the essential elements for plants. In this sense, the development of more efficient phosphorus fertilizers from alternative sources is a priority for the European Union. Struvite ($MgNH_4PO_4 \cdot 6H_2O$), obtained from the urban wastewater treatment plants is being considered an alternative phosphorus source. In this study, the fertilizing effect of struvite on a lettuce crop has been evaluated in comparison to three mineral fertilizers, NPK, superphosphate (SP) and ammonium phosphate (AP) in a pot experiment. A dose of 100 kgP/ha from the different fertilizer treatments was applied to a calcareous soil in 70 L pots. The growth and physiological state of *Lactuca sativa* L plants were evaluated after two successive growing cycles. Soils were sampled after each harvest to analyze the effect of the treatments on soil physic-chemical and biological properties. The results showed a similar production in plants from the first harvest growth in soils treated with struvite and NPK. Higher production values were found with AP and SP (Fig 1). The results in the second harvest showed a decrease in the plant yield in plants from AP and SP while struvite and NPK treatments maintained the values. In relation to the phosphorus content in plant, during the first harvest, plants showed the same pattern than in plant production, but in the second harvest, NPK and struvite treatments increased the phosphorus levels in the plant (Fig 2). In soil, struvite was able to maintain phosphorus level after two growing cycles due to the slow release of this nutrient to soil (Fig 3) whereas a significant decrease was observed for the other mineral fertilizer. These results are of great interest to avoid losses by lixiviation. Further studies are necessary to evaluate the mobilization mechanisms of phosphorus in soils treated with struvite in order to an adequate management of this product in a sustainable agriculture.

Acknowledgment:Project STRUVITE II (Canal de Isabel II) (2018-2019)

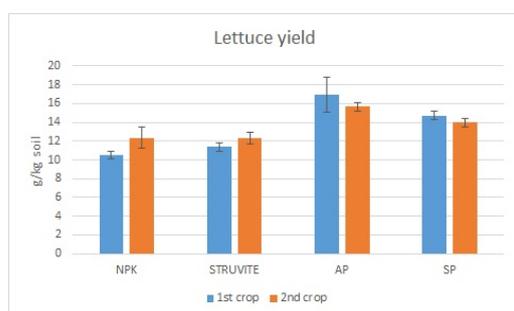


Figure 1.jpg

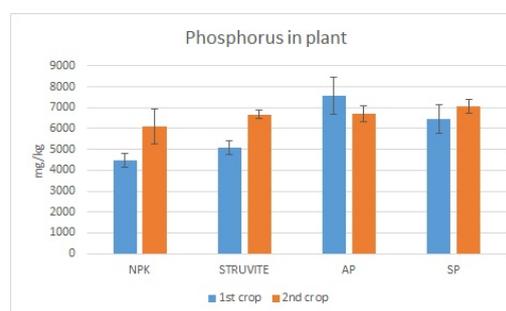


Figure 2.jpg

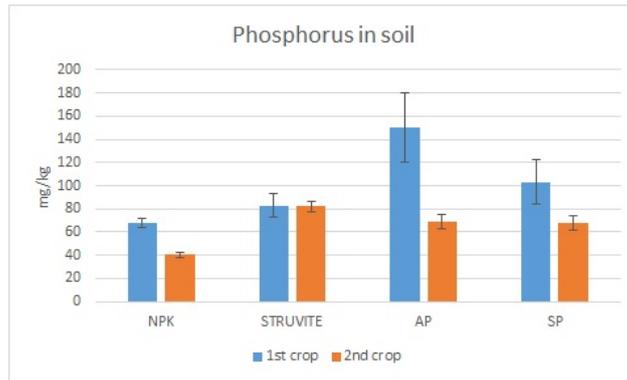


Figure 3.jpg

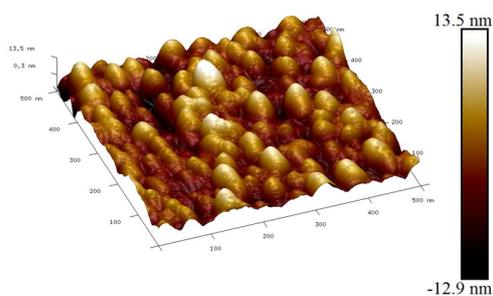
Facile synthesis of spray pyrolyzed ZnO/NiO nanocomposites thin films

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 120

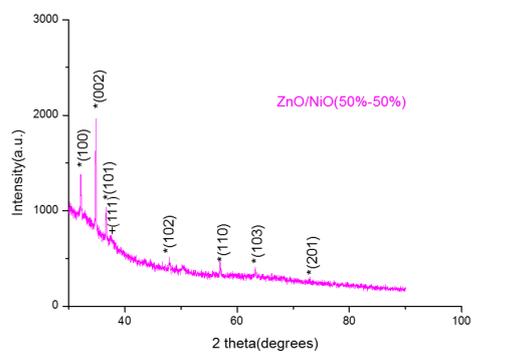
Mr. Antar Bouhank¹, Dr. Youcef Bellal¹, Mr. Hacene Serrar¹

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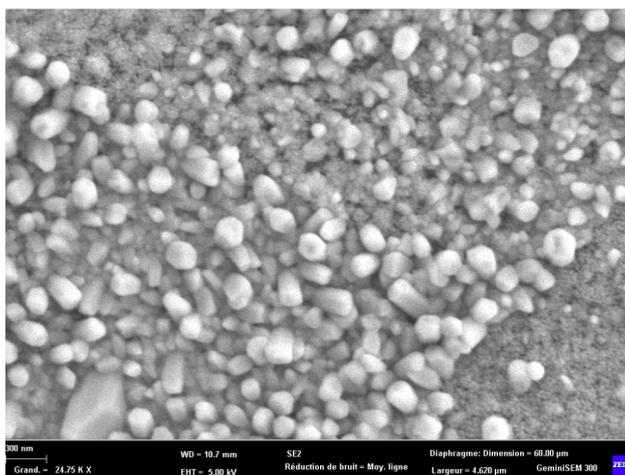
This study reviews ZnO, NiO and ZnO/NiO nanocomposites thin films deposition using the Spray Pyrolysis Technique (S.P.T). The thin films were deposited onto ordinary glass substrates heated at 500 °C from aqueous solutions of zinc chloride and nickel chloride dissolved in distilled water as precursors. The structural, morphological and optical properties of the ZnO, NiO, and ZnO/NiO thin films have been studied by X-ray diffraction, scanning electron microscopy, Raman spectroscopies and so on. The optical band gaps are 3.3 and 3.5 eV for ZnO and NiO thin films respectively obtained by UV-Vis spectroscopy. However, the optical band gaps of ZnO/NiO nanocomposites thin films, are noticeable out of the range (3.3–3.5 eV).



Afm.png



Xdr pattern.png



Meb.png

Mechanism of CO₂ activation by diaminophosphinoboranes

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 185

***Ms. Natalia Szykiewicz*¹, *Dr. Rafał Grubba*¹**

1. Gdansk University of Technology, Faculty of Chemistry

Monomeric diaminophosphinoboranes (*i*Pr₂N)₂B-PRR' (R, R' = *t*Bu, Ph) readily react with CO₂ under mild conditions to cleanly form products of the general formula (*i*Pr₂N)₂B-O-C(O)-PRR'. [1] Although diaminophosphinoboranes of this kind form stable products in the reaction with CO₂, the kinetics of these reactions are notably different - the time of complete conversion of substrates into products strongly depends on the type of substituents attached to the P atom. To investigate the mechanism of CO₂ capture and elucidate the differences in their reactivities, we carried out DFT calculations. Our mechanistic study reveals that the presence of a strong nucleophilic P center with an accessible lone pair is crucial for the activation of electrophilic CO₂. Moreover, the nucleophilicity of the P center not only influence the rate of reaction but also change the mechanism of the CO₂ insertion into the P-B bond. Hence, the reaction may proceed via two- or one-step process depending on the electron density at the P atom.

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The authors thank the National Science Centre NCN, Poland (Grant 2016/21/B/ST5/03088) for financial support.

New tertiary phosphines based on a 1,8-naphthalimide scaffold

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 164

Dr. Martin Smith¹, Mr. Luke Wilkinson¹

1. Loughborough University

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Compounds bearing the fluorescent 1,8-naphthalimide group have been widely used for example as frameworks for dyes, imaging and medical applications and in supramolecular chemistry. The easy tuneability of the planar naphthalimide scaffold, especially relevant for the synthesis of modified NHC ligands, has provided unique opportunities to explore their coordination properties.¹⁻⁵ Relative to those studies reported with NHC ligands, documented neutral phosphorus(III) ligands are sparse.⁶

Fig. 1

We report here our initial synthetic efforts, based on simple condensation reactions⁷, for tethering a polyimide group onto a P^{III} centre (see Fig. 1) and a survey of the coordination chemistry of these ligands towards selected late transition metal centres. All compounds have been characterised by a combination of spectroscopic and X-ray crystallographic techniques.

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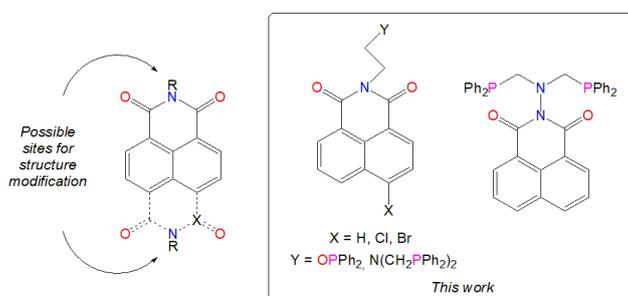


Fig. 1.png wilkinson .png

Novel synthetic approaches to cyclic and open-chained phosphasilenes

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 190

Mr. Daniel Mühlhausen¹, **Prof. David Scheschkewitz**¹, **Mr. Yannic Heider**²

1. Saarland University, 2. Saarla

Since the isolation of the first heavy alkene analogues, a class of compounds featuring heteronuclear heavy double bonds that has especially moved into focus of contemporary main group chemistry is that of phosphasilenes.^[1] Regarding the pivotal role of phosphorus as n-type dopant in the silicon semiconductor industry, the combination of these two elements on a molecular level is of particular importance. In view of their possible embedding in extended materials, the functionalization of phosphasilenes is desirable in this context. Recently, the *P*-amino functionalized electrophilic phosphasilene **1** was isolated in our group and proven to be a valuable substrate for the transfer of the P=Si moiety to various anionic nucleophiles.^[2,3] The scope of this reaction was now extended to several aryl- and alkyl lithium reagents with the dimethylamino-group in **1** acting without exception as a competent leaving group. *P*-Aryl and *P*-alkyl substituted phosphasilenes **2-5** were synthesized and isolated and fully characterized in selected cases (Figure 1). The newly synthesized phosphasilenes show an interesting correlation between the ratio of their *E/Z*-isomers and the steric demand of the substituent.

Very recently, we synthesized and isolated the first three-membered cyclic phosphasilene **6**, which is stabilized by the coordination of a donating *N*-heterocyclic carbene (NHC).^[4] Abstraction of the coordinated NHC with a Lewis-acid induces dimerization of the three-membered ring to a saturated Si₄P₂ cluster **7** (Figure 2). The scaffold of **7** is reminiscent of the Si₆TiP₆ global minimum isomer of hexasilabenzene.^[5]

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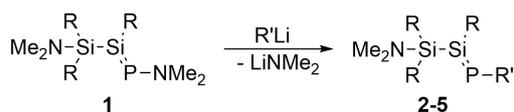


Figure 1 syntheses of p-substituted phosphasilenes 2-5.png

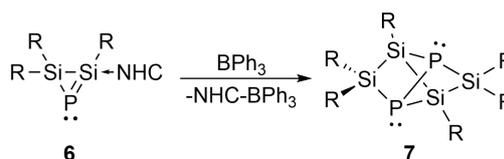


Figure 2 lewis-acid induced dimerization of the cyclic three-membered phosphasilene 6.png

Phosphorene and black phosphorus: the ^{31}P NMR view

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 192

Dr. Silvia Borsacchi¹, **Dr. Lucia Calucci**¹, **Prof. Marco Geppi**², **Dr. Francesca Martini**², **Dr. Giovanni Barcaro**³, **Dr. Maria Caporali**⁴, **Dr. Manuel Serrano-Ruiz**⁵, **Mr. Matteo Vanni**⁵, **Dr. Margherita Bolognesi**⁶, **Dr. Stefano Toffanin**⁶, **Dr. Francesca Cicogna**¹, **Dr. Serena Coiai**¹, **Dr. Elisa Passaglia**¹, **Dr. Maurizio Peruzzini**⁴

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Black phosphorus and phosphorene are attracting a large interest in the last years because of their great potential in many application fields [1]. In spite of this, the use of ^{31}P NMR spectroscopy for characterizing these materials has been very limited so far. By exploiting Magic Angle Spinning (MAS) NMR experiments we have characterized for the first time the ^{31}P - ^{31}P homonuclear dipolar couplings and the ^{31}P shielding interactions, responsible for the NMR properties of black phosphorus (bP) and of its few-layer exfoliated form (fl-bP). It has been possible to identify the network of ^{31}P nuclei more strongly dipolarly coupled and quantify their effective coupling. Moreover, with the support of DFT calculations, the ^{31}P chemical shift tensors have been fully determined, highlighting two kinds of magnetically nonequivalent ^{31}P nuclei [2]. ^{31}P MAS NMR experiments have been successfully applied to fl-bP derived materials both in suspension and in solid polymeric matrices, obtaining interesting information on the state, modifications and interactions of fl-bP with polymers and functionalizing agents, opening the way to a more extensive NMR application to phosphorene based innovative materials for improving their structural knowledge and control [3,4].

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Modeling of low non linearity and low confinement loss photonic crystal fiber by introducing asymmetric defect structures

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 205

Dr. Mohamed Benhaddad¹, Prof. Fouad Kerrou¹

1. laboratoire de Modélisation des dispositifs a énergies renouvelables et nanométrique, Université Frères Mentouri de Constantine1

Photonic crystal fiber (PCF) with minimum values of confinement loss, nonlinear coefficient, is used in optical communication. this paper proposes a small mode area with low confinement loss by introducing four rings solid core hexagonal structure which having both elliptical and circular air holes in cladding. The proposed (PCF) is simulated by using Comsol Multiphysics based on finite element method. The nonlinearity of proposed (PCF) is found to be varying with respect to wavelength range about 1200-1800[nm]. The variation of other parameters like effective refractive index, confinement loss and effective area with respect to wavelength is also investigated.

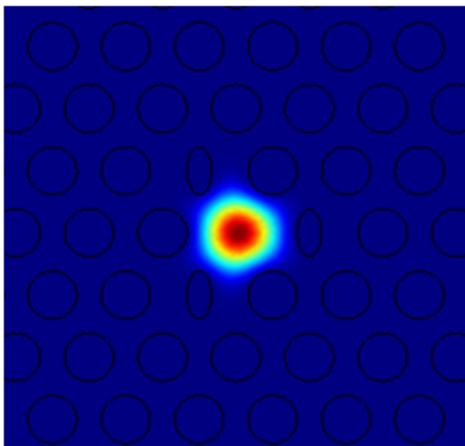


Fig.1. Typical mode pattern in the inner core of (PCF)

Concentration.png

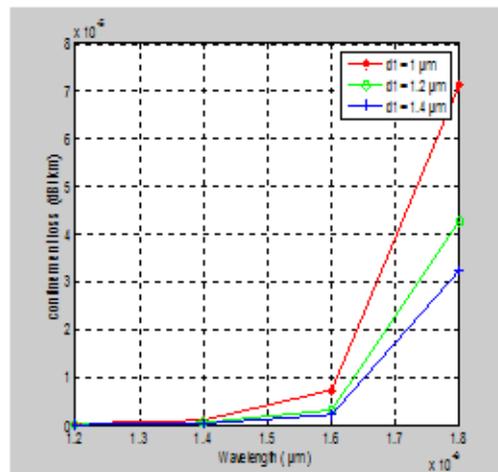


Fig.2. Plot of confinement loss vs. Wavelength

Confinement loss.png

Metallacarboranes as TNBC therapeutics

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 207

Mr. Neville Murphy¹, **Dr. Pau Farràs**¹, **Dr. Roisín Dwyer**¹, **Prof. Andrew Dove**², **Dr. Andrew Weems**²

1. National University of Ireland Galway, 2. University of Birmingham

Metallacarboranes are boron cluster's answer to 'sandwich complex' metallocenes, a group of polyhedral cluster compounds comprising of carbon, boron, hydrogen and a metal centre. Properties such as high stability in biological systems, amphiphilicity and tuneability has seen interest in these molecules surge in recent times.¹⁻³ Potential applications in anti-cancer and antimicrobial therapeutics are already being explored while both carborane and metallacarborane compounds have seen extensive testing as pharmacophores.⁴⁻⁷ This work investigates the efficacy of various metal centres (figure 1) in metallacarboranes against triple-negative breast cancer, which accounts for 20-25% of all breast cancers and has a generally poor prognosis.⁸

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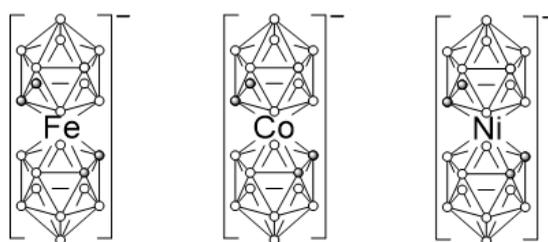


Figure 1: Iron, cobalt and nickel metallacarboranes.

Metallacarboranes for testing.png

Reactivity of silane compounds with few-layer black phosphorus

Monday, 2nd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 215

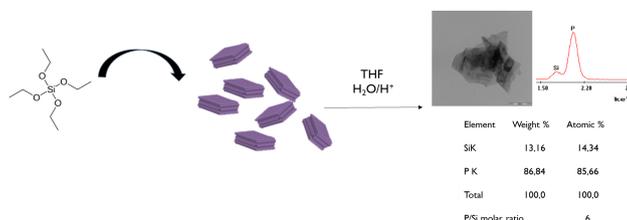
Mr. Iñigo Iglesias¹, **Dr. Andrea Ienco**², **Dr. Manuel Serrano-Ruiz**³, **Dr. Maria Caporali**³, **Dr. Maurizio Peruzzini**², **Dr. Martina Banchelli**⁴, **Dr. Paolo Matteini**⁴

1. University of Siena; Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR-ICCOM, Sesto Fiorentino, 2. Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR-ICCOM, Sesto Fiorentino, 3. Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR-ICCOM, Sesto Fiorentino, 4. CNR-IFAC

2D materials have attracted the interest of researchers around the world due to their outstanding properties and potential applications in many fields such as optoelectronics and sensing. Among those 2D materials, phosphorene, which consists on a single layer of bulk orthorhombic black phosphorus¹, seems to be promising due to its outstanding mechanical, optical and electrical properties. Yet, the instability of this material in air and its tendency to degrade very quickly via reaction with oxygen, water and light is a major drawback that impedes its direct application.² Therefore, for the last years, research efforts have been devoted to the chemical functionalization of this fascinating nanomaterial in order to improve its stability.³ It is known that SiO₂ coating is a common process that has been previously used in many nanomaterials, such as carbon nanotubes.⁴ This kind of coating does not alter its electronic structure significantly and improves their resistance to degradation. In this work, we have studied the reactivity of few-layer black phosphorus with various silane compounds such as TEOS and PDMS, with a focus on understanding the role of pH on the achievement of the final product. Characterization of the reaction products (Infrared spectroscopy, Raman, Transmission electronic microscopy, etc) shows the layers of BP are containing silicon compounds and that the flakes are free of SiO₂ nanoparticles on its surface. Analysis via Energy Dispersive X-ray spectroscopy confirmed the presence of Si whose quantity depends on the reaction conditions. Crystalline structure of silicon compounds formed after the reaction in both presence and absence of black phosphorus under the same conditions was also analysed via X-Ray powder diffraction.

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Sipgraphic.png

Heavier cyclopropenes

Monday, 2nd December - 14:30: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 72

Prof. David Scheschkewitz¹

1. Saarland University

Cyclopropene and its heavier homologues have attracted considerable interest as the smallest unsaturated cyclic species. The chemistry of both is dominated by a more or less facile ring opening due to the pronounced strain common to three-membered rings. In addition, the heavier congeners also display the generally enhanced reactivity of the inherently weak heavier double bond and therefore have to be kinetically protected by sterically demanding substituents.

The lecture will discuss numerous examples of heavier cyclopropenes based on silicon, germanium, tin and phosphorus at the borderline to insufficient kinetic stabilization. As will be demonstrated, the comparatively small substituents thus employed fine-tune the stability of heavier cyclopropenes with regards to other isomers such as cyclopropylidene- and vinyl carbene analogues. The application of this concept in the activation of small molecules (CO, isonitriles, alkenes and alkynes) as well as the construction of larger (saturated and unsaturated) oligomeric species will be showcased. Particular attention will be devoted to the reversibility of such processes with a view to catalysis and materials.

A stable N-heterocyclic silylene with a 1,1'-ferrocenediyl backbone: reactivity towards carbonyl compounds and fundamentally important small molecules

Monday, 2nd December - 15:04: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 20

*Ms. Nadine Weyer*¹, *Dr. Michael Leibold*¹, *Dr. Clemens Bruhn*¹, *Prof. Ulrich Siemeling*¹

1. University of Kassel

We recently demonstrated that stable ferrocene-based N-heterocyclic carbenes (NHCs) of the type $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NR}\}_2\text{C:}]$ can add NH_3 and CO under mild conditions.[1, 2] Such small-molecule activation reactions are typical of (alkyl)(amino)carbenes, but were completely unprecedented for diaminocarbenes. In view of the surprising reactivity of these NHCs, which is due to their ambiphilic nature, we surmised that their heavier analogues, N-heterocyclic tetrylenes of the type $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NR}\}_2\text{E:}]$ ($\text{E} = \text{Si} - \text{Pb}$), will show unconventional chemical behaviour, too.

Due to the availability of suitable divalent starting materials, the synthesis and isolation of such compounds was easily possible for $\text{E} = \text{Ge}, \text{Sn}$ and Pb .[3, 4] N-heterocyclic silylenes are significantly more challenging. Nevertheless, we have been able to obtain the stable congener $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NDipp}\}_2\text{Si:}]$ by using bulky aryl substituents ($\text{Dipp} = 2,6\text{-diisopropylphenyl}$). We have started to investigate its reactivity towards fundamentally important small molecules (Scheme 1). Facile H-X bond activation is observed with H_2O , NH_3 and H_3BNH_3 , affording 1,1-addition products of the type $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NDipp}\}_2\text{SiHX}]$ ($\text{X} = \text{OH}, \text{NH}_2$ and BH_2NH_3 , respectively). $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NDipp}\}_2\text{Si:}]$ readily reacts with the heterocumulenes N_2O and CO_2 , respectively liberating N_2 and CO . The reaction with N_2O furnishes $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NDipp}\}_2\text{SiO}]_2$, which is the head-to-tail dimer of the corresponding silanone. We surmise that this silanone is also formed as an intermediate in the reaction with CO_2 , but is efficiently trapped by unreacted CO_2 , affording the spiro-type orthocarbonate $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NDipp}\}_2\text{SiO}_2]_2\text{C}$. $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NDipp}\}_2\text{Si:}]$ undergoes addition reactions with a variety of ketones (Scheme 2). Its reaction with acetone leads to $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NR}\}_2\text{SiH}\{\text{OC}(=\text{CH}_2)\text{Me}\}]$, which is the product of a 1,1-addition of the corresponding enol tautomer $\text{H}_2\text{C}=\text{C}(\text{OH})\text{Me}$. Other enolizable ketones show analogous reactions. In contrast, the non-enolizable ketone fluorenone affords a silaoxirane in a formal [2+1] cycloaddition. In the same vein, the reaction with diphenylketene furnishes a silaallene oxide (Scheme 2). All silicon compounds shown in Schemes 1 and 2 have been structurally characterised by single-crystal X-ray diffraction.

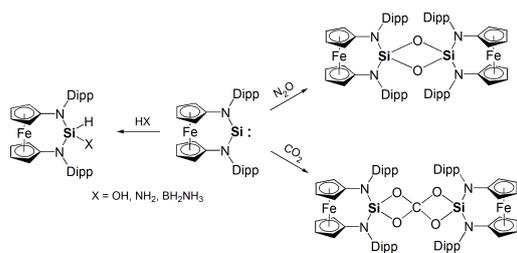
In summary, the stable N-heterocyclic silylene $[\text{Fe}\{\eta^5\text{-C}_5\text{H}_4\text{NDipp}\}_2\text{Si:}]$ has been synthesised and investigated. Due to its 1,1'-ferrocenediyl backbone it can be viewed as containing a six-membered $\text{FeC}_2\text{N}_2\text{Si}$ ring. Its reactivity is unusual for N-heterocyclic silylenes with dicoordinate Si^{II} and reminiscent of that of the ambiphilic "Kira silylene".

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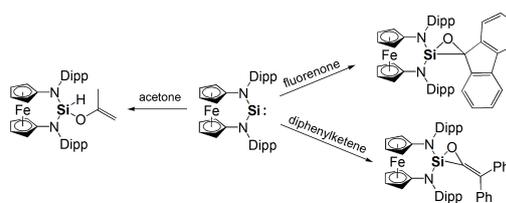
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Scheme 1 reactions with small molecules.png



Scheme 2 reactions with carbonyl compounds.png

ESi5 heterosiliconoids (E = B, P): Stable n- and p-doped unsaturated silicon clusters

Monday, 2nd December - 15:38: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 180

Mr. Yannic Heider¹, Prof. David Scheschkewitz¹

¹. Saarland University

Unsaturated silicon clusters (siliconoids) are short-lived intermediates during the transition from molecules to the elemental bulk; stable representatives reiterate surface features of silicon materials.^[1] The incorporation of suitable heteroatoms into the cluster scaffold of stable siliconoids extends this analogy to the technological process of silicon doping. Very recently, we were able to isolate the first boron- and phosphorus-containing heterosiliconoids with BSi₅ and PSi₅ cluster cores, respectively.

While the reductive cleavage of a Tip group from the global minimum Si₆R₆ benzpolarene **1** (R = Tip = 2,4,6-ⁱPr₃C₆H₂) gives the anionic siliconoid **2**,^[2] which serves as precursor for various functionalized Si₆ siliconoids, the usage of two further equivalents of reducing agent results in the dianionic Si₅R₄²⁻ cluster **3** with formal loss of the *privo* SiR₂ moiety (Figure 1). X-ray diffraction and multinuclear NMR spectroscopy of **3** underlined its reminiscence of small Zintl-anions of silicon in terms of structural and electronical properties.^[3,4]

In a proof-of-principle reaction **3** was treated with TMSCl to afford the corresponding TMS-substituted derivative **4**. The reaction of **3** with ⁱPr₂NECl₂ (E = B, P) yields the unprecedented p- and n-doped heterosiliconoids **5** and **6** (Figure 2).

Full characterization including NMR spectroscopy, X-ray diffraction and DFT calculations confirmed the integrity of the electronic benzpolarene signature despite the substitution of the *privo* silicon vertex by boron or phosphorus atoms, respectively.

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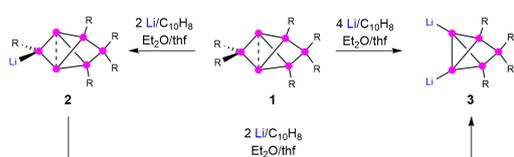


Figure 1 synthesis of dianionic si5r42 cluster
3.png

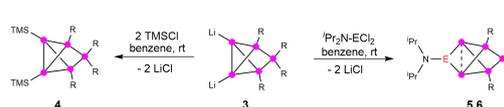


Figure 2 syntheses of bis tms -substituted
si5-cluster 4 and boron and phosphorus doped
siliconoids 5 and 6.png

Diphosphination and phosphinoboration of carbon dioxide

Monday, 2nd December - 15:55: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 188

Dr. Rafał Grubba¹, **Ms. Natalia Szykiewicz**¹, **Ms. Anna Ordyszewska**², **Dr. Łukasz Ponikiewski**¹,
Prof. Jarosław Chojnacki¹

1. Gdansk University of Technology, Faculty of Chemistry, 2. Gdansk University of Technology

Introduction

The activation of small molecules constitutes one of the main frontiers of the modern inorganic chemistry. For many years this field was the exclusive realm of transition metals chemistry, however since the first decade of this century, great number of non-metallic systems for activation of small molecules were discovered. Among the great variety of systems based on the main group elements capable of activating H₂, CO₂, SO₂ or nitrogen oxides, compounds containing phosphorus and boron atoms have a significant contribution to this field. In our research group, we design and synthesize compounds containing P-P or P-B functionalities and investigate their reactivity towards small molecules.

Methods

The isolated products were fully characterized by multinuclear NMR spectroscopy, IR spectroscopy, and X-ray diffraction.

Results and discussion

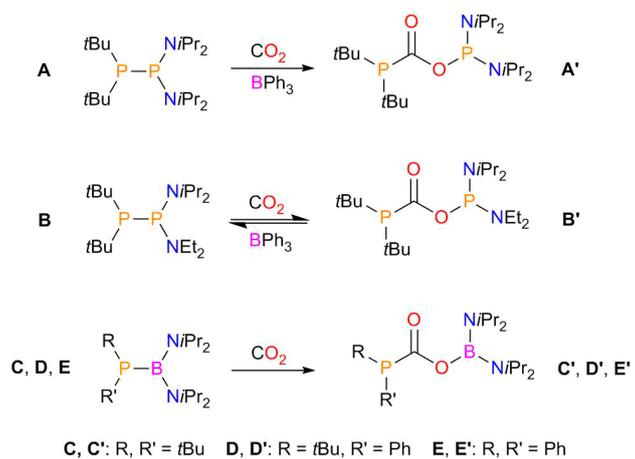
We obtained a range of new diphosphanes with diversified nucleophilic properties of P-atoms and applied them as basic components in frustrated Lewis pairs (FLP).¹ The unsymmetrical diphosphanes with polarized P-P bond react at room temperature with CO₂ with the presence of stoichiometric or catalytic amounts of BPh₃ with insertion of CO₂ into P-P bond (Scheme 1A-B).² These results are in strong contrast to the reactivity of known FLPs where a formation of zwitterionic species containing tetracoordinated phosphorus and boron was observed. We found that the presence of long and polarized P-P bonds is crucial for the activation of CO₂ by diphosphanes. This synthetic approach can be also applied to trivalent phosphorus and boron compounds with direct P-B bonds. For this purpose we have synthesized a series of new diaminophosphinoboranes, which are structural analogs of unsymmetrical diphosphanes, where one P atom has been replaced by a B atom (Scheme 1C-E).³ The monomeric diaminophosphinoboranes readily react with CO₂ under mild conditions to form products of the general formula R₂P-C(=O)-O-B(NR₂)₂.

Acknowledgments

The authors thank the National Science Centre NCN, Poland (Grant 2016/21/B/ST5/03088) for the financial support.

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Scheme 1. Diphosphination and phosphinoboration of CO₂.

Scheme1.png

Boron clusters on the road to detection and anticancer therapies

Monday, 2nd December - 14:30: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 65

***Prof. Clara Viñas*¹, *Prof. Francesc Teixidor*¹, *Dr. Elena Oleshkevich*¹, *Ms. Isabel Fuentes*¹, *Ms. Arpita Saha*¹**

1. ICMAB-CSIC

The twelve-vertex *closo* C₂B₁₀H₁₂ icosahedral carboranes have been the most widely studied polyhedral Boron clusters because are solids that rank among the most stable molecular compounds known. Moreover, despite showing remarkable chemical inertness, they can be functionalized by different straightforward reactions.¹ Icosahedral carboranes act as strong electron-withdrawing ligands through substitution on carbon and as electron-donating moieties when substitution is through the boron vertices² in a regioselective manner, and have many possible sites of substitution, up to twelve.^{2c} Carboranes, which are 3D aromatic and highly stable species can be visualized as hollow spheres.³ The unique stability and geometrical properties of the isomeric *closo* C₂B₁₀H₁₂ carboranes suggested these hollow spherical cages as building blocks for stereo precise structural platforms of novel reaction centers having properties that cannot be achieved with organic hydrocarbon compounds.

The aim of this presentation is to show the ability of boron clusters in producing new molecules for targeted applications in nanomaterials and nanomedicine: the incorporation of spherical carboranes as capping agents for magnetite/maghemite NPs⁴ and the interaction between metallabis-(dicarbollide) with double-stranded DNA as well as “*in vitro*” and “*in vivo*” studies will be presented.⁵The simple protein stabilization through its encapsulation by an inorganic molecule capable for anchoring and self-assembling will be also reported.⁶

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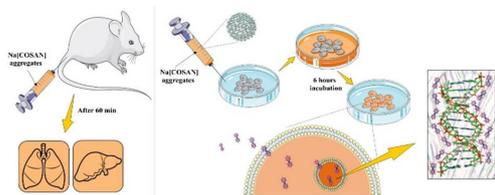


Figure 1.jpg

ChemPubSoc Europe DOI: 10.1002/chem.201803178 CHEMISTRY A European Journal Full Paper

DNA Recognition

Metallacarboranes on the Road to Anticancer Therapies: Cellular Uptake, DNA Interaction, and Biological Evaluation of Cobaltabisdicarbollide [COSAN]

Isabel Fuentes,^[a] Tania García-Mendiola,^[a, b, c, d] Shinichi Sato,^[d] Marcos Pita,^[a] Hiroyuki Nakamura,^[a] Encarnación Lorenzo,^[b, c, d] Francesc Teixidor,^[d] Fernanda Marques,^[d] and Clara Viñas^[a, d]

Chem. Sci., 2018, 24, 17239–17254 Wiley Online Library 17239 © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 2.jpg

Carboranes in medicinal chemistry

Monday, 2nd December - 15:04: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract
ID: 75

***Prof. Evamarie Hey-Hawkins*¹, *Dr. Menyhárt-Botond Sárosi*¹**

1. Leipzig University

Since the discovery of polyhedral carboranes more than fifty years ago, their potential for various applications has been unlocked. Mainly, their use as pharmacophores is due to their remarkable biological stability and hydrophobicity. The cage framework of these clusters can be easily modified with a variety of substituents both at the carbon and at the boron atoms. It has been shown that the implementation of the carboranyl moiety, as a phenyl mimetic, in biologically active molecules results in compounds that can exhibit improved biological stability and activity in comparison to their generic paradigms. However, up to now, the use of carboranes as pharmacophores is limited to just a few examples.^[1] Our research focuses on several types of enzyme inhibitors, such as cyclooxygenase (COX) or lipoxygenase (LOX) inhibitors.

A highly coveted approach in the design of novel nonsteroidal anti-inflammatory drugs that are applied in the treatment of various inflammatory processes is achieving cyclooxygenase (COX) 2 selectivity. By implementing a carboranyl moiety in the structures of known COX inhibitors more selective and robust COX-2 inhibitors were obtained (Figure 1).^[2]

5-Lipoxygenase (5-LOX) is an enzyme of the extracellular matrix and plays a role in increased metastasis and angiogenesis. Numerous reports show the overexpression of 5-LOX in several cancer cell lines. For the activation of 5-LOX, the 5-LOX-activating protein (FLAP) is necessary. Therefore, inhibition of 5-LOX or FLAP could inhibit tumour growth and angiogenesis. Replacement of phenyl rings in selected 5-LOX inhibitors by carboranes resulted in a similar enzymatic inhibitory behaviour but markedly increased cytotoxicity against several melanoma and colon cancer cell lines (Figure 2).^[3] Selected examples will be presented.

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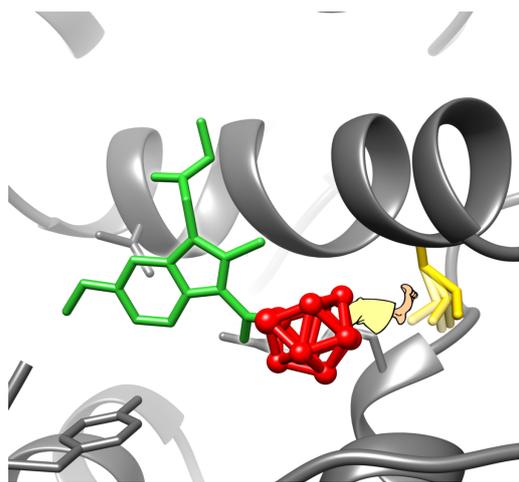


Figure 1.png

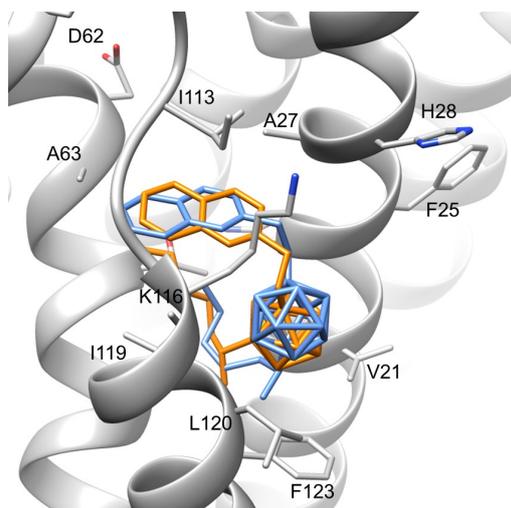


Figure 2.jpg

Multidentate ligands with phosphorus pendant arms in the synthesis of potential antitumor agents based on rhenium(I) complexes

Monday, 2nd December - 15:38: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 129

Dr. Diana Aleksanyan¹, **Dr. Svetlana Churusova**¹, **Dr. Ekaterina Rybalkina**², **Prof. Vladimir Kozlov**¹

1. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 2. Blokhin National Medical Research Center of Oncology of the Ministry of Health of the Russian Federation

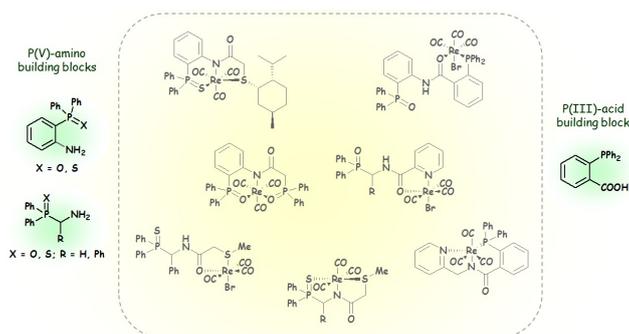
(Thio)phosphoryl-substituted aromatic and aliphatic amines as well as *o*-diphenylphosphinobenzoic acid were used as convenient key precursors for the synthesis of new multidentate ligands with central amide units *via* modular assembling of building blocks—functionalized amines and carboxylic acids. The ligands obtained readily formed complexes with Re(I) ions, adopting either neutral bidentate or monoanionic tridentate pincer-type coordination mode depending on the nature of pendant phosphorus arms and reaction conditions (Fig. 1). In turn, the syntheses of the phosphorus-containing precursors were accomplished either by the published procedures or facile approaches developed by our group.

Recently, organometallic rhenium(I) complexes with bidentate heterocyclic, alkoxide, hydroxide and organophosphorus ligands were found to display promising cytotoxic properties against several cancer cell lines [1, 2]. At the same time, the efficiency of their multidentate analogs is still almost unexplored. Therefore, the complexes obtained were tested for *in vitro* cytotoxic activity on a range of human cancer cells, including human colon (HCT116), breast (MCF7), and prostate (PC3) cancers (see, *e.g.*, Ref. [3]). Most of the compounds explored demonstrated prominent cytotoxic properties, with IC₅₀ values falling into a low-micromolar range. In general, the tridentate pincer-type coordination provided higher efficiency, which is likely to be connected with the higher stability of such complexes in biological environment. The results of cytotoxicity studies on transformed breast cells HBL100 and their doxorubicin-resistant subline showed the potential for development of Re(I) therapeutic agents that could overcome multidrug resistance. The main structure–activity relationships for a new class of promising antitumor agents as well as some mechanistic aspects of their biological action will be discussed.

This work was supported by the Russian Science Foundation, project no. 18-73-00310.

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3. D. V. Aleksanyan, S. G. Churusova, E. Yu. Rybalkina, O. I. Artyushin, A. S. Peregudov, Yu. V. Nelyubina, Z. S. Klemenkova, O. V. Bykhovskaya, V. A. Kozlov, *J. Organomet. Chem.*, **2019**, 892, 66.



Rhenium i complexes based on multidentate ligands with phosphorus pendant arms.jpg

Development of tumor-targeting boron-containing compounds for Boron Neutron Capture Therapy

Monday, 2nd December - 15:55: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 169

Mr. Cheng-Ying Hsieh¹, Ms. Jui-Hsun Chang², Mr. Zong-Kai Xue², Ms. Yi-Hsiu Chung², Prof. Chun-Yi Wu³, Prof. Jen-Kun Chen⁴, Prof. Ming-Hua Hsu², Prof. Jia-Cherng Horng¹

1. Department of Chemistry, National Tsing-Hua University, Taiwan, 2. Department of Chemistry, National Changhua University of Education, Taiwan, 3. Department of Biomedical Imaging and Radiological Science, China Medical University, Taiwan, 4. Institute of Biomedical Engineering & Nanomedicine, National Health Research Institutes, Taiwan

Boron Neutron Capture Therapy (BNCT) is a potential treatment for brain cancer, head and neck cancer, and melanoma. BNCT is a treatment through the nuclear reaction of boron atoms. It will produce lithium atoms and α -particles. The α -particles can only go forward a few micrometers in the living system but are enough to kill the cancer cells (fig. 1). The effect of the BNCT is based on the selectivity of boron-containing drugs. The 4-dihydroxy-boryl-L-phenylalanine (BPA) is the most commonly used drug to perform the BNCT clinical trial. But these are not good enough to become ideal drugs in formal treatment. As such, it is essential to develop a novel high boron-containing drug.

To targeting tumor cells, here we select phosphatidylserine and hypoxia targeting based on the pathological characterization of tumor cells. In a normal situation, the surface net charge of the cell membrane will approach to zero. When the cell occurs inflammation or apoptosis, the surface net charge changes to negative due to the phosphatidylserine exposed. Zinc(II)-dipicolylamine group is a receptor for anionic membranes in cell culture and living subjects (fig. 2). Here, we design and synthesize the boron cluster conjugated zinc(II)-dipicolylamine (ZnDPA) to approach the aims of increasing T/N ratio and rising boron concentration of the tumor region. On the other hand, the abnormal cell growth will cause oxygen shortage around the tumor cells. 2-nitroimidazole derivatives such as [¹⁸F]FMISO are used in PET imaging to detect tumor hypoxia (fig. 3). Here, we conjugate a boron cluster with 2-nitroimidazole through click reaction. We will evaluate the biodistribution of the boron cluster-based derivatives described above, so we already attached an iodine atom on the boron cluster. Mean-time, we can label the iodine-123 onto the boron cluster using Sodium iodine-125 by iodo-exchange reaction. The biodistribution and accumulation of boron agents will be assessed by radiation imaging. We will also evaluate the cell viability and cell uptake of synthesized products.

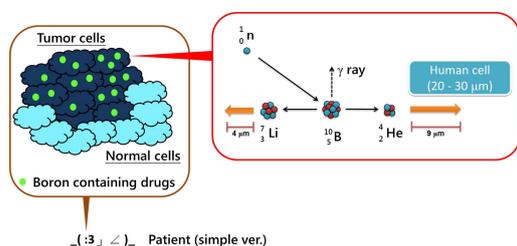


Fig. 1.jpg

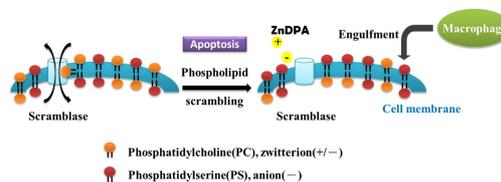


Fig. 2.jpg

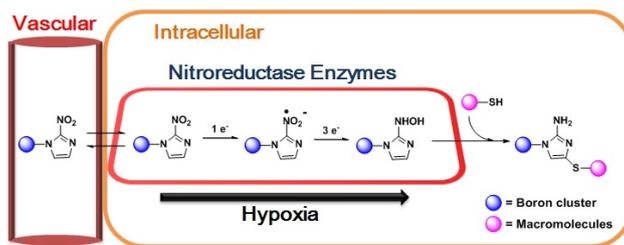


Fig. 3.jpg

Novel synthetic approach to charge-compensated nido-carborane ligands

Monday, 2nd December - 16:40: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 123

Dr. Marina Stogniy¹, **Ms. Svetlana Erokhina**¹, **Prof. Igor Sivaev**¹, **Prof. Vladimir Bregadze**²

1. A.N. Nesmeyanov Institute of Organoelement Compounds, 2. A.N. Nesmeyanov Institute of Organoelement Compounds, RAS

The 7,8-dicarba-*nido*-undecaborate anion due to its unique physical and chemical properties and unusual three-dimensional π -character plays an important role in the development of the metallocarborane chemistry.^{1,2} Another important property of this anionic cluster is the capability to form charged-compensated compounds that can provide the ligating of transitional metal ions.

In this work we present the new synthetic approach to the obtaining of charged-compensated *nido*-carborane derivatives *via* the reactions of nucleophilic addition to its nitrilium derivatives.^{3,4} The proposed method allows obtaining wide range of *nido*-carborane ligands with simple substituents as well as ligands with additional functional groups in the side-chain.

The prepared compounds can be used for the synthesis of transitional metals half-sandwich complexes.

Acknowledgments

This work was supported by Russian Science Foundation (Grant 19-73-00229)

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3. M. Yu. Stogniy, S. A. Erokhina, K. Yu. Suponitsky, A. A. Anisimov, I. B. Sivaev, V. I. Bregadze, *New J. Chem.* **2018**, 42, 17958.
4. M. Yu. Stogniy, S. A. Erokhina, I. B. Sivaev, V. I. Bregadze, *Phosphorus, Sulfur, and Silicon and the Related Elements* **2019**, <https://doi.org/10.1080/10426507.2019.1631312>.

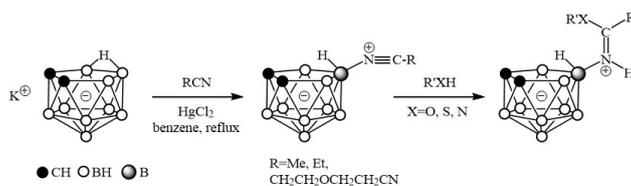


Fig. 1. the synthetic route to charged-compensated nido-carborane derivatives.jpg

Metal-free nucleophilic substitution of iodine in nido-carborane

Monday, 2nd December - 16:57: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 158

Prof. Igor Sivaev¹

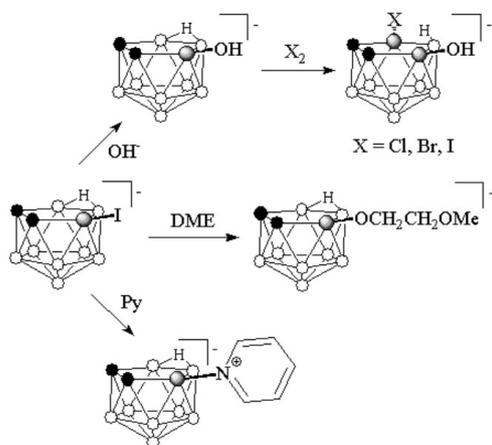
1. Nesmeyanov Institute of Organoelement Compounds

Iodo derivatives of carboranes are widely used in metal-catalyzed reactions for formation of derivatives with B-C [1], B-N [2], B-P [3], B-O [4] and B-S bonds. On the best of our knowledge, there is only one report on metal-free substitution of iodine in the carborane chemistry describing reactions of iodo derivatives of metallacarboranes [8-I-3,3'-M(1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)]⁻ (M = Co, Fe) with pyridines [6].

We found that reactions of 9-iodo-*nido*-carborane [9-I-7,8-C₂B₉H₁₁]⁻ with nucleophiles under basic conditions result in nucleophilic substitution of iodine with formation of the corresponding *nido*-carborane derivatives with B-O and B-N bonds (Scheme 1). These reactions can be applied to generation of *nido*-carborane derivatives in situ followed by formation of the corresponding substituted metallacarboranes (Scheme 2). The synthesized compounds were characterized by mass-spectrometry, multinuclear NMR spectroscopy and single crystal X-ray diffraction.

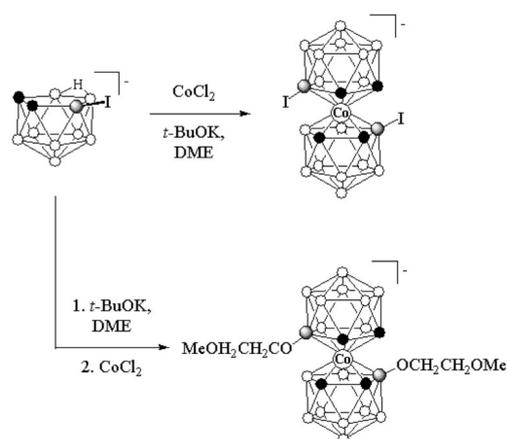
This work was supported by Russian Science Foundation (16-13-10331).

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Scheme 1

Scheme1.jpg



Scheme 2

Scheme2.jpg

Synthesis of fluorescent water-soluble phosphorus dendrimers excited by two photons for biological uses

Monday, 2nd December - 17:14: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 78

Mr. Artem Zibarov¹, Dr. Aurelien Hameau¹, Dr. Kathleen Moineau-Chane Ching², Dr. Anne-Marie Caminade¹, Dr. Jean-Baptiste Verlhac³, Dr. Mireille Blanchard-Desce³, Dr. Maxime Klausen⁴

1. Laboratoire de Chimie de Coordination du CNRS UPR 8241; Université Toulouse III Paul Sabatier, **2.** Laboratoire de Chimie de Coordination du CNRS UPR 8241, **3.** Institut des Sciences Moléculaires, Université de Bordeaux, CNRS UMR 5255, **4.** Institut des Sciences Moléculaires, Université de Bordeaux, CNRS UMR 5255

There is always a need for new water-soluble fluorescent tools in biology, for different purposes. In recent years Two-Photon Excited (TPE) fluorophores have obtained a widespread popularity in the biology community due to the fact that this type of fluorophores provides improved spatial selectivity in three dimensions, and can be excited at a frequency of half the actual energy gap, thus at longer wavelengths (typically 700–1300 nm), but the fluorescence occurs at the same wavelength than when excited with one photon. Thanks to this it's possible to increase the penetration depth and decrease the photo damage to tissues at the same time.

The most widely used TPE-fluorophores are quantum dots (inorganic nanocrystals) but they raised a number of questions related to toxicity, biocompatibility and environmental issues. Besides, organic TPE fluorophores cannot be as brilliant as quantum dots and their fluorescence could be quenched by water.

Fluorescent water-soluble dendrimers containing several TPE chromophores may help to solve both problems^{1,2}. Indeed, dendrimers³ are molecules with an arborescent structure. Despite the fact that dendrimers, like polymers, consist of tens, hundreds and even thousands of units, they have a strictly defined structure because they are synthesized step by step. The dendrimers are thus composed of a core on which branches with points of divergence and surface functions are attached.

Fluorescent properties of fluorophores, attached to the branches of the dendrimer, might be protected due to a shielding effect of dendritic structure, revealed by photophysical studies. Moreover when several fluorophores are attached to dendrimer branches, the problem of low brilliance of an individual molecule is solved.

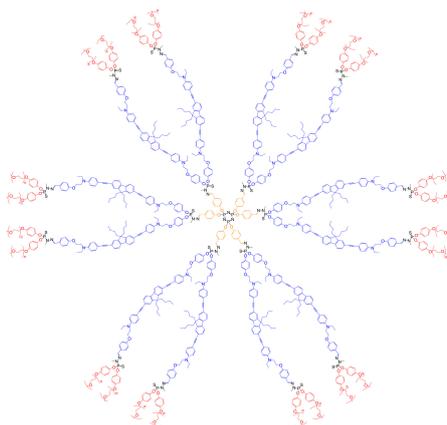
The solubility in water can be obtained by using fluorophores (if they are end groups) with ionic functions or by adding cationic (ammoniums), anionic (carboxylates or phosphonates) or neutral groups (PEG) to the dendrimer molecule.

We will present water-soluble fluorescent dendrimers with TPE fluorophores, that have been synthesized and investigated and their use for biology holds great promises for the future.

¹ T. R. Krishna, M. Parent, M. H.V. Werts, L. Moreaux, S. Gmouh, S. Charpak, A.-M. Caminade, J.-P. Majoral, M. Blanchard-Desce, *Angew. Chem. Int. Ed.*, 2006, 45, 4645-4648.

² A. Sourdon, M. Gary-Bobo, M. Maynadier, M. Garcia, J.-P. Majoral, A.-M. Caminade, O. Mongin, M. Blanchard-Desce, *Chem. Eur. J.* 2019, 25, 3637-3649.

³Dendrimers. Towards Catalytic, Material and Biomedical Uses. A.-M. Caminade, C.-O. Turrin, R. Laurent, A. Ouali, B. Delavaux-Nicot (Eds), John Wiley & Sons, Chichester, UK, 2011



Structure of the water-soluble dendrimer. dendrimer heart orange the chromophores blue peg derivative red.jpg

Bisphosphonyl-substituted α -amino acids: Synthetic route to new potentially active compounds

Monday, 2nd December - 17:31: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 57

Dr. Romana Pajkert¹, **Ms. Isabeau Lüddecke**¹, **Prof. Jianlin Han**², **Dr. Haibo Mei**², **Prof. Gerd-Volker Rösenthaller**¹

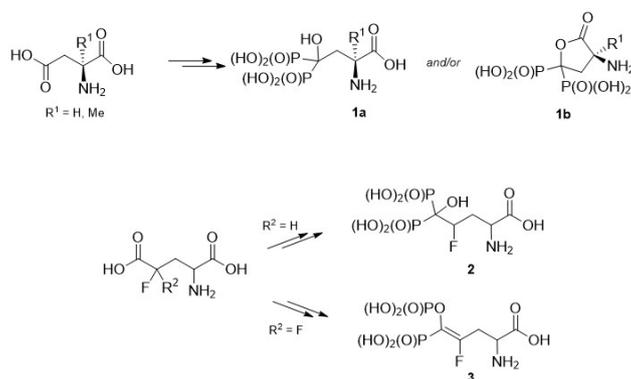
1. Jacobs University Bremen, 2. Nanjing Forestry University

Bisphosphonates (BPs), analogues of the naturally occurring diphosphates with a metabolically stable P-C-P structure and hydroxybisphosphonates are important and effective class of clinically used drugs developed for the treatment of metabolic bone disorders associated, such as osteoporosis and Paget's disease. They are effective inhibitors of tumor-induced bone destruction and significantly reduce the incidence of skeletal complications in patients with bone metastases from several forms of cancer, including breast and prostate cancer. BPs especially hydroxybisphosphonates with an additional hydroxy anchor-group have a high affinity for calcium and therefore specifically target bone mineral. They are also effective against parasites, sleeping sickness, Chagas disease, malaria and Leishmaniasis.¹

In this context, the synthetic route to selected α -amino acids (**1**, **2**) bearing bisphosphonic moiety will be presented. This methodology included the hexafluoroacetone-protection of α -functionalized carboxyl group, activation of the remained carboxyl group with thionyl chloride, bisphosphonylation of the resulting acyl chlorides, hydrolysis and deprotection of the obtained bisphosphonic acids. In the case of difluorinated amino acids, such as β -difluoroglutamic acid, a rearrangement to furnish alkenyl phosphato-phosphonate (**3**) was observed² (Scheme).

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2. I. Lüddecke, G.-V. Rösenthaller, R. Pajkert, J. Han, H. Mei, *Eur. J. Org. Chem.* submitted.



Pajkert.jpg

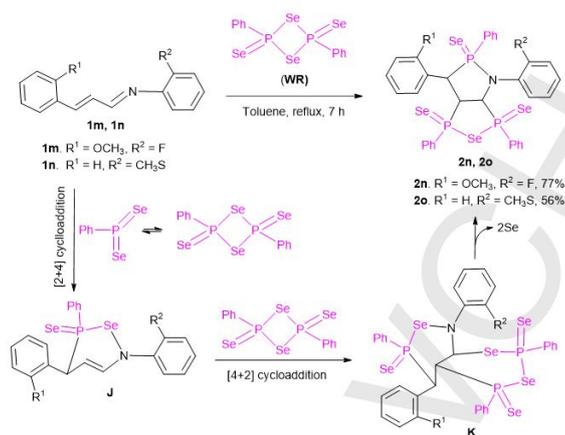
Reactivity of Woollins' reagent with Schiff bases

Monday, 2nd December - 17:48: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 206

Prof. Derek Woollins¹, Dr. Guoxiong Hua²

1. Khalifa University, 2. University of St Andrews

Woollins' Reagent serves as a reductive cycloaddition reagent with 2-en-1-imines containing a conjugated C=C bond group (Schiff bases) leading to a series of four-, five-, six-membered 1,2-azaphospholidines incorporating one or two N-P=Se linkages.



Capture.jpg

Stable cAAC–phosphonyl radicals adducts

Monday, 2nd December - 18:05: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 34

Mrs. Yulia Livshits Kritsman¹, Dr. Boris Tumansky¹, Dr. Roman Dobrovetsky¹

1. Tel Aviv University

[P=O][•]-type radicals and their adducts are proposed as intermediates in a number of important chemical transformations. As well as, these paramagnetic species are of an interest in electronic organic material field. Despite the interest in these species, the examples of their stable paramagnetic derivatives are scarce, in fact, only one example of stable [R₃P=O]^{•-} anion-radical is known in the literature. Here we report the synthesis, EPR and theoretical study of stable phosphonyl radical – cyclic alkyl amino carbene (cAAC) adducts, [R₂P(O)–cAAC][•]. Experimental and computational data indicate that most of the spin density in these radicals is localized on the carbon atom from the cAAC unit. However, intriguingly the chemistry of some of these radical species is typical for phosphorus-centered radicals.

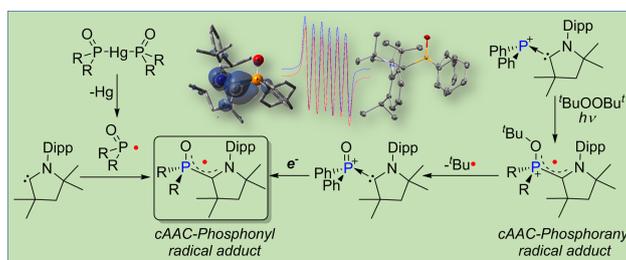


Fig1new1.png

Building blocks for “carbonphosphides” and related P,C,N compounds

Monday, 2nd December - 18:22: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 221

*Prof. Hansjoerg Gruetzmacher*¹, *Mr. Moritz Scharnhoezl*¹, *Prof. Zhongshu Li*², *Dr. Jaap Borger*¹

1. ETH Zürich, 2. Sun Yat-Sen University

Introduction: Carbon nitrides are old compounds described by Liebig already in 1834[1] but rediscovered recently as graphitic-C₃N₄ which may become one of the most promising materials of the 21st century.[2] Little is known about corresponding “carbon phosphides” which are likewise predicted to have remarkable optoelectronic properties.[3]

Methods and results: We could prepare compounds **A** and **B** which can be viewed as N-heterocyclic carbene adducts of C₂P₂. [4] Calculations show that the dissociation energies required to remove the ligands L from **A** and **B** are relatively moderate. Especially **A** allows to attach a broad range of transition metal fragments giving new complexes such as shown in **C**. These compounds represent the first transition metal complexes with a four-membered inorganic ring as 6p-aromatic ligand. Starting from the salt Na[OCP], a straight forward synthesis of Na[RPCN] **D** was developed which can be regarded as an analogue of the phosphacyanamide, [PCN]²⁻. [5] Salt **D** serves as precursor to new heteroallenes such as **E** which contains a linear new P=C=N=B unit.

Conclusion: On the way to molecular precursors of carbon phosphides new phosphorus building blocks such as L₂C₂P₂ and M[RPCN] were discovered. These show an especially rich and unprecedented chemistry and may well help to develop new synthetic techniques to explore C_nP_m and C_nN_mP_k materials.

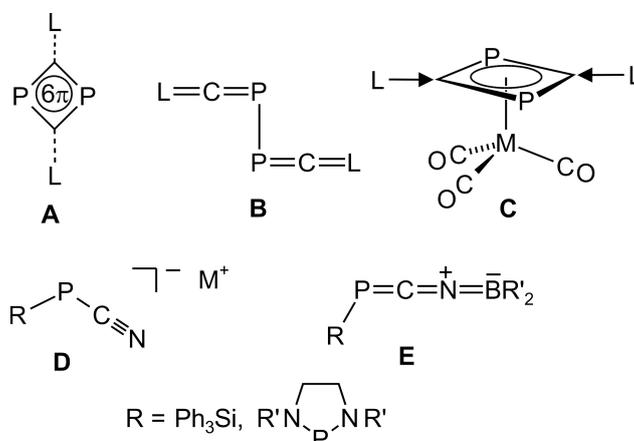
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Scheme 1 h gruetzmacher.jpg

Synthesis of new siloxane sulfur-containing monomers and oligomers based on carvone

Monday, 2nd December - 16:40: Materials science: polymers, thin films, nanopowders, ceramics, crystals, composites etc. (Room 1) - Oral - Abstract ID: 131

Dr. Fedor Drozdov¹, Dr. Alexandr Tarasenkov¹, Dr. Georgij Cherkaev¹, Prof. Aziz Muzafarov¹

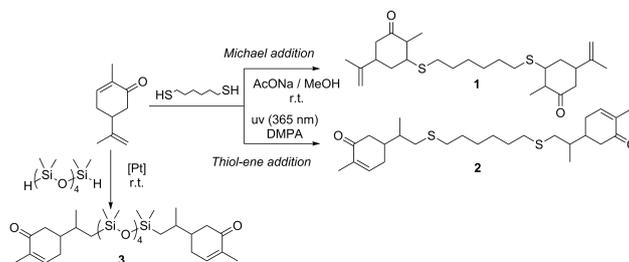
1. N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences

Recently, a large number of works have been devoted to the application of natural functional compounds for the synthesis of polymers. One of the most interesting classes of natural compounds in the field of polymer synthesis is terpenoids, especially large-scale pinene, limonene, and carvone [1]. In this work, it was shown that carvone is able to attach thiols either via the conjugated double bond according to the Michael reaction or through the isoprenyl double bond in the case of thiol-ene addition (Scheme 1). This approach can be used to obtain various sulfur-containing carvone derivatives, including symmetric monomers. It was shown that using obtained monomers, polymerization either by the Michael reaction or by the thiol-ene addition reaction is possible.

Scheme 1. Synthesis of various carvone derivatives using Michael reactions, thiol-ene addition and hydrosilylation
Moreover, symmetric siloxane derivatives were synthesized based on carvone and polymerized by the thiol-ene reaction. The possibility to perform a hydrosilylation reaction on sulfur-containing carvone derivatives without any side reactions has also been shown.

The work was supported by the Russian Foundation for Basic Research (Project No. 19-29-05227 МК)

1. F.V. Drozdov, G.V. Cherkaev, A.M. Muzafarov. *J. Organomet. Chem.*, **2019**, 880, 293-299.



Scheme.png

Towards silica-phosphazene based hybrid nanoparticles with controlled degradability

Monday, 2nd December - 16:57: Materials science: polymers, thin films, nanopowders, ceramics, crystals, composites etc. (Room 1) - Oral - Abstract ID: 60

***Ms. Vanessa Poscher*¹, *Prof. Ian Teasdale*¹, *Dr. Yolanda Salinas*¹**

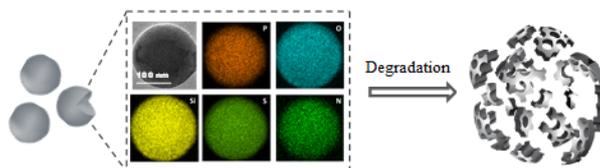
1. Johannes Kepler University Linz

Silica-based materials are very promising materials for many nanotechnology areas, especially for nanomedicine as drug delivery systems. Such silica-based nanoparticles are well-demonstrated to be inert and therefore biocompatible materials, but they are not known to show biodegradability, an important requirement for biomedical applications.¹ To overcome the issue of non degradability, we created novel degradable hybrid silica nanoparticles through an incorporation of phosphazene moieties. Polyphosphazenes are unique polymers with a phosphorous-nitrogen backbone, which degrade under hydrolytic conditions in an appropriate time frame into non-toxic products and intermediates.² Through a degradation of the phosphazene moieties the particles disintegrate (see Figure 1³). To achieve a faster degradation compared to compact nanoparticles, we attempted to synthesize novel mesoporous silica nanoparticles containing phosphazene moieties.

¹Asefa T., Tao Z., *Chem. Res. Toxicol.* **2012**, 25, 2265-2284.

²Rothmund S., Teasdale I., *Chemical Society Reviews* **2016**, 45, 5200-5215.

³ Poscher V., Teasdale I., Salinas Y., *ACS Appl. Nano Mater.*, **2019**, 2, 655-660.



Tem-eds elemental mapping images of the novel hybrid organosilica-phosphazene based particles and their proposed degradation behaviour.png

Rhodium(I) and iridium(III) complexes as catalysts for obtaining silicone rubber with improved properties

Monday, 2nd December - 17:14: Materials science: polymers, thin films, nanopowders, ceramics, crystals, composites etc. (Room 1) - Oral - Abstract ID: 174

Mr. Mikhail Dobrynin¹, Prof. Regina Islamova¹

1. St. Petersburg State University

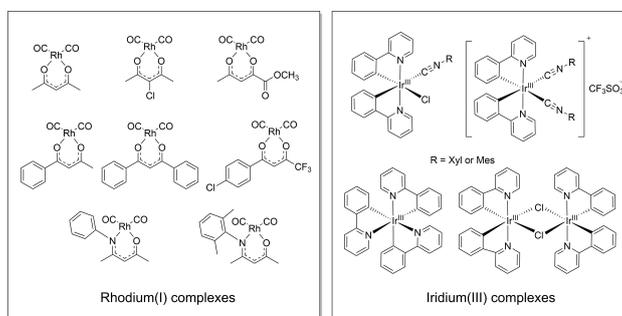
Silicone rubber is widely used both in industry and everyday life. Compared to other rubbers, it has outstanding thermal resistance, electrical insulation and weather stability [1]. One of the systems used to obtain rubber from linear polysiloxanes include vinylcontaining polysiloxanes, hydride-containing (poly)siloxane crosslinker and hydrosilylation catalyst. In industry platinum(0) complex – Karstedt’s catalyst – is often used, however it is unstable and needs inhibitor to cross-link silicones effectively at heating. To solve these problems other complexes of platinum group metals can be used.

Our work concerns the use of acetylacetonate rhodium(I) and cyclometalated iridium(III) complexes as hydrosilylation catalysts for reaction of vinyl-terminated polydimethylsiloxane and poly(dimethylsiloxane-co-methylhydrosiloxane) to yield silicone rubber. Unlike Karstedt’s catalyst, these complexes allow to obtain silicone rubber without inhibitors. Acetylacetonate rhodium(I) complexes allowed to crosslink polysiloxanes at RT and to improve their elastic properties (elongation at break increased by 90–100%) [2]. Cyclometalated iridium(III) complexes did not need inhibitors to store reaction mixture at RT without visible changes and they catalyzed crosslinking only at temperatures above 80 °C; rubbers obtained with iridium(III) complexes possessed luminescent properties and increased thermal stability (by 80–120 °C).

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[2] M. V. Dobrynin, C. Pretorius, D. V. Kama, A. Roodt, V.P. Boyarskiy, R.M. Islamova, *J. Catal.* 372 (2019) 193–200. doi:10.1016/j.jcat.2019.03.004.

This work was supported by Russian Foundation for Basic Research (RFBR) grant mol_a 18-33-00769. Physico-chemical measurements were performed at Chemical Analysis and Materials Research Centre, Center for Magnetic Resonance, Center of Thermal Analysis and Calorimetry of Saint Petersburg State University.



Complexes used as catalysts.png

Cyclic organosilicon triperoxides as new curing agents for silicones

Monday, 2nd December - 17:31: Materials science: polymers, thin films, nanopowders, ceramics, crystals, composites etc. (Room 1) - Oral - Abstract ID: 179

Mr. Konstantin Deriabin¹, Prof. Regina Islamova¹

1. St. Petersburg State University

Free radical peroxide induced curing is one of the most famous methods in polymer industry to obtain 3D networks from polysiloxanes. It is relevant to search for new initiators for peroxide curing, which are close in nature to silicones. Silicon-containing peroxides satisfy these requirements. The use of these peroxides is made possible by the development of large-scale methods for their synthesis from cheap and available reagents.[1] In this work, we report that cyclic organosilicon triperoxides (Figure 1) allow curing liquid linear PDMSs (notably mixtures of trivinyl-terminated PDMS and polymethylhydrosiloxane) leading to high-quality silicone rubbers without using a roll mill and inhibitors.[2]

Cyclic organosilicon triperoxides are vinyl-selective initiators for thermal curing at 150–180 °C of vinyl-containing PDMS and polymethylhydrosiloxane obtaining homogeneous transparent silicone rubbers. Silicone curing was monitored by the following data: curing times, IR spectroscopy and the DSC method. The organosilicon peroxide with the Me–Si–Me moiety is a more active curing agent than other organosilicon peroxides with bulkier substituents on the silicon atom. The optimal concentrations of the peroxides are 0.09–0.22 M. The usage of polymethylhydrosiloxane in curing mixtures leads to a noticeable acceleration of curing by 2–3 times, and can be explained by the formation of cross-links for a relatively short period of time by the mechanism of radical hydrosilylation (Figure 2).[2]

Cured samples obtained with the addition of polymethylhydrosiloxane have improved mechanical properties (elongation is more than 200%, compression sets are less than 1.0%). All the silicone rubbers showed antibacterial activity against Escherichia coli. Thus, the results of this study can be useful in the creation of surfaces for possible applications in the food industry and medicine.

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Acknowledgements. This work was supported by the Russian Foundation for Basic Research (project № 18-33-00769 mol_a). Measurements were performed at the Magnetic Resonance Research Centre, the Chemical Analysis and Materials Research Centre, the Thermogravimetric and Calorimetric Research Centre and the Centre for Culture Collection of Microorganisms (all in Saint Petersburg State University).

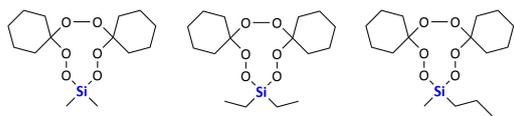


Figure 1. cyclic organosilicon triperoxides.png

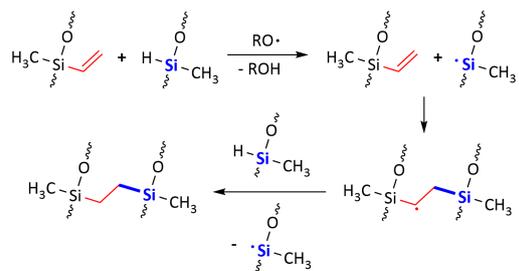


Figure 2. free radical induced curing using polymethylhydrosiloxane.png

Effect of phosphorus-, nitrogen- and silicon-based coatings on the flammability of cotton textiles

Monday, 2nd December - 17:48: Materials science: polymers, thin films, nanopowders, ceramics, crystals, composites etc. (Room 1) - Oral - Abstract ID: 222

Prof. Joelle Levalois-Grutzmacher¹

1. ETH-Zurich

Introduction

With the increasing concern of their toxicity and environmental-friendliness, a recent global ban on the use of halogenated flame retardants [1] points to an increasing demand and need to develop new classes of wash resistant and environmentally friendly flame retardants. This is especially important for cellulose-based cotton textiles, since they are mostly used in the production of clothes and fabrics for everyday use by the human population.

In recent years, phosphorus-nitrogen (P-N) flame-retardant synergism has received considerable attentions because it provides excellent fire protection with less harm to the environment [2-3].

On the other hand, it is wellknown that the silicon compounds can enhance the thermal stability and char yield of cotton fabrics [4]. Therefore, investigations on the synergistic effects of phosphorus, nitrogen and silicon are recently receiving increasing attention in the literature [5].

Method

In view of the potential of such combination on cotton textiles, we have designed new P-N monomers containing silylesters side groups and compared their flame retardant properties versus their non-silylated analogs (Figure 1).

Figure 1

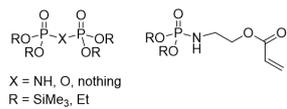
The coating of the different monomers applied by various techniques onto the surface of the textiles was monitored by IR-ATR, NMR, EDX and XPS measurements. The flammability and the thermal behavior of the treated fabrics were assessed by means of Limiting Oxygen Index (LOI), Microscale Combustion Calorimetry (MCC) measurements and Thermogravimetric Analyses (TGA).

Results and Discussion

A significant increase of the oxygen indexes and char formation were observed which correlates with synergistic effects between the three elements. Moreover, surface characterization and comparison of the reactions with model compounds reveal a partial phosphorylation of the -OH groups of the cellulosic moieties at room temperature. This is thought to be the origin of the improved flame retardant properties for phosphate silyl esters when applied on cotton fabrics.

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Chemical structures of phosphate silyesters and their non-silylated analogs

Figure 1.png

Black phosphorus functionalization with organometallic precursors

Monday, 2nd December - 18:05: Materials science: polymers, thin films, nanopowders, ceramics, crystals, composites etc. (Room 1) - Oral - Abstract ID: 237

Dr. Matteo Vanni¹, **Dr. Manuel Serrano-Ruiz**², **Dr. Stefano Caporali**³, **Dr. Andrea Giaccherini**⁴, **Dr. Francesco D'Acapito**⁵, **Dr. Antonio Massimiliano Mio**⁶, **Dr. Giuseppe Nicotra**⁶, **Dr. Gabriele Manca**⁷, **Dr. Andrea Ienco**¹, **Dr. Werner Oberhauser**¹, **Dr. Maria Caporali**⁷, **Dr. Maurizio Peruzzini**⁷

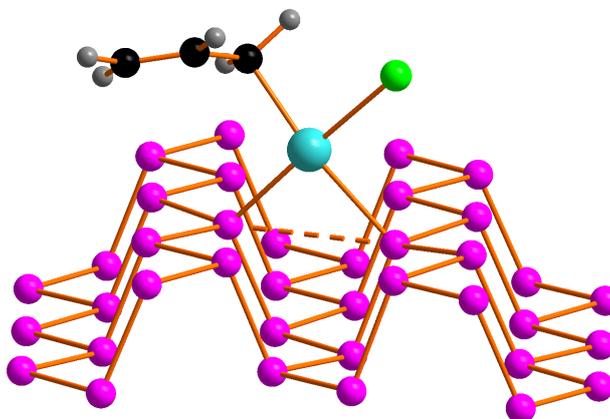
1. Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR-ICCOM, Sesto Fiorentino, 2. Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR-ICCOM, Sesto Fiorentino, 3. Department of Industrial Engineering, University of Florence, Via di S. Marta 3, 50139 Florence, Italy, 4. Department of Earth Sciences, University of Florence, Via La Pira 4, 50121 Firenze, Italy, 5. CNR IOM OGG c/o ESRF - LISA CRG, Grenoble, France, 6. CNR-IMM Istituto per la Microelettronica e Microsistemi, VIII strada 5, I-95121, Catania Italy, 7. Institute for the Chemistry of OrganoMetallic Compounds, Italian National Council for Research, CNR-ICCOM, Se

Over the last few years many research efforts have been devoted toward the study of new bidimensional materials such as black phosphorus and molybdenum disulfide, marking the beginning of a post-graphene era.^[1] Black phosphorus (bP) features a puckered honeycomb structure reminiscent of graphene, however the sp^3 hybridization and the formal presence of a lone pair on each phosphorus atom offers the potential to get involved in strong interactions with metal fragments.^[2] We report here a survey on the use of a labile organometallic Pd complex to decorate the bP surface. Based on DFT models of possible Lewis acid-base adducts between bP and the palladium fragment, we carried out an experimental investigation in order to isolate and characterize the functionalized material. Different solid state characterization techniques (XRD, HRTEM, XPS, XANES, EXAFS) have been applied trying to shade light on the chemical environment of palladium.

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Acknowledgements: This work was supported by an ERC Advanced Grant PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" (Grant Agreement No. 670173) to M. P.



Pbsi graphic content.png

From bulk to nanosized ammonia borane

Monday, 2nd December - 18:22: Materials science: polymers, thin films, nanopowders, ceramics, crystals, composites etc. (Room 1) - Oral - Abstract ID: 191

Prof. Umit B. Demirci¹

1. University of Montpellier

Ammonia borane NH_3BH_3 (AB) is one of the most promising BNH materials for chemical hydrogen storage. In pristine state it is not suitable for the targeted application, but when nanosized, the dehydrogenation properties of AB are so improved that the material shows how its potential is high in the field.

Up to recently, nanosizing was possible only with the help of a host material, i.e. a porous scaffold. Nevertheless, the use of the scaffold has a negative impact on the gravimetric storage capacity of AB. In other words, nanosizing must be done differently, in a way that maximizes the storage capacity of AB.

Recently we have shown that nanoparticles of AB can be obtained by using a commercial surfactant like CTAB or oleic acid. In doing so attractive dehydrogenation results were measured. To further improve our approach we have then developed a new type of surfactants, more compatible, and our preliminary results have shown comparable performance.

PBSi 2020 will be a good opportunity to show our achievements and discuss about the challenges ahead.

New perspectives in small molecule activation using low valent main group compounds

Tuesday, 3rd December - 09:00: Plenary speech (Auditorium) - Oral - Abstract ID: 256

Prof. Simon Aldridge¹

1. University of Oxford

The activation and functionalization of chemical bonds represent fundamental processes that underpin chemical synthesis. While such transformations have been exploited in catalysis primarily through the application of late transition ('Noble') metal catalysts, other approaches based on 'base' 3d metals, frustrated Lewis pairs and *s/p*-block elements have recently begun to emerge.¹

We have been interested in developing compounds of the group 13 and 14 elements which show unusual electronic structure and/or patterns of reactivity towards E-H bonds (E = H, B, C, N, O, Si). These include highly reactive analogues of carbenes and vinylidenes featuring the heavier group 14 elements,²⁻⁴ and unusual 5- and 6-valence electron species featuring the Group 13 metals.^{5,6} We have applied these systems to a range of challenging functionalization processes including the activation of 'difficult' E-H bonds (N-H bonds in ammonia, unactivated C-H bonds, C-C bonds in benzene)^{3,7,8} and the pairing of oxidative addition processes with subsequent reductive generation of functionalized products.³

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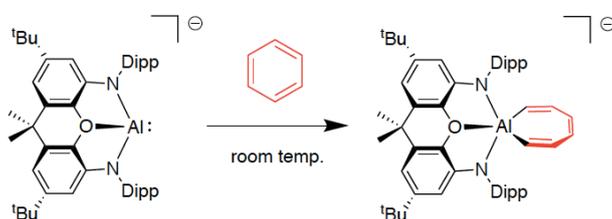
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Screen shot 2019-10-27 at 15.54.56.png

Phosphorus: a key role in mineralized human tissues and the new perspective in Regenerative Medicine

Tuesday, 3rd December - 09:40: Plenary speech (Auditorium) - Oral - Abstract ID: 262

Dr. Anna Tampieri¹

1. CNR

TBD

Why scientists forget boron clusters?

Tuesday, 3rd December - 10:45: Plenary speech (Auditorium) - Oral - Abstract ID: 252

Prof. Francesc Teixidor¹

1. ICMAB-CSIC

Five are the platonic solids: tetrahedrane, cube, octahedron, dodecahedron and icosahedron. Interestingly there are three that are matched by the platonic hydrocarbons C₄H₄, C₈H₈, and C₂₀H₂₀. The corresponding platonic solids are characterized by three edges meeting at each corner. In octahedron and icosahedron four and five edges, respectively, meet at each corner. This is too much for the electron precise C-H and C-C bonds and consequently, C₆H₆ and C₁₂H₁₂ have taken other structural alternatives. Interestingly the octahedron and the icosahedron are occupied by boron hydrides [B₆H₆]²⁻ and [B₁₂H₁₂]²⁻. Thus boron hydrides and hydrocarbons hoard the five platonic solids in a complementary manner. Remarkably *closo* boron clusters are 3D-aromatic [1] species abiding the 4n+2 aromatic Hückel rule that is 2D whose main archetype is C₆H₆. If the focus is given to the icosahedron [B₁₂H₁₂]²⁻ this is 3D-aromatic, and one of the most stable molecular compounds, but C₁₂H₁₂, [12]annulene, is non-aromatic. This little story on the five platonic solids shows nicely how boron and carbon complement themselves. But this is not what happens in reality. Scientists seldom come upon boron clusters when having unusual needs. We speak not about organic boron, or more appropriately Lewis acid boron, that has got an extraordinary influence in synthetic organic chemistry, but on boron clusters. For instance, C₆₀ has extraordinary difficulty to solubilize; contrarily, the dimetallacarborane shown in the figure solubilizes practically in every organic solvent, while keeping a pattern of redox processes very similar to C₆₀. [2]

One particularity of boron clusters is that they are polyhedral, and particularly the twelve vertexes have a shape that is very similar to a sphere. And this particular shape ideally permits a hexagonal or square packing. There are geometrical constraints in their application. By using these spheres with CdSe it has been possible to produce morphologies only practicable with physical methods with low throughput. In this way, Quantum Rings, Rods, Dots and Tetrapods have been made. [3] This presentation aims to show the ability of boron clusters in producing new molecules for targeted applications in nanomaterials and nanomedicine.

Acknowledgements: Thanks to the MINECO CTQ2016-75150-R and Generalitat de Catalunya 2017 SGR 1720

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Towards green chemistry of silicones

Tuesday, 3rd December - 11:25: Plenary speech (Auditorium) - Oral - Abstract ID: 258

Dr. Maxim Temnikov¹, **Dr. Alexandra Kalinina**², **Dr. Aleksandra Bystrova**¹, **Prof. Aziz Muzafarov**¹

1. Nesmeyanov Institute of Organoelement Compounds, 2. N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences

Silicones are continuously growing type of polymer materials having great potential for further development. Being biocompatible, chemically inert and recyclable they are one of the most promising candidates for the polymers of the future. The main problem which impedes the realization of this optimistic forecast is the chlorine cycle of the initial monomers manufacture and processes of polymers synthesis based on those chlorosilanes. Two synthetic strategies of chlorine-free silicones manufacture will be presented in the presentation. First deals with mechanochemical synthesis of alkoxy silanes from silicon and alcohols. High conversion of silicon and good yields of tri- and tetraalkoxy silanes were achieved. The second strategy consists in chemical transformations of alkoxy silanes to the siloxanes of different structure. The variety of polymethylsilsesquioxanes of various architectures will be considered and discussed. Other aspects of green chemistry of silicones will be analysed.

Attempted synthesis of silylenes leads to the formation of a hitherto unknown tricyclooctasilane

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 91

*Dr. Michael Haas*¹, *Prof. Cameron Jones*²

1. Technische Universität Graz, 2. Monash University

The reduction of 1,1-dibromocyclopentasilane with the mild magnesium(I) dimer[$\{(MesNacnac)Mg\}_2$] was examined, which gave rise to the formation of an endocyclic disilene **1.1** was found to dimerize slowly to **1-dimer**. The formation of **1** was further confirmed by a trapping experiment with MeOH. Furthermore, the formation of the homocyclic silylene was demonstrated by performing the reduction in the presence of Et₃SiH as a trapping agent. To prevent the 1,2-trimethylsilyl shift, which causes a rapid degradation of the silylene a second synthetic strategy was established. Therefore, two different tetrasilanes **4** and **5** were synthesized. **4** and **5** were subsequently reacted with 2.1 eq. of trifluoromethanesulfonic acid to the corresponding bis(trifluoromethanesulfonates) **6** and **7**. 1,4-dihalo-tetrasilanes **8a,b** and **9** as well the hexasilanes **10** and **11** were obtained by a subsequent nucleophilic substitution of the triflate substituent with X⁻ (X = Cl⁻, Br⁻ or R₃Si⁻). The dianionic species **12** and **13** were synthesized by the reaction of the corresponding hexasilanes **10** and **11** with KOtBu. Surprisingly the salt metathesis reaction of the dianionic compound **13** does not lead to the formation of the expected 1,1-halocyclopentasilanes. Instead the formation of cyclobutasilane **14** was observed. The reaction of **9** with lithium led again to the formation of **14** alongside with the formation of a cyclohexasilane **15**. Interestingly **14** underwent a ring opening formation by the reaction with gaseous HCl in the presence of AlCl₃ and compound **16** was formed. The reduction of **16** allowed the straightforward access to **17** as a structurally complex hitherto unknown tricyclic polysilane.

Mesoporous silica material functionalized with calixarenes

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 177

Prof. Ovidiu Nemes¹, Dr. Raluca Septelean², Mr. Marius Olteanu³, Dr. Gyorgy Deak³, Dr. Ancuta Elena Tiuc¹

1. Technical University of Cluj-Napoca, Faculty of Materials and Environmental Engineering, 28 Memorandumului Street, 400114, Cluj-Napoca, **2.** Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, 1 Mihail Kogălniceanu Street, 400084, Cluj-Napoca, **3.** National Institute for Research and Development in Environmental Protection, Blvd Splaiul Independenței 294, Sector 6, 060031, Bucharest

Calixarenes, organic macrocycles properly substituted at the upper and lower rim can be used as coupling agents in systems such as inorganic substrate/coupling agent/inorganic substrate or inorganic substrate/coupling agent/organic substrate [1,2,3]. The high versatility of calixarene compounds is based on the adjustability of the macrocycles cavity by controlling the number of phenolic monomers or the functional groups grafted at the upper or lower rim of the system.

Due to the connection capacity of calixarenes to inorganic substrate and the extensive use of calixarenes in separation sciences [4,5] we focused our study on the preparation of silica materials modified with calixarenes that can be used for the extraction of metals from waste waters. We present here some results regarding the preparation, thermal behavior and SEM analysis of new products obtained through the coupling of calix[4]arene derivatives to two types of mesoporous silica materials.

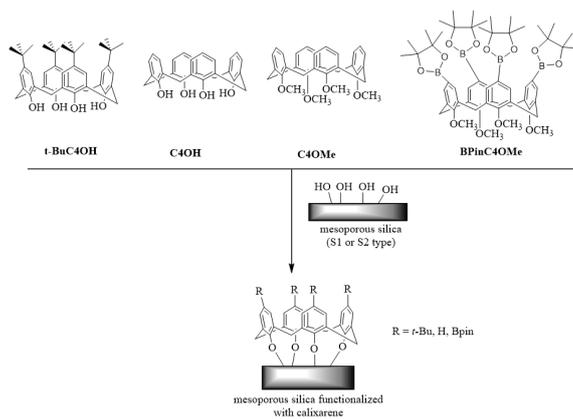
Scheme 1.

For the modification of the silica substrate we have used 4 different calixarenic systems functionalized at the upper or lower rim: tetra-hidroxy-*para*-tert-butylcalix[4]arene (t-BuC4OH), tetra-hidroxy-calix[4]arene (C4OH), tetra-methoxy-calix[4]arene (C4OMe) and tetra-boronpinacolato-tetra-methoxy-calix[4]arene (BPinC4OMe) (scheme 1).

All the newly obtained materials were characterized through thermogravimetric methods and their morphology was determined through SEM and TEM imaging.

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Scheme 1.png

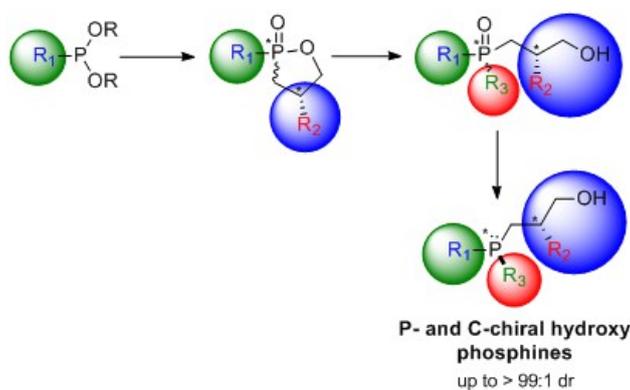
A concise stereoselective route to C- and P- chiral phosphines via optically active oxaphospholane-2-oxide

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 197

*Dr. Orit Keisar*¹, *Dr. Nissan Ashkenazi*¹

1. IIBR

A facile, stereoselective method for the synthesis of both carbon- and P-chirogenic phosphine oxides and phosphines bearing a hydroxyl chelating arm was developed. A carefully designed oxaphospholane was constructed via tandem Arbuzov- intramolecular cyclization reaction, using commercially available compounds. Regioselective ring opening alkylation/arylation provided optically active phosphine oxides within two synthetic steps. An additional step of stereospecific deoxygenation produced P-chirogenic tertiary phosphines in high dr.



Abstract graphic.jpg

The influence of metal (I/II) salts on the properties of the phosphonoformate anion

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 128

***Ms. Mara Egenhöfer*¹, *Ms. Sara Barile*², *Prof. Vito Capriati*², *Prof. Konstantin Karaghiosoff*¹**

1. Ludwig-Maximilian-University, 2. University of Bari Aldo Moro

Phosphonic acids and phosphonates are of great importance to medical and pharmaceutical science. So they find wide application in various drugs as medicines against osteoporosis or antiviral agents.^[1,2] An antiviral agent with a broad activity against varicella-zoster virus (VZV), herpes simplex virus type 1 and type 2 (HSV-1 and HSV-2) and cytomegalovirus (CMV) is the trisodium phosphonoformate hexahydrate (Foscarnet, Foscarvir (CH), Triapten (GER)).^[2] Despite of these important pharmaceutical applications and despite the fact, that various metal ions are present in living systems, very little is known about the coordination properties of the phosphonoformate anion and the structures of coordination compounds with this anion. However knowledge and understanding of the ligand properties of the phosphonoformate anion is of great importance and is one of the main topics of ongoing investigations on metal phosphonates. In the course of our investigations we prepared different metal (I/II) salts of the phosphonoformate anion *via* hydrolysis of corresponding esters under basic conditions.^[3]

Figure 1: General reaction equation of the ester hydrolysis.

The salts were structurally characterized by single crystal X-ray diffraction and are presented. The influence of the different cations on crystal structure is reported and discussed together with the impact on the toxicological properties of the compounds.

Figure 2: Molecule structure of the monoprotonated trisodium phosphonoformate monohydrat.

Figure 3: Molecule structure of the trisodium phosphonoformate hexahydrat (symmetry operation $i: 0.5-x, 0.5+y, 0.5-z$).

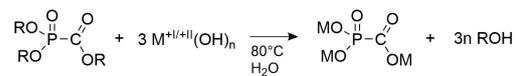
Figure 4: Molecule structure of the trisodium phosphonoformate dodecahydrat.

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[3] Hoechst AG **1987**, *Verfahren zur Herstellung von Alkali-phosphonoformiaten*, DE 3607445 A1.



R: Alkyl, M: Metal^{+I/+II}, n: 1,2

Figure1 general reaction equation of the ester hydrolysis.png

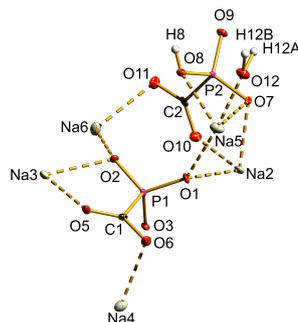


Figure2 crystal structure of the monoprotonated trisodium phosphonoformate monohydrat.png

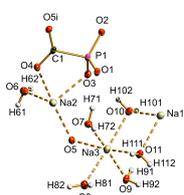


Figure3 crystal structure of the trisodium phosphonoformate hexahydrat.png

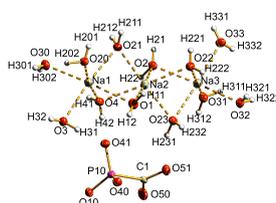


Figure4 crystal structure of the trisodium phosphonoformate dodecahydrat.png

Novel PEGylated nedaplatin liposomes with enhanced cytotoxicity and genotoxicity

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 36

Mr. Sherif Ashraf Fahmy¹, Mrs. Salma El-Shafei¹, Ms. Nada Elzahed¹, Dr. Andreas Kakarougkas¹, Prof. Tamer Shoeib¹

1. American University in cairo

Introduction: Following the discovery of cisplatin over 50 years ago, this platinum based drug (PBD) has been a widely used and effective form of cancer therapy, primarily causing cell death by inducing DNA damage and triggering apoptosis [1]. However, the dose limiting toxicity of cisplatin has led to the development of second and third generation PBDs that maintain the cytotoxicity of cisplatin but have more acceptable side-effect profiles [1]. Nedaplatin, a second generation PBD, has been exclusively used in Japan for the treatment of non-small cell lung cancer, head and neck, esophageal, bladder, ovarian and cervical cancer [1]. In addition to the creation of new analogues, tumor delivery systems such as liposome encapsulated platinum drugs have been developed and are currently in clinical trials [2].

Methods: In this study we have designed the first PEGylated liposomal formulations of nedaplatin (LND) using thin film hydration method (Figure 1) [3]. The prepared liposomes were characterized with respect to their entrapment efficiency (EE), size distribution, zeta potential, stability, morphology and release kinetics. Furthermore, we report on the cytotoxic and genotoxic effects of free and liposomal nedaplatin on human non-small cell lung cancer cell line (A549) and human osteosarcoma cell line (U2OS).

Results & discussion: The formulations showed Zeta potential of -40.7 mv which is favorable for increasing liposomes stability and reducing the aggregation of particles. LND had a homogenous particle size distribution around 150 nm and transmission electron microscopy (TEM) images showed liposomes with uniform, homogenous and spherical shape vesicles with smooth surfaces with no observed aggregation (Figure 2). The entrapment efficiency (EE) of LND reached nearly 90%. The LND formulations were shown to have a slightly slower drug release rate relative to the free nedaplatin in PBS media (Figure 3). Data from several assays examining drug internalization and quantifying DNA damage induction are presented. Encapsulation of nedaplatin in PEGylated liposomes significantly increased the cytotoxicity and genotoxicity of nedaplatin in A549 and U2OS cell lines (Figure 1).

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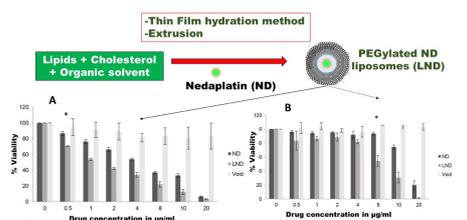


Figure 1. Figure illustrating the design of PEG-ylated nedaplatin and evaluating cytotoxicity of free and liposomal nedaplatin after 72 hours of drug encapsulating MTT assay in (A) A549 and (B) U2OS. An overall statistically significant decrease in cell viability was observed with LND compared to ND (p value<0.05) and multiple pair-wise t tests showed the lowest concentration of treatment starting from which a significant difference between LND and ND survival curves is observed. These points are indicated by asterisks * in the charts above; at 0.5 µg/ml for A549 and 8 µg/ml for U2OS. The differences were significant for all increasing doses past these points.

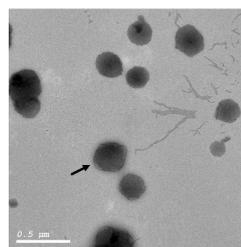


Figure 2. TEM image for LND formulation showing uniform spherical structures. The coating PEO layers are also shown as lighter outer circles (see arrow)

Figure 1-design evaluation.jpg

Figure 2-tem.jpg

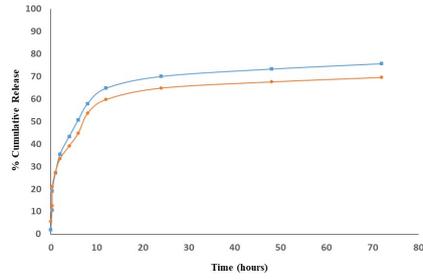


Figure 3: Nedaplatin and formulated nedaplatin release profiles in PBS and FBS media. Circles represent liposomal nedaplatin in PBS and squares are free nedaplatin in PBS.

Figure 3-release profiles.jpg

Novel catalytic methodologies for the synthesis of functionalized silsesquioxanes

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 96

Ms. Joanna Kaźmierczak¹, Prof. Grzegorz Hreczycho¹

1. Adam Mickiewicz University, Poznań, Poland

In recent years, silsesquioxanes have attracted considerable attention due to their nano-sized, hybrid structure and versatile applications in material science. These organosilicon compounds are of considerable interest for creating hybrid organic-inorganic materials.

The aim of this poster is to demonstrate our highly efficient and selective catalytic approach to functionalized silsesquioxanes *via* the coupling reaction of completely as well as partially condensed POSS silanols with allyl-substituted organometallic compounds catalyzed by scandium(III) trifluoromethanesulfonate ($\text{Sc}(\text{OTf})_3$)¹. Moreover, we also developed heterogeneous catalytic method for modification of silsesquioxanes, using Nafion as heterogeneous and reusable catalyst of this process.²

This methodology opens up a possibility to introduce a wide variety of functional groups into silsesquioxanes with excellent yields and selectivity, under mild conditions (rt, air atmosphere) with evolution of no reactive by-products.

We also present the first catalytic approach to the corner-capping reaction of incompletely condensed silsesquioxanes which enables for the synthesis of heterosilsesquioxanes, containing heteroatoms in silsesquioxanes framework.¹

This methodology can be of great importance and practical use for the functionalization of silsesquioxanes which have the potential for wide applications in many fields of material science.

Acknowledgements

This work was supported by a National Science Centre Grant UMO-2017/27/N/ST5/00091.

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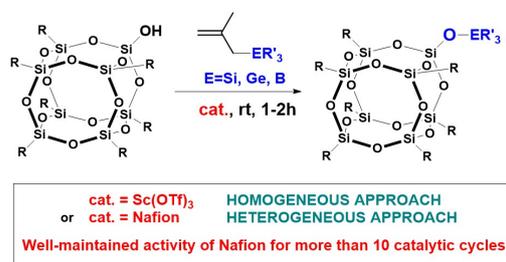


Figure 1. Functionalization of silsesquioxanes catalyzed by $\text{Sc}(\text{OTf})_3$ or Nafion

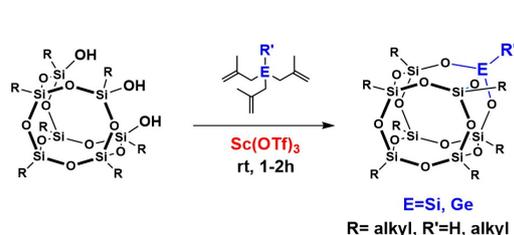


Figure 2. The first catalytic corner-capping reaction of POSS trisilanols

Figure1.jpg

Figure2.jpg

Access to P*-chiral tertiary diphosphines via asymmetric catalytic hydrophosphination reaction

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 151

Mr. Ronald Teo¹, Dr. Jeremy Chen¹, Dr. Yongxin Li¹, Dr. Sumod A. Pullarkat¹, Prof. Pak-Hing Leung¹

1. Nanyang Technological University

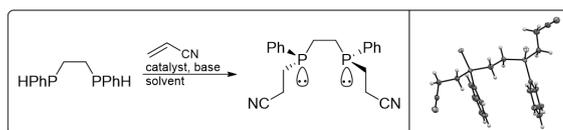
Chiral P*-tertiary diphosphines are ubiquitous in numerous asymmetric metal-mediated and organocatalytic reactions.¹ While catalytic generation of P-chiral monophosphines are prevalent,² synthesis to P-chiral diphosphines is often limited. The asymmetric hydrophosphination procedure presents a valuable methodology to the synthesis of these phosphines with its simple, yet atom economical approach.³ Herein, we present a regio- and stereo-selective protocol to the catalytic hydrophosphination of electron-deficient olefins from secondary 1,2-diphosphines to afford P*-tertiary diphosphines.

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[1] A. Grabulosa, in *P-Stereogenic Ligands in Enantioselective Catalysis*, ed. A. Grabulosa, RSC Publishing, United Kingdom, 2011, ch. 5, pp. 235–291, and the references therein.

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General 1 2-dihydrophosphination protocol.png

Synthesis of chiral bidentate mixed phosphine-N-heterocyclic carbene precursors

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 152

Mr. Jeffery Seah Wee Kiong¹, Dr. Yongxin Li¹, Dr. Sumod A. Pullarkat¹, Prof. Pak-Hing Leung¹

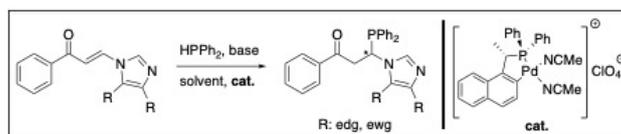
1. Nanyang Technological University

Phosphines and N-heterocyclic carbenes (NHCs) are ubiquitous in asymmetric homogenous catalysis.¹ Phosphines are useful as their electronic and steric effects can be easily fine-tuned even though the dissociation of monodentate phosphines during catalysis presents a disadvantage as phosphines are prone to oxidation. However, this problem can be solved by using NHCs which form very strong metal-carbon bonds and do not readily dissociate from the metal center. Reactions involving both phosphines and NHCs as ligands have also been widely reported.² To add on, the steric effect imposed by NHCs is different from that of phosphines due to its unique bent geometry.³ In this study, a novel method involving the synthesis of chiral bidentate mixed phosphine-NHC precursors with high enantioselectivity up to 96% will be reported.

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Reaction.jpg

Tris(aminomethyl-1-pyrenyl)phosphine: a new air stable ligand with metal coordination capabilities

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 162

Dr. Martin Smith¹, Mr. Christopher Miles¹

1. Loughborough University

Mark R. J. Elsegood, Christopher R. Miles, Martin B. Smith

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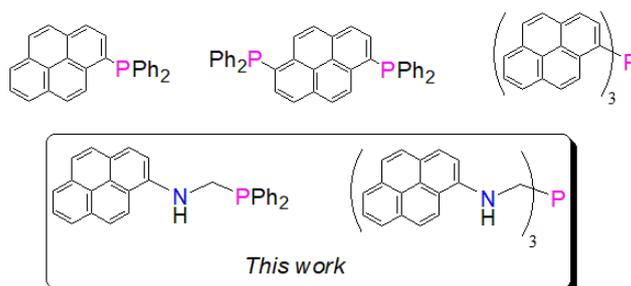
The simplest triarylphosphine, PPh₃, has a rich and varied background that continues to attract much interest in academia and industry. Phosphines with polycyclic aromatic hydrocarbons such as naphthyl, anthracenyl or 1-pyrenyl groups (as shown in Fig. 1) have not received the appeal as seen with PPh₃ possibly due to their more challenging syntheses. One common theme displayed by the 1-pyrenylphosphines shown in Fig. 1 is their fluorescent properties^{1,2} and their pi-pi stacking interactions with carbon-based materials to facilitate catalyst recycling.³

Fig. 1

The preparation of known 1-pyrenylphosphines, as shown in Fig.1, often requires the need for pyrophoric bases, lengthy syntheses and/or work up procedures. We recently described the facile syntheses of a small library of trisubstituted naphthyl phosphines in two steps that can be performed under aerobic conditions.⁴ We show here that this route can be extended to the preparation of tris(aminomethyl-1-pyrenyl)phosphine and illustrate some coordination chemistry with this and the related, singly substituted, aminomethyl-1-pyrenylphosphine. All compounds were confirmed by a combination of multinuclear NMR and single crystal studies.

References

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Chris chemdraw rome .png

Exploiting non-covalent interactions in catalysis using 1-pyrenyl bearing phosphines

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 163

Dr. Martin Smith¹, Mr. Peter De'Ath¹

1. Loughborough University

Peter De'Ath, Mark R. J. Elsegood, Garrett D. Jackson, Martin B. Smith
Department of Chemistry, Loughborough University, Loughborough, Leics, LE11 3TU
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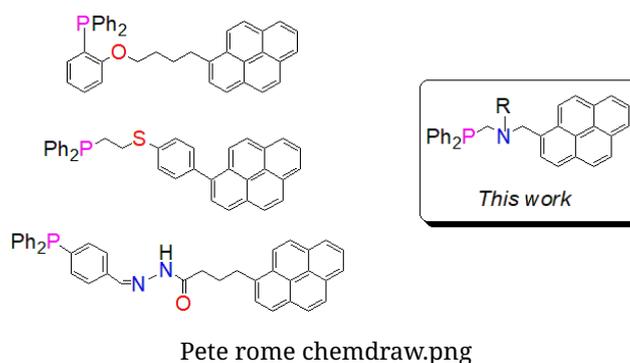
Tertiary phosphine and NHC (N-heterocyclic carbene) ligands are quintessentially important in metal chemistry and catalysis for their unique properties e.g. physical, stereoelectronic, coordination, solubility, chirality control. The chemical nature by which these ligands can be chemically modified through standard synthetic methodologies has facilitated their widespread appeal. The groups of Peris¹ and Mata² have recently shown that pyrenyl modified NHC Ru^{II}, Ir^{III} and Pd^{II} complexes can be grafted onto rGO (reduced graphene oxide) and evaluated as (de)hydrogenation catalysts. Furthermore, the recycling capability was effective and suggested to us, that 1-pyrenylphosphines (see Fig. 1 for three known examples)³⁻⁵ may behave similarly in this respect.

Fig. 1

In this poster, we will present the synthesis of some new 1-pyrenyl functionalised tertiary phosphines based on known procedures,^{6,7} their coordination capabilities towards Ru^{II}, Rh^{III}, Pd^{II} and Pt^{II} and a brief study of the catalytic behaviour of these complexes. All new compounds were characterised by NMR, IR and in some cases, by single crystal X-ray crystallography.

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Two ways of boron and gadolinium coupling

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 229

Dr. Sergey Anufriev¹, Prof. Igor Sivaev¹

1. A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow

BNCT (boron neutron capture therapy) is a type of binary radiation therapy for the treatment of cancer, especially of malignant brain tumors, based on the capture of thermal neutrons by ^{10}B nuclei that have been selectively delivered to tumor cells. There are two primary tasks to solve: the selective delivery of high payloads of boron at the target site and the assessment of the amount of boron reached the target sites.

It is assumed that the introduction of gadolinium will make it possible to use magnetic resonance imaging to monitor the agent distribution in the patient's body and to plan the irradiation time. In addition, since natural isotopes gadolinium-157 (15.65%) and gadolinium-155 (16.80%) have very high thermal neutron capture cross sections, this can lead to a significant increase in the effect of neutron capture therapy.

To solve these tasks, we have developed two ways of synthesis of theranostics containing boron and gadolinium atoms. The first way is based on modification of DO3A ligand (1,4,7-tris(carbonylmethyl)-1,4,7,10-tetraazacyclododecane), which makes very strong complexes with various heavy metals including gadolinium. Using simple methods of organic synthesis, we can attach to DO3A ligand not only boron-containing moiety, but also a functional group like azide-group, which can be used for conjugation with modified biomolecule (Fig.1). The second way is based on the introduction of additional chelating groups into a boron-containing moiety — carborane-based ligand. It is expected that this should significantly improve stability of gadolinium bis(dicarbollide) complexes. To such groups a moiety for biomolecule conjugation also can be attached (Fig. 2).

This work was supported by grants of the President of the Russian Federation (MK-910.2019.3) and Russian Foundation for Basic Research (19-53-50001).

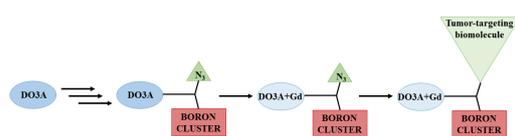


Figure 1.png

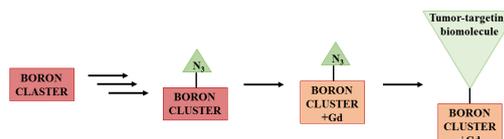


Figure 2.png

Multilayered Cu-Ti deposition on silicon substrates for chemiresistor applications

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 255

*Dr. Alfio Torrisi*¹, *Dr. Pavel Horák*¹, *Dr. Antonino Cannavò*¹, *Dr. Giovanni Ceccio*¹, *Dr. Jiri Vacík*¹,
*Dr. Jan Vanis*², *Dr. Jan Grym*², *Dr. Roman Yatskiv*²

1. Nuclear Physics Institute, CAS, Hlavní 130, 25 068 Husinec-Řež, Czech Republic, 2. Institute of Photonics and Electronics, CAS, Chaberska 57, 182 51 Prague, Czech Republic

Introduction

Metal-oxide based sensors (MOS) can be used for several technological applications in microelectronic devices, due to their low cost and sensitive capabilities to different chemical species.

Methods

On the perspective to develop such CuO-TiO₂ MOS, tens of Cu and Ti thin layers were alternatively deposited on silicon crystal substrates using Ar ion beam sputtering and, subsequently, oxidized by the thermal annealing treatments in air. By this technique the samples were prepared with a total film thickness of ~ 150 nm on the Si substrate. The deposited films have different ratio of Cu and Ti phases ranging from 20:80 to 90:10. Such samples were characterized by the AFM and SIMS analyses, which will be commented and discussed in this work.

Results and Conclusions

In particular, AFM gives information on the surface sample morphology, and SIMS allows to observe the Cu/Ti multilayers and thickness of each phase, and further to exploit the copper diffusion and phase separation of CuO and TiO₂ in the samples. The reasons of this effect represent an issue that has to be deeply investigated, in order to improve the MOS preparation.

Carbosilane dendritic amphiphiles for the preparation of liposomal drug delivery systems

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 267

Mr. Antonín Edr¹, Dr. Tomáš Strašák¹

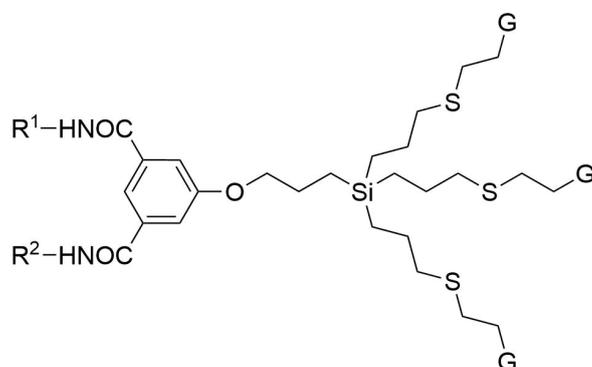
1. Institute of Chemical Process Fundamentals of the CAS, v.v.i., Prague, Czech Republic

Recently, we discovered a high biomedical potential of carbosilane dendrimers with phosphonium groups on their periphery [1, 2]. Thus, one of the aims of my work is a preparation of phosphonium dendritic amphiphiles such as **1** which could be assembled into liposomes that can serve as drug delivery systems. However, the synthesis is designed so that different groups can be chosen as a polar domain of the amphiphile and so as a periphery group of the liposome. The main goal is to find a drug delivery system for defined siRNA (short interfering RNA) but other applications are possible as well.

In the meantime, a synthesis of unsymmetrical analogues (e.g. **2**) of the mentioned amphiphiles was discovered. The idea is to connect a fluorescent tag to one of the lipophilic arms of the unsymmetrical analogues of the amphiphiles with the best biomedical results and then assemble the final liposomes from a mixture of symmetrical and unsymmetrical molecules e.g. 100:1. That should enable an easy detection of the liposomes in living systems whilst keep their assembly possible and preparation economical.

References:

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2. R. Herma, D. Wrobel, M. Liegertova, et al., Int. J. Pharm., 562 (2019) 51-65



- 1** - $R^1 = R^2 = C_{12}H_{25}$; $G = PPh_3^+I^-$
2 - $R^1 = C_{12}H_{25}$; $R^2 = C_8H_{16}NH_2$; $G = PPh_3^+I^-$

Carbosilane dendritic amphiphiles for the preparation of liposomal drug delivery systems.png

Four-channel optical demultiplexer based on X shaped photonic crystal ring resonators

Tuesday, 3rd December - 13:30: Poster session (Hall) - Poster - Abstract ID: 264

Dr. Merzoug Ammari¹, **Dr. Ahlem Benmerkhi**¹, **Prof. Touraya Bouchemat**¹, **Prof. Mohamed Bouchemat**¹, **Prof. Fouad Kerrou**²

1. Freres Mentouri, constantine1, 2. laboratoire de Modélisation des dispositifs a énergies renouvelables et nanométrie,
Université Frères Mentouri de Constantine1

The proposed structure of four channels demultiplexer consists of triangular lattice with circular silicon rods placed in a background of air. In triangular lattice, the number of rods in X and Z directions are 60 and 21 respectively. The lattice constant is 630 nm which is a distance between the two neighbor rods, denoted by 'a'. The radius of the rod is 106 nm. The relative permittivity of the dielectric rods in the structure is $\epsilon_r = 11.97$ (Refractive Index = 3.46).

The schematic diagram of our proposed demultiplexer is shown in figure 1a. This demultiplexer contains an input port, four output ports (A, B, C, D) and 4 X-shaped ring resonators for the purpose of filtering the proposed wavelengths.

As the designated wavelength is dropped by having distinct refractive index, the refractive index of the structure is varied. The first PCRR is having the index difference of 3.6, the second one is having 3.58, the third one is having 3.56 and the fourth one is having 3.54.

The 2D-FDTD method is used to simulate the proposed structure. To use this method, the structure should be meshed precisely. Thus, the meshing size of the structure is $\Delta x = \Delta z = a/16$,

The normalized transmission power spectrum is obtained at port A, B, C, and D respectively. As the change in refractive index will change the resonant wavelength, the different resonant wavelength is dropped at its designated port. The Fig.1b shows that normalized transmission spectra of proposed four port demultiplexer. The resonant wavelength of channel A, B, C, D are 1.5255 μm , 1.5195 μm , 1.5136 μm and 1.5078 μm , respectively and other functional parameters such as quality factor, transmission and crosstalk are tabulated in Table.1.

Fig. 1: (a) Four-channel demultiplexer based on ring resonators, (b) Output spectra of the demultiplexer.

Table 1 Simulation results of the proposed demultiplexer

Decaborate: A smaller cousin of dodecaborate in supramolecular chemistry

Tuesday, 3rd December - 14:30: General aspects of inorganic chemistry (Auditorium) - Oral - Abstract ID: 29

***Prof. Detlef Gabel*¹, *Dr. Suzan El Anwar*², *Dr. Bohumir Grüner*², *Ms. Barbara Begaj*³**

1. Jacobs University, 2. Institute of Inorganic Chemistry, Czech Academy of Science, 3. Jacobs University Bremen

We have recently described the supramolecular properties of the dodecaborate cluster and its derivatives^[1-4]. There is strong association with cyclodextrins, and the association is dependent on the size of the cluster – halogenated clusters require larger cyclodextrins than hydrogen-substituted clusters.

Decaborate is smaller than dodecaborate, and less symmetrical. Halogen derivatives can be prepared, as well as derivatives with organic residues. We found that the parent cluster did not bind with any measurable affinity to any of the cyclodextrins, in stark contrast to dodecaborate. Halogenation improves binding, and further substitution increases the interaction forces. Structure-activity relationships will be presented.

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d¹⁰-Metal complexes of novel, hemilabile phosphine oxide ligand

Tuesday, 3rd December - 15:04: General aspects of inorganic chemistry (Auditorium) - Oral - Abstract ID: 157

*Ms. Christin Kirst*¹, *Prof. Konstantin Karaghiosoff*¹

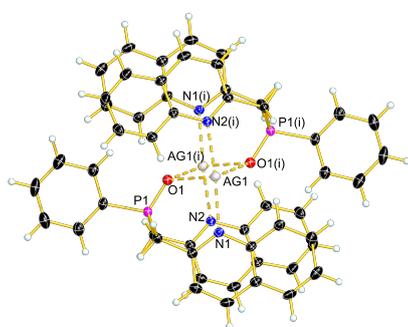
1. Ludwig-Maximilian-University

Hemilabile chelating ligands offer a unique opportunity to generate complexes, in which a coordination site can be provided *on demand* for the selective coordination of further ligands within metal centered chemical reactions. For this reason, they are of great importance for transition metal catalyzed processes in industry and laboratory. The development of new hemilabile phosphine based ligands with tunable coordination properties is a challenging task in phosphorus chemistry.

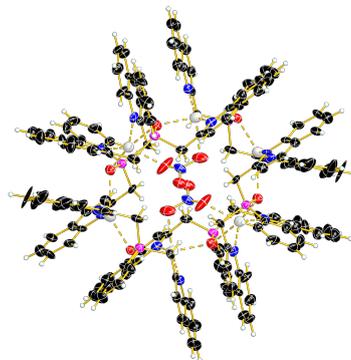
Our concept is based on tertiary phosphines, which have pyridine or pyridine derivatives in the organic part. The pyridine containing part is bonded to phosphorus via a methylene bridge, which offers flexibility in the orientation of this part of the molecule when coordinating to a metal. The coordination properties of the dicoordinate nitrogen can be fine tuned by suitable substitution. The conversion of the phosphine to the corresponding phosphine oxide ensures air stability and is important for possible practical applications. The resulting multi-dentate O,N ligand combines flexible coordination of rigid sites and is anticipated to display a rich coordination chemistry. Here we present the synthesis and first complexes of this new ligand with d¹⁰ transition metals and in particular with Cu(I), Ag(I) and Zn(II).

The new ligand is readily prepared from the corresponding dichlorophosphine and suitable trimethylsilylmethyl derivative of the nitrogen containing organic substituent and is isolated in high yields. Through oxidation with hydrogen peroxide it is converted to the air stable phosphine oxide. The reaction of this ligand with selected Cu(I), Ag(I) and Zn(II) salts yields a variety of novel metal complexes, which are isolated in high yields and characterized by multinuclear NMR spectroscopy, MS and vibrational spectroscopy. X-ray diffraction studies on single crystals of the complexes reveal fascinating structures in the solid state.

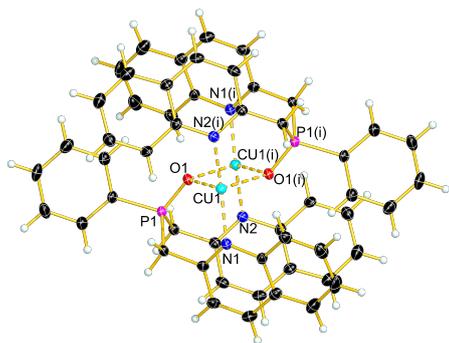
In most of the cases multinuclear complexes are formed. On coordination, nitrogen and oxygen take over different tasks with the oxygen atom often acting as a bridge between two metal atoms. The coordination ability of the anion also plays an important role and influences the formed solid-state structures considerably. Regarding the Ag(I) complexes, the structures found indicate no possible metal-metal interactions. Synthesis, structures and further properties of the new complexes will be presented and discussed.



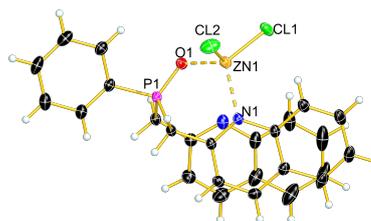
Agbf4 complex chk.png



Agno3 complex chk.png



Cubf4 complex chk.png



Zncl2 complex chk.png

Fragmentation and ring opening reactions of the imidazoliumyl-substituted [(LC)₄P₄]⁴⁺ tetracation (LC = NHC)

Tuesday, 3rd December - 15:21: General aspects of inorganic chemistry (Auditorium) - Oral - Abstract ID: 218

Dr. Kai Schwedtmann¹, Ms. Jan Haberstroh¹, Mr. Sven Roediger¹, Dr. Antonio Bauza², Dr. Antonio Frontera², Dr. Felix Hennersdorf¹, Prof. Jan J. Weigand¹

1. Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, 2. Departmet of Chemistry, Universitat de Illes Balears, 07122 Palma de Mallorca

The element phosphorus tends to assemble into homo-nuclear cyclic and cage-like structural motifs which is illustrated by the multitude of known polyphosphanes.^[1] Particularly, neutral monocyclic polyphosphanes with the general formula P_nR_n (n = 3-5) are already known for decades and their chemistry is well established.^[2] The replacement of all substituents R in *cyclo*-P_nR_n by imidazoliumyl-substituents gives cationic *cyclo*-phosphanes of type [(LC)_nP_n]ⁿ⁺ where the substituents L_C are expected to have a significant influence to the reactivity.^[3] In this contribution we present the formation of a tetracationic *cyclo*-tetraphosphane [(LC)₄P₄]⁴⁺ as triflate salt via the reduction of L_CPCl₂⁺.^[4,5]

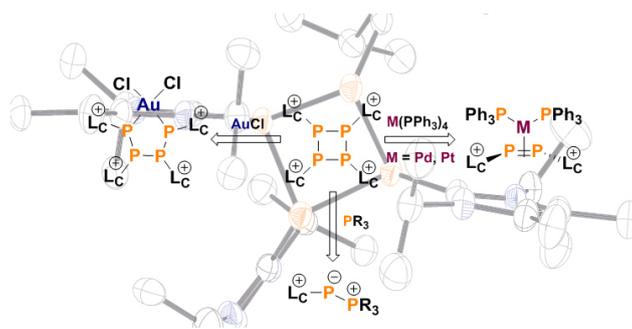
Selective transition metal mediated fragmentation and ring opening reactions as well as reactions with main group element compounds where [(LC)₄P₄]⁴⁺ acts formally as L_CP⁺-synthon will be discussed.

Acknowledgment:

We thank the Deutsche Forschungsgemeinschaft (DFG grant numbers WE4621/3-1 and WE4621/6-1) for financial support.

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Abstract pbsi figure.jpg

A new diversified family of diphosphinoboranes - synthesis and classification

Tuesday, 3rd December - 15:38: General aspects of inorganic chemistry (Auditorium) - Oral - Abstract ID: 30

Ms. Anna Ordyszewska¹, **Ms. Natalia Szykiewicz**¹, **Prof. Jarosław Chojnacki**¹, **Dr. Rafał Grubba**¹

1. Gdansk University of Technology, Faculty of Chemistry

Introduction

Only a few diphosphinoboranes were isolated in a crystalline form and therefore there are hardly any X-ray structures reported in the literature. The first well-described example reported in 1988 is $(PPh_2)_2BMe_3$ which was synthesized by Power in the metathesis reaction¹. Karsch reported on the synthesis and isolation of $(Mes_2P)_2BX$ ($X=Br, OEt$)². The first and only aminodiphosphinoborane with provided crystallographic data is $Ph_2NB[P(SiMe_3)_2]_2$ synthesized and characterized by Paine³.

Methods

The obtained compounds were characterized in the solution and in the solid state by means of NMR spectroscopy and X-ray diffraction, respectively.

Results

We have synthesized, isolated and characterized two precursors $(tBu_2P)(Br)BNiPr_2$, $(Cy_2P)(Br)BNiPr_2$ and seven diphosphinoboranes, which can be divided into three groups (Scheme 1.): **A** – $(tBu_2P)_2BPh$; **B** – $(tBuPhP)_2BPh$, $(Cy_2P)_2BPh$; **C** – $(Ph_2P)_2BNiPr_2$, $(tBu_2P)(Ph_2P)BNiPr_2$, $(Cy_2P)_2BNiPr_2$, $(Cy_2P)(Ph_2P)BNiPr_2$. These species were obtained in the salt elimination reaction of lithium phosphide R_2PLi ($R_2P= tBu_2P, Cy_2P, Ph_2P, tBuPhP$) and dibromoborane $R'BBr_2$ ($R' = NiPr_2, Ph$). The synthesis is inspired by the previously described methods of Power¹ and Paine³.

Discussion

Obtained diphosphinoboranes were classified into three groups: **A** – in which P-atoms are carrying strong electron-donating substituents and B atom possesses electron-accepting phenyl group, which further leads to the structure with one double and one single P-B bond and diversified planar and pyramidal geometry of P-atoms; **B** – in which the P-B distances are comparable and both phosphorus atoms are pyramidal; **C** – in which B-atom is attached to amino group with strong donor abilities which further allows obtaining compounds with two very long P-B bonds and two pyramidal P-atoms. In the majority of cases, the synthesis is very clean and the crude product may be used for further applications without additional purification.

Acknowledgments

The authors gratefully acknowledge the National Science Centre, Poland (NCN) for financial support (Project No. 2017/25/N/ST5/00766).

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Substituted thiaboranes establish the class of non-covalent organic framework materials

Tuesday, 3rd December - 15:55: General aspects of inorganic chemistry (Auditorium) - Oral - Abstract ID: 198

Prof. Ales Ruzicka¹

1. Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 573, CZ-532 10, Pardubice, Czech Republic

Microporous materials with cavities of diameter < 2 nm such as charcoal, ceramics, zeolites, porous coordination polymers (PCP) with subclass of metal organic frameworks (MOF), porous organic frameworks (POF) with subclass of covalent organic frameworks (COF) gained much attention of scientists both in academia and industry. As it is clear from the common names of some of these materials, the subunits (metals and organic molecules in MOFs or purely organic molecules in COFs) are interconnected by very strong coordination or covalent bonds with dissociation energies of 40 - 150 kcal/mol.

Contradictory, there is also one more group of molecular assemblies, so-called hydrogen-bonded organic frameworks (HOF), where the aggregates were supposed to be too unstable with no effective permanent porosity, because the strengths responsible for molecular association are too weak of about 10 kcal/mol only. Recently, some strategies how to prepare these materials available for various applications by employment of oligo-carboxylic or sulfonic acids, heterocycles or oligoamides were developed. With the respect to named families of compounds, the aggregation of molecules in order to make the extrinsic porosity or cavities within the supramolecular architectures is not probable without a guest molecule holding the system together. Five years ago, we started the investigation of the chalcogen bonding, made possible by the σ -hole localized on the sulfur atom and the π -system of phenyl ring interaction, within the group of thiaboranes. Now we would like to report on the chemistry of thiaboranes going from interactions and reactivity with various bases up to template controlled porosity and selective carbon dioxide capture.

Fluorescent dendritic nanotools especially designed for biology

Tuesday, 3rd December - 14:30: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 115

Dr. Anne-Marie Caminade¹

1. Laboratoire de Chimie de Coordination du CNRS UPR 8241; Université Toulouse III Paul Sabatier

Phosphorus-containing dendrimers of type phosphorhydrazone are a special class of dendrimers, possessing multiple properties, in particular for biology.[1] These dendrimers can be especially engineered to permit the introduction of fluorophores at different locations in their structure (core, branches, surface, Figure 1), essentially for bioimaging.[2] Fluorescence helped in particular for deciphering the interaction of anti-inflammatory dendrimers with human monocytes [3,4] (Figure 2a) or with mannose receptors [5] (Figure 2b) and of anti-cancer dendrimers with different strains of cancerous cells [6] (Figure 2c). Furthermore, fluorescent dendrimers can be used in vivo for imaging the repartition of bioactive dendrimers in different organs of small animals. [7] An overview of the biological properties of fluorescent phosphorus dendrimers will be given.

[1] Phosphorus dendrimers in biology and nanomedicine, Caminade, A.M., Turrin, C.O., Majoral, J.P. (Eds), Pan Stanford Publishing, Singapore, **2018**

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Acknowledgements: the ANR (Agence Nationale de la Recherche, grant ANR 2017 PRC SLOW2) and the CNRS (Centre National de la Recherche Scientifique) are acknowledged for financial support.

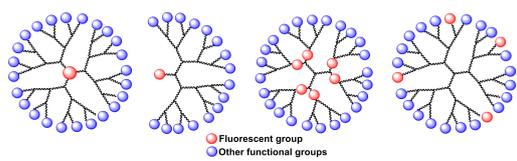


Fig 1.png

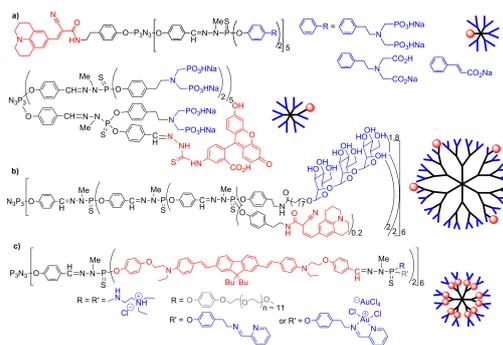


Figure 2.png

Novel fluoroborate-functionalised polyazamacrocycles for the specific detection of tumour hypoxia by ^{19}F -MRI

Tuesday, 3rd December - 15:04: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 50

Dr. Thibault Troadec¹, **Dr. Richard Knighton**¹, **Dr. Lorenzo Tei**², **Prof. Raphaël Tripier**³

1. CNRS-Université de Bretagne Occidentale, Brest, 2. Università del Piemonte Orientale Alessandria, 3. Université de Bretagne Occidentale, Brest

Hypoxia (oxygen deficiency) is characteristic of rapidly growing tumours, which do not have sufficient blood supply during their fast proliferation. These cellular environments have been proven to be highly aggressive and resistant to usual therapies, and their specific detection is key in the design of appropriate therapeutic protocols for affected patients.[1]

Positron Emission Tomography (PET) tracers, such as ^{18}F -Miso or ^{64}Cu -ATSM are currently the best specific imaging agents available.[2] However, compared to PET which requires radioisotopes and thus suffers from inherent cost and constraining preparation of radiotracers, MRI benefits from widely deployed equipment, alongside cheaper and storable tracers. Therefore, the development of hypoxia-specific MRI probes is highly desirable. Although a few ^1H -MRI techniques have been investigated,[3] ^{19}F -MRI has emerged as a promising alternative, thanks to the high MR sensitivity of this nucleus (83% compared to ^1H) and its absence in soft tissues, resulting in excellent signal-to-background ratio.

As Cu(II) is reduced in hypoxic environments, copper complexes bearing pendant fluorinated groups are good candidates for such an application. Paramagnetic Cu(II) broadens the ^{19}F -MRI signal, representing the “off” state of the probe, that is turned “on” specifically upon reduction to Cu(I) in hypoxic media (Figure 1). Proof-of-concept probes from E. L. Que *et al.* have demonstrated the viability of the concept with trifluoromethyl groups.[4]

Our work, presented herein, aims at improving the *in vitro/in vivo* behaviour and magnetic resonance properties of such complexes thanks to Boron, with trifluoroborate groups as the platform for the ^{19}F -MRI signal, as well as the strength of copper coordination to allow future *in vivo* applications (Figure 2).

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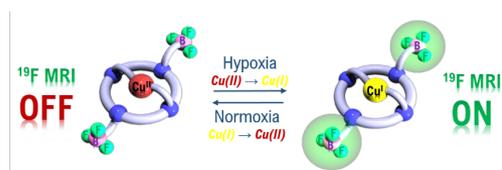


Figure 1 - redox on-off switch for hypoxia-specific ^{19}F -mri.png

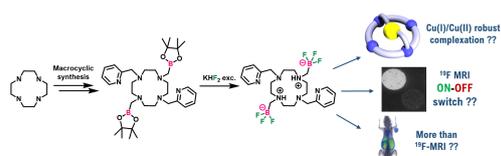


Figure 2 - fluoroborate-functionnalised macrocycle synthesis and applications.png

Synthesis of phosphonic analogues of phenylalanine and homophenylalanine including fluorine and bromine in aromatic moiety.

Tuesday, 3rd December - 15:21: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 52

Ms. Weronika Wanat¹, Prof. Pawel Kafarski¹

1. Wroclaw University of Science and Technology

α -Aminophosphonic acids are known as molecules with broad ability to influence biological and pathological processes in living organisms. The unique structure of these compounds (analogues of naturally occurring α -amino acids) determined their high potential during inhibition of enzymatic catalysis. Due to stabilization of the transition state, which play the key role for the hydrolytic mechanism, molecules with N-C-P scaffold are considered as promising protease inhibitors, especially metalloaminopeptidases[1]. Introduction of fluorine and other atoms into phenyl ring brings

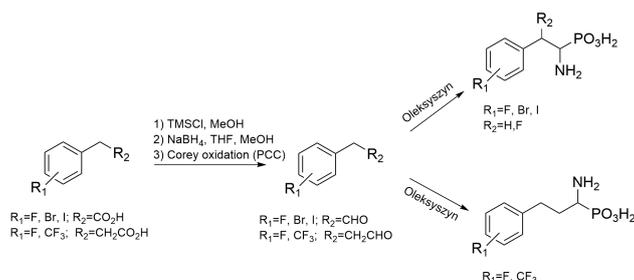
the permission of improving pharmacokinetic properties of the designed α -aminophosphonic acids. Furthermore, implemented substituents stand out the possibility of formation of the additional interactions with amino acid residues in the active and binding centers, which can improved their inhibitory potency.

New series of aromatic α -aminophosphonic acids have been synthesized by using multistep synthetic route. In general, commercially available carboxylic acids were converted into methyl esters, alcohols and aldehydes[2]. Finally, aldehydes were used as substrates in condensation with benzyl carbamate and triphenyl phosphite (Oleksyszyn reaction)[3] in order to receive the title products. Developed methodology ensured satisfactory reaction yields and resistance to hydrogenation of bromine atoms located at aromatic ring, which is usual obstacle observed when using synthetic schemes requiring hydrogenation process.

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General procedure.png

Influence of phosphorus content on bioactivity of SiO₂-CaO-P₂O₅ nanoparticles

Tuesday, 3rd December - 15:38: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 87

***Dr. Beata Borak*¹, *Ms. Iga Jakobowska*², *Ms. Jolanta Gasiorek*¹, *Dr. Justyna Krzak*¹, *Dr. Maciej Ptak*³, *Dr. Anna Lukowiak*³**

1. Department of Mechanics, Materials Science and Engineering, Wrocław University of Science and Technology, Wrocław, 2. Department of Chemistry, Wrocław University of Science and Technology, Wrocław, 3. Institute of Low Temperature and Structure Research, PAS, Wrocław

Introduction

The bioactivity of glasses or ceramics derives from their ability to *in vivo* formation of a hydroxyapatite surface layer which show adhesion to living bones. The bioactivity depends on many factors including materials' composition, structure, and morphology. This study aims to investigate the effects of different content of phosphorus in SiO₂-CaO-P₂O₅ material and thermal treatment (600-800 °C) on the morphology and *in vitro* bioactivity of nanoparticles.

Methods

In this work, bioactive glass (or glass-ceramic) nanoparticles based on ternary (SiO₂-CaO-P₂O₅) system were prepared by wet chemistry methods.

Results

Materials consisting of round shaped particles with diameter sizes of about 100 nm were obtained (Fig. 1). Their shape and size were evaluated by SEM and DLS method.

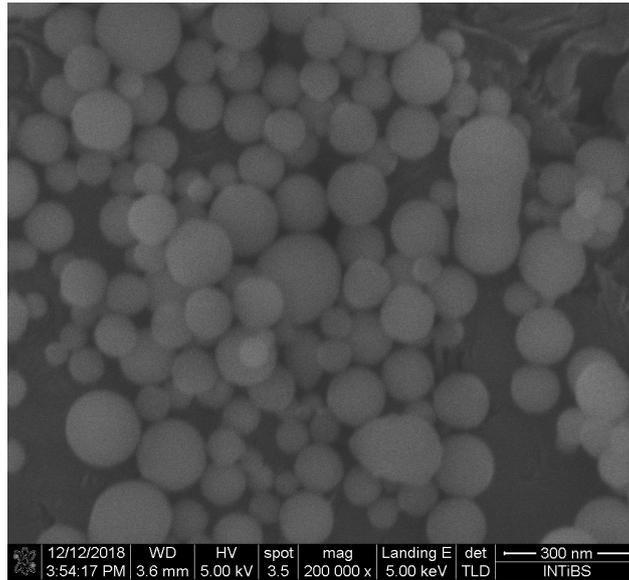
The bioactive character of obtained materials was accessed by analyzing the ability for hydroxyapatite formation on the surface after being immersed in SBF solution at 37 °C for different time (4 hours - 4 week). The ability to induce mineralization is a desired characteristics of biomaterials used in bone tissue engineering. The best bioactivity results are observed for the samples prepared as a ternary system (SiO₂-CaO-P₂O₅) in the comparison to the binary (SiO₂-CaO) system. XRD, EDX, ICP-OES, SEM, FTIR and Raman spectroscopy were utilized to recognize and confirm the formation of hydroxyapatite layer on the prepared nanoparticles.

Discussion

It was observed that the presence of phosphorus have influence of the better formation of hydroxyapatite layer – responsible for bioactivity of glasses but it has also influence on the crystallization process of these materials. Crystallized materials show a lower dissolution rate what could have a undesirable effect on bioactivity.

Acknowledgements

This research was performed in the framework of the National Science Centre grant No. 2016/22/E/ST5/00530.



Sem image of sio2 cao-p2o5 particles.png

Efficient light emitters based on icosahedral boron clusters. Structure, photophysics and bioimaging studies.

Tuesday, 3rd December - 15:55: Bioinorganic chemistry and application in medicine (Room 1) - Oral - Abstract ID: 59

***Dr. Rosario Nunez*¹, *Dr. Mahdi Chaari*¹, *Dr. Albert Ferrer-Ugalde*¹, *Prof. Francesc Teixidor*¹, *Prof. Clara Viñas*¹, *Dr. Gerard Tobias*¹**

1. ICMA-B-CSIC

Icosahedral boron clusters are very robust compounds characterized by a three-dimensional (3D) s-delocalization,¹ high thermal and chemical stability, hydrophobicity and low toxicity in biological systems.² The versatility toward functionalization of boron clusters makes them suitable building blocks easily linkable to organic molecules and another scaffolds. Due to their unique structural and electronic properties, carborane clusters are excellent entities when applying them to tailor the fluorescence emission of any fluorophore group.³

We have designed efficient light emitters carborane-containing molecules, whose emission in solution depends critically on the cluster isomer (ortho- or meta-) and the substituents attached to the carbon cluster atom.⁴ Molecules bearing *m*-carborane clusters exhibit high fluorescence efficiency in solution while maintaining a moderate emission in aggregate state. In this way, and depending on the application of choice, we are capable of preparing highly fluorescent materials in both states.

We have synthesised boron cluster-based conjugates as fluorescent probes for in vitro studies, by linking different neutral or anionic boron clusters (carborane C₂B₁₀H₁₂, metallocarboranes [M(C₂B₉H₁₁)₂]⁻ (M = Co, Fe), and *closo*-dodecaborate [B₁₂H₁₂]²⁻ moieties) to BODIPY derivatives.⁵ Their exceptional cellular uptake and intracellular boron release, together with their fluorescent and biocompatibility properties make these compounds good candidates for cell tracking and boron delivery systems. **Figure 1** shows confocal microscopy images of HeLa cells incubated with metallocarborane-BODIPY conjugates emitting green fluorescence. Furthermore, a set of boron-enriched hybrids that combine the advantages of boron clusters and their platforms (GO, nanoparticles) have also been prepared. They could be tagged with imaging contrast agents to assess their accumulation in vivo experiments.

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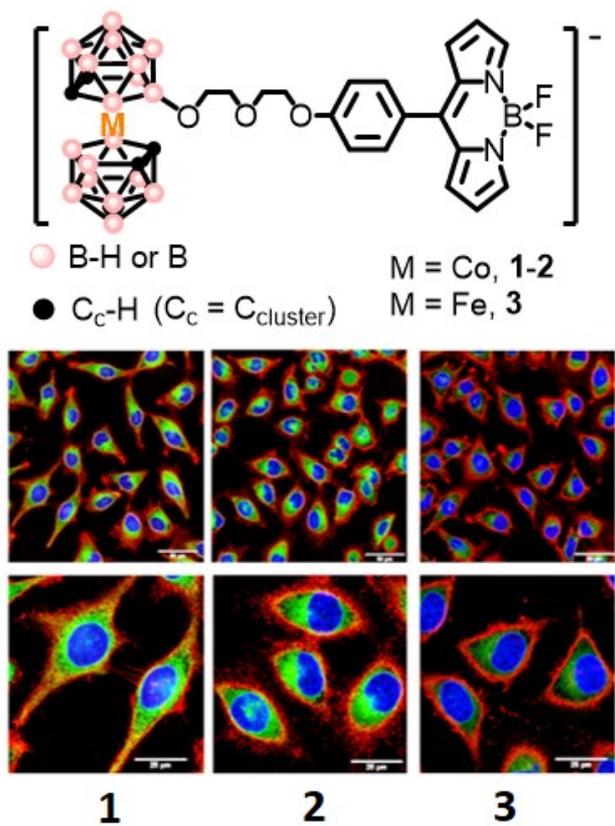


Figure 1def.jpg

Combining frustrated lewis pair Reactivity with boron-ligand cooperation: reversible hydrogen activation and gem selective dimerization of terminal alkynes by a pyridonate borane complex

Tuesday, 3rd December - 16:50: Catalysis processes & applications (Auditorium) - Oral - Abstract ID: 89

Dr. Urs Gellrich¹, Mr. Max Hasenbeck¹

¹ Justus-Liebig-Universität Giessen

In recent years, metal-ligand cooperation has emerged as a powerful tool for sigma-bond activation by transition-metal complexes.^[1] In this work, a pyridone borane complex that liberates dihydrogen under mild conditions is described.^[2] The reverse reaction, dihydrogen activation by the formed pyridonate borane complex, is achieved under moderate H₂ pressure at room temperature (Figure 1). DFT and DLPNO CCSD(T) computations reveal that the active form of the pyridonate borane complex is a boroxypyridine that can be described as a single component Frustrated Lewis Pair (FLP). Significantly, the computations and experiments show that the boroxypyridine undergoes a chemical transformation to a neutral pyridone donor ligand in the course of the hydrogen activation. This unprecedented mode of action may thus, in analogy to metal-ligand cooperation, be regarded as an example of boron-ligand cooperation. The unique reactivity of this system enabled the first metal-free *gem* selective dimerization of terminal alkynes (Figure 2).^[3] The key step of the catalytic cycle is a rare 1,2-carboration. Each individual step of the catalytic cycle was explored experimentally and substantiated by accurate DLPNO-CCSD(T) computations.

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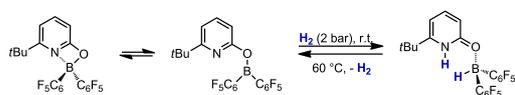


Figure1.png

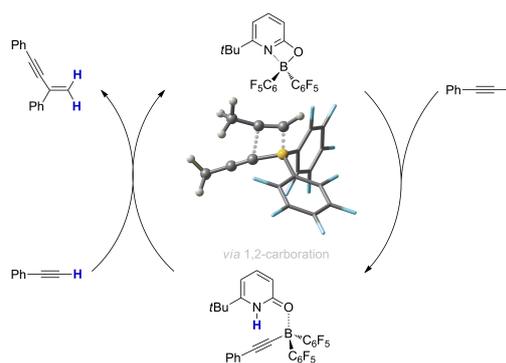


Figure2.png

Towards convenient methodologies for the synthesis and use of organophosphorus derivatives

Tuesday, 3rd December - 17:07: Catalysis processes & applications (Auditorium) - Oral - Abstract ID: 54

Dr. Julia Deschamp¹, Dr. Jade Dussart¹, Dr. Margery Cortes-Clerget¹, Dr. Olivier Gager¹, Dr. Evelyne Migianu-Griffoni¹, Prof. Marc Lecouvey¹

1. Université Paris 13, Sorbonne Paris Cité

Organophosphorus compounds are an important class of molecules which have manifold applications in the fields of catalysis, agronomy, material and life sciences. [1]

In this context, the development of more eco-compatible chemical methodologies represents a major challenge in the field of synthetic organophosphorus chemistry in order to fulfill the principles of green chemistry. [2]

For many years, our group studied the syntheses and uses of various bisphosphonate derivatives which have potent biological activities. More recently, we have focused on the development of convenient methodologies allowing the easy access to other organophosphorus compounds like phosphinates, bisphosphinates or phosphino-phosphonates.[3] On the other hand, we have also aimed to elaborate novel chiral peptidophosphonate catalysts for the selective formation of C-C bonds. [4]

In this communication, we will disclose an overview of our latest advances and contribution in the field of P(III) and P(V) chemistry.

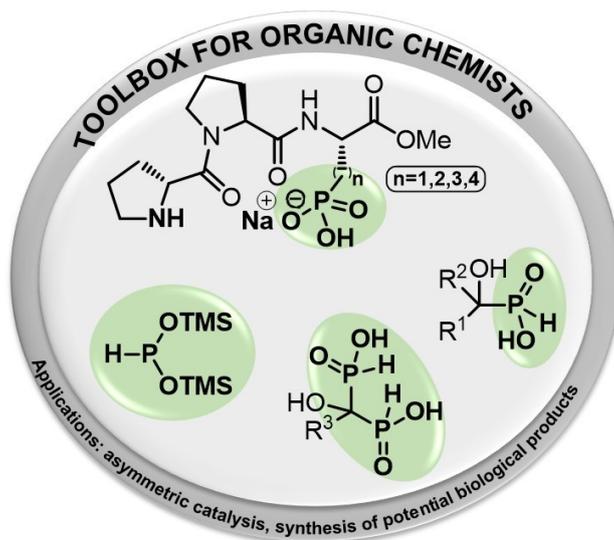
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[2] P. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, 39, 301-312

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Scheme1.jpg

Aerobic [M]-/organo-catalyzed oxidation of siloxanes – perspective way to the functionalized siloxanes

Tuesday, 3rd December - 17:24: Catalysis processes & applications (Auditorium) - Oral - Abstract ID: 134

Ms. Irina Goncharova¹, **Dr. Ashot Arzumanyan**¹, **Dr. Sergey Milenin**², **Prof. Aziz Muzafarov**³

1. A.N.Nesmeyanov Institute of Organoelement Compounds, RAS, 2. Enikolopov Institute of Synthetic Polymeric Materials, 3. N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences

Synthesis of organosilicon products with a “polar” functional group within organic substituents is one of the most fundamentally and practically important challenges in today’s chemistry of silicones. Incorporation of a “polar” function into organosilicon compounds opens quite unique opportunities for their subsequent modification and preparation of new copolymers, MOFs, HOFs and other hybrid materials. In addition, modification by incorporation of functional groups would also allow other problems to be solved, namely, the low mechanical strength and “incompatibility” of silicones with organic polymers.

To solve these problems obtaining of functionalized (–OH, –C₆H₄C(O)OH) siloxanes *via* the aerobic oxidation of hydride or *p*-tolyl-siloxanes was suggested (Scheme 1). This approach is based on “green”, commercially available, simple, and inexpensive reagents and employs mild reaction conditions: Cu(OAc)₂ or Co(OAc)₂ /NHPI or NHSI – catalytic system, O₂ as the oxidant, process temperature from 30 to 60 °C, atmospheric pressure.

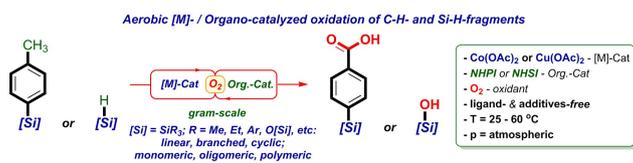
It was shown that it is principally possible to perform the gram-scale aerobic [M]-/organo-catalyzed oxidation of a Si–H group to a Si–OH group with retention of the organosiloxane core. This method allows various monomeric, oligomeric and polymeric siloxanols of linear, branched and cyclic structures to be synthesized.¹ This approach was later extended to *p*-carboxyphenyl-siloxanes synthesis.² The reaction is general and allows to synthesize both mono- and di-, tri-, and poly(*p*-carboxyphenyl)siloxanes. Furthermore, it was shown that the suggested method is applicable for the oxidation of organic alkylarene derivatives (Ar–CH₃, Ar–CH₂–R) to the corresponding acids and ketones (Ar–C(O)OH and Ar–C(O)–R).

All the organosilicon products were obtained and isolated in gram amounts (up to 15 g) and characterized using complex of physico-chemical methods (1D- and 2D-NMR, IR, ESI-HRMS, GPC, X-ray). Molecular structure of bis(trimethylsiloxy)methylsilanol that is liquid at room temperature was confirmed using *in situ* crystallization. X-ray data also confirmed that *para*-carboxyphenylsiloxanes in crystalline state tend to form hydrogen-bonded polymers (HOF-like structures).

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This work was supported by the RSF project № 19-73-10172.



Scheme 1

Scheme 1.jpg

Highly selective hydrosilylation of alkynes by platinum(0) complexes bearing bulky dialkylbiaryl phosphine ligands

Tuesday, 3rd December - 17:41: Catalysis processes & applications (Auditorium) - Oral - Abstract ID: 58

*Mr. Ruslan Lukin*¹, *Dr. Dmitry Yakhvarov*¹, *Mr. Alexander Kachmarzhik*¹

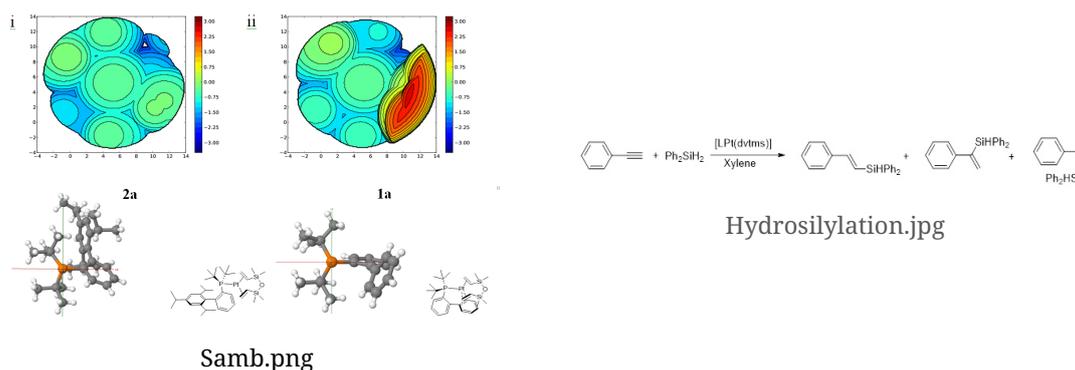
1. Kazan Federal University

A series of 7 platinum(0) dialkylbiarylphosphine complexes with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS) were synthesized with 72-96% yield and structurally characterized using NMR, IR and XRD. Prepared complexes found to be efficient catalysts in hydrosilylation reaction between phenylacetylene and diphenylsilane in mild conditions and in cross-linking process of PDMS. The ligand set was based on dialkylbiaryl phosphines and their tailored derivatives and in total contained 7 ligands. These catalysts sufficiently increased the selectivity of β -(*E*) isomer formation up to 98% with increasing of the total yield up to 95%.

For complex **1a** platinum(0)-*ortho* carbon atom from aryl group distance averages 3.204 Å platinum(0)-*ipso* carbon distance was 3.293 Å, these values are less than the sum of platinum and carbon Van der Waals radii (3.57 Å) [1]. The same effect, when $d(\text{metal-C}_{\text{ortho}})$ is quite shorter than $d(\text{metal-C}_{\text{ipso}})$ observed in palladium(0) diphosphine complexes [18], in contrast to gold(I) complexes of JohnPhos [2] which prefers interactions with *ipso* atom rather than *ortho*, preferred *ipso*-coordination also occurs in allylpalladium complexes of dialkylbiarylphosphines with formation of strong Pd-C_{ipso} bond, as it seems from bond length varying from 2.3 to 2.5 Å which refers to η^1 -coordination of palladium to benzene ring [3]. Estimation of hapticity for Pt-arene interaction in **1a** using Kochi and co-workers proposed equation [4] equation gave hapticity value of $x=1.68$, this is comparable with gold(I) complexes with x in range 1.55-1.95.

The structural parameters were extracted from both XRD structures and optimized phosphine oxide derived template structures. Parameters were set as percent buried volume, sterimol values, and percent buried volume values of phosphines in 4 quadrants. Constructed library of complexes allow to include other types of ligands with the same structural scaffold for further optimization of hydrosilylation processes and study QSPR for selectivity and activity of homogeneous catalysts in Si-H activation processes.

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Investigating the reduction and reactivity of cobalt diphosphine complexes

Tuesday, 3rd December - 17:58: Catalysis processes & applications (Auditorium) - Oral - Abstract ID: 16

*Ms. Claire Brodie*¹, *Dr. Andrei Batsanov*¹, *Dr. Phil Dyer*¹

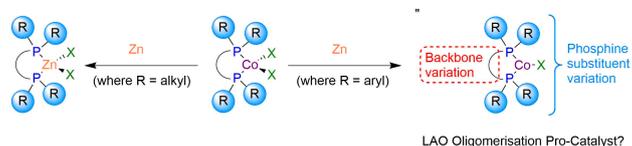
¹. Durham University

Recently, there has been significant interest in the synthesis and reactivity of chelate diphosphine cobalt(I) complexes. These systems have: been explored as pro-catalysts to mediate coupling of ethylene with CO₂,¹ been shown to catalyse heterodimerisation of acrylates with 1,3-dienes,² and been demonstrated to be pro-catalysts in the asymmetric hydrogenation of enamides.³

In tandem with these studies, we initiated an investigation of the application of chelate diphosphine cobalt(I) complexes in regio- and stereo-selective linear α -olefin (LAO) to LAO oligomerisation reactions. It was envisaged that the chelating diphosphine motif would provide a sterically and electronically tuneable metal scaffold, to engineer selective oligomerisation, not only through substituent variation at phosphorus, but also by alteration of the P[^]P backbone.

Here, the synthesis and characterisation of the necessary precursor cobalt(II) [(P[^]P)CoX₂] complexes and transformation to the target cobalt(I) derivatives is discussed. The reduction chemistry of [(P[^]P)CoX₂] systems is thoroughly explored and shows that single electron reduction of such species using Zn metal is governed by steric and electronic effects imposed by the diphosphine ligand (Scheme 1). In addition, the direct synthesis of chelating diphosphine complexes from cobalt(I) sources such as [(PPh₃)₃CoCl] is investigated. Structural, spectroscopic and spectrometric techniques are utilised to gain insight into the ligand-olefin oligomerisation selectivity relationship between diphosphine ligands.

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Scheme 1 example of observed ligand-dependant reactivity of p p cox2 with zn.png

Detecting and identifying the first reaction intermediates in hydrolysis of sodium borohydride

Tuesday, 3rd December - 18:15: Catalysis processes & applications (Auditorium) - Oral - Abstract ID: 93

Prof. Umit B. Demirci¹

1. University of Montpellier

Sodium borohydride is a hydrogen source discovered in the 1940s during the context of the World War II that re-emerged in the early 2000s owing to its propensity to spontaneously generate “pure” hydrogen by reacting with water [1]:



Sodium borohydride, when stabilized in alkaline aqueous solution, is also a potential anodic liquid fuel that is able to be oxidized in the presence of a suitable electrocatalyst; typically, it has been considered to develop the technology called “direct borohydride fuel cell”:



However, one of the issues of this latter application is the occurrence, in some extent, of (heterogeneous) hydrolysis that is considered as a detrimental side reaction [2]. More specifically, it is believed that the formation of the intermediate BH_3OH^- , known to be instable, plays an important role in the occurrence of heterogeneous hydrolysis [3]:



Accordingly, we aimed at detecting and identifying this intermediate by setting up an in situ study based on the systematic use of 11-boron NMR. In parallel, we developed a new protocol to synthesize the elusive anion BH_3OH^- via the formation of the sodium salt NaBH_3OH , in order to investigate it in hydrolysis and oxidation conditions.

The collected NMR spectra revealed that the formation of BH_3OH^- from BH_4^- in the presence of H_2O is not as simple as shown by Eq. (3). Besides the signals belonging to these two anions, at least two additional signals were observed, suggesting the formation of other intermediates species. The PBSi 2019 meeting will be a good opportunity for presenting our last results about these hydrolysis intermediates.

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Polycyclic Aromatic Hydrocarbons (PAHs) with P-containing six and seven membered rings

Tuesday, 3rd December - 16:50: Optical, electrical and magnetic properties (Room 1) - Oral - Abstract ID: 27

Mr. Thomas Delouche¹, Prof. Muriel Hissler¹, Dr. pierre-antoine bouit¹

1. Institut des Sciences Chimiques de Rennes (ISCR)

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Contact @:thomas.delouche@univ-rennes1.fr

Polycyclic Aromatic Hydrocarbons (PAHs) are organic molecules featuring a bidimensional backbone composed of sp^2 -C atoms. This particular structure confers them unique properties in term of reactivity, optical/redox activity, self-assembly and opto-electronic device performances.¹ They are thus an important class of organic semi-conductors. In order to modify their properties, PAHs including heteroatoms (S, N, B, P, Si) have been studied.² Our research group has also worked on PAHs and especially on PAHs featuring phospholes (aromatic five member P-rings).³ Indeed, P-derivatives have several advantages: they are stable and it is possible to tune their chemical environment and they can be used as ligand for coordination complexes with transition metals.

In this project, we synthesized two whole families of PAHs including a P-atom with 6 (phosphaphenalenenes) and 7 (phosphepines 1, Figure1) membered ring. They were fully characterized including X-ray diffraction. The optical and the electrochemical properties were experimentally studied (UV-vis abs/emission, cyclic voltammetry) and theoretically (DFT calculations). In particular, the effect of the P-heterocycle on the optical/redox properties was investigated. Finally, these compounds are suitable for their insertion in opto-electronics devices and a phosphepine was successfully inserted in a blue-emitting OLED's (Organic Light-Emitting Diodes).

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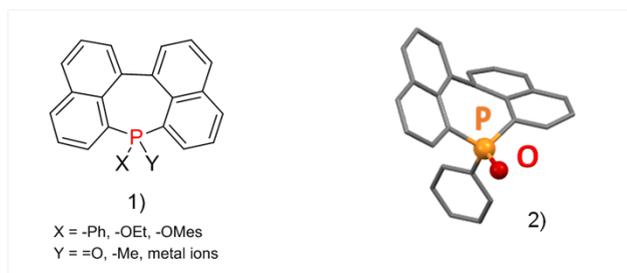


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Configurational landscapes of hydrido iron (II) complexes with chiral diphosphanes

Tuesday, 3rd December - 17:07: Optical, electrical and magnetic properties (Room 1) - Oral - Abstract ID: 51

Prof. Francisco Estevan¹, **Dr. Marta Feliz**²

1. Departament de Química Inorgànica, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain, **2.** Instituto de Tecnología Química (Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas), Avd. de los Naranjos s/n, 46022 Valencia, Spain

The substitution of the dihydrogen ligand is one of the simplest reactions of dihydrogen complexes and it plays an important role in some catalytic cycles. The iron (II) hydrido dihydrogen $[\text{FeH}(\eta^2\text{-H}_2)(\text{diphos})_2]^+$ (diphos = dmpe, dppe, (*R,R*)- or (*S,S*)-Me-DuPhos) show fluxional character at room temperature, and the dissociation of the dihydrogen ligand does not seem to be so favorable, owing to the intramolecular exchange between dihydrogen and hydrido ligands.^[1] Dihydrogen substitution reactions by neutral monodentated ligands (L = CO, MeCN) afford the *trans*- $[\text{FeH}(\text{L})(\text{diphos})_2]^+$ (diphos = dmpe, dppe) complexes, and kinetic experiments show that the substitution mechanism involves the initial opening of a chelate ring instead direct dihydrogen substitution.^[2] In this work, we present the $\eta^2\text{-H}_2/\text{L}$ (L = CO, CH₃CN, THF, Et₂O) ligand exchange reactions from the chiral $[\text{FeH}(\eta^2\text{-H}_2)((\text{R,R})\text{-Me-DuPhos}^*)_2]^+$ or $[\text{FeH}(\eta^2\text{-H}_2)((\text{S,S})\text{-Me-DuPhos}^*)_2]^+$ isomers to afford *cis* or *trans* reaction products (see Figure). Their formation and structure elucidation are investigated by NMR and single-crystal X-ray diffraction, and the reaction mechanisms are proposed.

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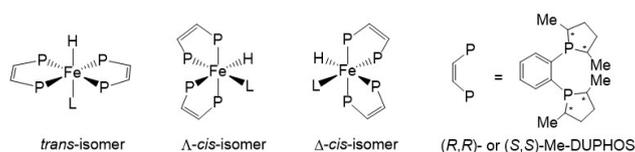


Figure 1.jpg

Modulation of dual emission in donor-acceptor phosphonium fluorophores

Tuesday, 3rd December - 17:24: Optical, electrical and magnetic properties (Room 1) - Oral - Abstract ID: 194

Mr. Andrei Beliaev¹, Prof. Igor Koshevoy¹, Prof. Pi-Tai Chou²

1. Department of Chemistry, University of Eastern Finland, 2. National Taiwan University

Materials that exhibit intriguing photophysical phenomena are of primarily importance in fundamental and applied research due to their potential application in the development of smart materials, photonic devices and bioimaging probes. Phosphorus containing dyes represent a prominent class among organic luminophores. Evidently, it's a result of the rich chemistry of the $\lambda^3\sigma^3$ phosphines (*e.g.* coordination or oxidation), which probably serve as the main sources for engineering organophosphorus chromophores of diverse architectures (*i.e.* phospholes, phosphinines or acyclic P-oxides). Remarkably, compared to largely utilized organic $\lambda^5\sigma^4$ phosphine-derived units ($R_3P=E$, $E = O, S, Se$), $\lambda^4\sigma^4$ phosphonium configuration (R_4P^+) has been largely ignored in the construction of luminophores. Being strong and tunable acceptor (*A*) by nature, phosphonium group significantly perturbs LUMO orbitals affecting the emission properties, and in combination with donor functions (*D*) can modulate efficient intramolecular charge transfer (*ICT*).

In our recent study we described a family of “push-pull” phospho-fluorophores, decorated by pendant electron-accepting phosphonium ($-R_3P^+$) and amine donor ($-NPh_2$ /carbazole) blocks connected by the aromatic spacers with altering π -conjugated systems (Figure 1A).[1] In polar solvents, these dyes behave as typical *D*- π -*A* molecules, and demonstrate variation of the emission color from sky-blue to orange (487–687 nm), pronounced solvatochromism, large Stokes shift (6900–13693 cm^{-1}), and extreme quantum efficiency up to unity, assigned to the *ICT* process.

Figure 1. Molecular design of the *D*- π -*A* phosphonium salts (A); absorption (dashed) and emission (solid) profiles of the salts 1^1 - 3^1 in toluene (B); variation of the emission spectra upon counterion exchange for salt 2^1 (C).

Unexpectedly, in non-polar solvents, dyes 1^1 - 3^1 display dual fluorescence (F_1 and F_2 bands; Figure 1B). Panchromatic emission was found to be strongly dependent on the counterion nature (Figure 1C), viscosity and temperature of the medium, as well as the length of the π -conjugated spacer. In view of experimental observations, the result, most plausibly, can be ascribed to the *ICT*-driven counterion migration, resulting in sequential formation of two different excited states. To extend the concept, we intended to analyze the effect of different $^+A-(\pi-D)_n$ configurations on the anion migration and, consequently on the optical features. For this purpose, the amount of the donor moieties ($-\pi-D$) linked with central phosphorus atom was varied to give a family of multipolar 2^1 - 2^4 and 3^2 - 3^3 chromophores (Figure 1A). The diversified photophysical and dynamic behavior provides new unconventional means for controllable panchromatic light generation.

[1] A. Belyaev, et. al, *Angew. Chemie*, 10.1002/anie.201906929, Jul. 2019.

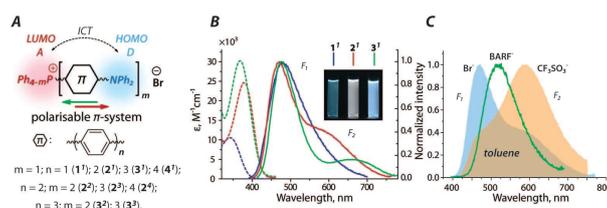


Figure 1.jpg

Anellated 3a,6a-diaza-1,4-diphosphapentalene as a form of stabilized phosphinidene

Tuesday, 3rd December - 17:41: Optical, electrical and magnetic properties (Room 1) - Oral - Abstract ID: 76

Prof. Alexander Kornev¹

1. G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences

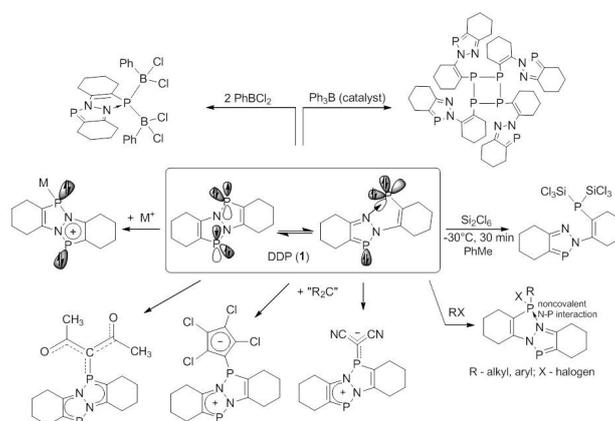
Anellated 3a,6a-diaza-1,4-diphosphapentalene (DDP, **1**) [1] which has an aromatic 10π e system, turns into a unit resembling the stabilized singlet phosphinidene when polarized by the action of weak Lewis acids or bases. This is the most likely reason for explaining the chemical properties of diazadiphosphapentalenes. DDP very easily enters into addition reactions to the phosphorus atom. In particular, hexachlorodisilane adds to the dicoordinated phosphorus atom at $-30\text{ }^\circ\text{C}$ with the Si-Si bond cleavage to form the bis(trichlorosilyl) derivative. DDP reacts with halocarbons providing 1,1-addition products without $\text{P}^{\text{III}} \rightarrow \text{P}^{\text{V}}$ transition, whereas addition reactions to the phosphorus atom for the usual aromatic azaphospholes are unknown.

DDP reacts with organoboranes depending on the steric and electronic properties of the latter. So, PhBCl_2 forms 2:1 complex with DDP, whereas Ph_3B , forming weak complex, serves as a catalyst of oligomerization. It was found that the oligomerization of DDP is a reversible process that is affected by concentration of the solution, type of solvent, light exposure.

DDP tends to form adducts with carbenes in such a way that the lone electron pair of the phosphorus atom is not affected. Adducts with the simplest carbenes (CCl_2 , CH_2) are unstable and quickly produce oligomers, while carbenes with stabilizing substituents show interesting chemical properties. So, the adduct of diacyl carbene with DDP showed unusual dimerization with the formation of a P-P bond. R_2C -derivatives of DDP containing electron delocalizing groups $(\text{ClC})_4\text{C}$, $(\text{NC})_2\text{C}$ are quite stable and have a zwitterionic structure. DDP possesses a much higher coordination activity with metal ions, which is caused by a novel type of complexation: heteroaromatic 10π -electron system provides two electrons for $\text{P} \rightarrow \text{M}$ bond formation, whereas the phosphorus lone pairs are not involved in the coordination.

[1] A. N. Kornev, et al, *Inorg. Chem.* **2014**, *53*, 3243.

This work was supported by the Russian Science Foundation, grant № 19-13-00400.



Chemical properties of ddp.jpg

Synthetic study towards diiodinated diaryl ether and thioether derivatives

Tuesday, 3rd December - 17:58: Optical, electrical and magnetic properties (Room 1) - Oral - Abstract ID: 167

***Prof. Khaled Shawakfa*¹, *Dr. Raed AlZoubi*², *Ms. Reem Altamimi*³**

1. Jordan University of Science & Technology, 2. Department of Chemistry, Jordan University of Science and Technology, PO. Box 3030, Irbid, 22110, Jordan., 3. Jordan University of Science Technology

A regioselective Copper-Catalyzed Ullmann-type Cross-Coupling reaction between phenol or thiophenol derivatives with 5-substituted-1,2,3-triiodobenzenes gave in moderate to good yields the hitherto unknowns diiodinated diarylether and thioether derivatives. In most cases the successful cross coupling Ullmann reaction were observed when triodobenzene derivatives bears electron withdrawing groups coupled with better nucleophile like phenol bearing electron donating groups or even better nucleophile like thiophenol and gave the isolated products selectively at the terminal position. However, the opposite regioselectivity was observed in the case of methyl 3,4,5-triiodobenzoate where only the internal products were isolated.

Light element boron based energy materials for batteries and hydrogen storage

Wednesday, 4th December - 09:00: Plenary speech (Auditorium) - Oral - Abstract ID: 147

Prof. Torben Jensen¹

1. Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University

A wide variety of complex metal borohydrides have been discovered and characterized during the past decade, revealing an extremely rich chemistry including fascinating structural flexibility and a wide range of compositions and physical properties [1-3]. Metal borohydrides, *closo*-borates and carborates receive increasing interest within the energy storage field due to their extremely high hydrogen density and possible uses for hydrogen storage or as battery materials [4]. New classes of boron based electrolytes for batteries have recently been discovered [5, 6].

Here we present new design criteria of functional electrolytes developed by analysis of the underlying phenomena responsible for the high ion conductivity. This is both useful for mono- and divalent cations including Mg^{2+} [7]. Structural dynamics in the solid state, i.e. entropy effects, are of extreme importance for ionic conductivity [4,5]. Disorder of high temperature polymorphs often lead to increased dynamics. The structure of high temperature polymorphs can be stabilized to lower temperatures by anion substitution [5]. Disorder in the solid state can also be created by stabilization of eutectic molten states by nano-structuring. Neutral molecules and a 3D network of dihydrogen bonds may increase the coordination flexibility and thereby increase cation mobility [7]. We conclude that the chemistry of boronhydrides is very diverse, towards rational design of multi-functional materials, including new ion-conductors for batteries, hydrogen storage materials, and possibly materials with new types of optical properties.

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[3] P. Schouwink, et al, Nature Comm. **5**, 5706 (2014).

[4] K. T. Møller, et al, Energies, **10**, 1645 (2017).

[5] M. Paskevicius, et al, Nature Comm. **8**, 15136 (2017) [6] B. R. S. Hansen, et al, Coord. Chem. Rev. **323**, 60 (2016).

[7] Y. Yan, et al, Fast magnesium ion conductivity promoted by neutral molecules, Submitted 2019.

Advances in P- based molecular materials for opto-electronic application

Wednesday, 4th December - 09:35: Plenary speech (Auditorium) - Oral - Abstract ID: 132

Prof. Muriel Hissler¹

1. Institut des Sciences Chimiques de Rennes (ISCR)

Since the pioneering work of Shirakawa, Heeger and McDiarmid in the 1970's, the interest for organic π -conjugated systems has grown tremendously. Indeed organic materials offer the possibility to process light-weight, flexible electronic devices, however, they have to satisfy a large number of technical requirements in order to be stable and efficient in the device. The insertion of a heteroelement into the backbone has appeared as an appealing way to tune the properties of the materials. Heterocycles like thiophene, pyrrole, and their derivatives are now widely used to modify chemical and physical properties of π -conjugated systems. Interestingly, while organophosphorus derivatives have been investigated for decades, their insertion into devices has only been achieved recently. The high reactivity and toxicity of many P-derivatives is one of the reason but the ability of chemists to stabilize and protect the P-atom allowed the introduction of organophosphorus derivatives into opto-electronic devices. Here, we will report on phosphorus based molecular materials: their synthesis, their unique properties useful for organic electronic materials, and the devices that they have been incorporated in so far. For example, we have shown that phosphorus heterocycles (phospholes, phosphetes, phosphepines...) are appealing building blocks for the construction of π -conjugated systems. Effectively, the reactivity of the P-center allows a straightforward HOMO-LUMO gap tuning as evidence by photophysical and electrochemical studies. The coordination ability of the P-center allows unprecedented coordination-driven assembly of π -systems onto transition metals. All these physical properties make phosphorus heterocycles valuable building blocks for the development of material for optoelectronic applications.

Keywords: Heterochemistry, Phosphorus heterocycles, Aromaticity, π -systems, Organic Optoelectronics

References:

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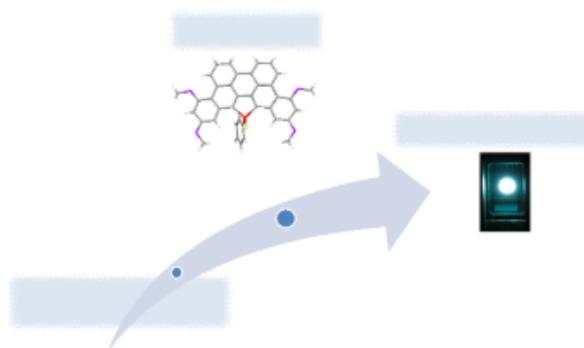


Figure 1 mh.png

Recent progress in the chemistry of heavy aromatics

Wednesday, 4th December - 10:45: Plenary speech (Auditorium) - Oral - Abstract ID: 253

Prof. Norihiro Tokitoh¹

1. Institute for Chemical Research, Kyoto University

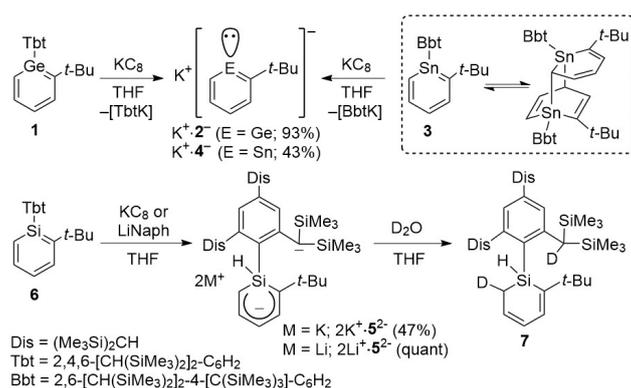
We have recently reported the synthesis and isolation of 2-*tert*-butylgermabenzenylpotassium ($K^+ \cdot 2^-$) the first example of heavy phenyl anion, *i.e.*, a Ge analogue of phenylpotassium, by the reaction of 1-*Tbt*-2-*tert*-butylgermabenzene **1** with KC_8 .¹ Spectroscopic and X-ray crystallographic analysis together with theoretical calculations revealed that $K^+ \cdot 2^-$ exhibits not only aromatic character due to the C_5Ge π -system but also germylene character due to the delocalization of negative charge on the five ring carbon atoms.¹⁻³ Stannabenzenylpotassium the Sn analogue of $K^+ \cdot 4^-$, was also synthesized and isolated by the treatment of an equilibrated mixture of the corresponding stannabenzene **3**⁴ and its dimer with KC_8 .⁵

Next, we attempted the synthesis of the corresponding silabenzenyl anion. However, the treatment of 1-*Tbt*-2-*t*-Bu-silabenzene **6** with KC_8 or $LiNaph$ resulted in the formation of dianion **5**²⁻ as yellow crystals as shown in Scheme 1.⁶ The formation of dianions ($2K^+ \cdot 5^{2-}$ and $2Li^+ \cdot 5^{2-}$) was evidenced by their X-ray crystallographic analysis and the trapping with D_2O giving the deuterated product **7**.

The structures, properties, and formation mechanisms of metallabenzenyl anions ($K^+ \cdot 2^-$ and $K^+ \cdot 4^-$) and dianions ($2K^+ \cdot 5^{2-}$ and $2Li^+ \cdot 5^{2-}$) will be discussed in detail.

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Scheme 1.

Pbsi tokitoh gra01.jpg

Structures of phosphates, borates, and silicates from surface enhanced NMR spectroscopy

Wednesday, 4th December - 11:25: Plenary speech (Auditorium) - Oral - Abstract ID: 257

Prof. Lyndon Emsley¹

1. Ecole Polytechnique Fédérale de Lausanne

A fundamental challenge in materials chemistry relates to the determination of three-dimensional structures with atomic-level precision.

We demonstrate how surface enhanced NMR spectroscopy (SENS) can be achieved by using dynamic nuclear polarization (DNP). In this approach, electron polarization is transferred from an organic radical to the rare nuclei (at natural isotopic abundance) at the surface, yielding up to a 200-fold signal enhancement for many materials.¹

Combining DNP SENS with structure prediction methods and DFT chemical shift calculations we show the full atomic-level characterization of materials including cementitious calcium silicate hydrates, borosilicate zeolites, GaP and InP nanoparticles, or nucleic acids on surfaces.

1. A. Rossini, A. Zagdoun, M. Lelli, A. Lesage, C. Copéret and L. Emsley “Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy,” *Acc. Chem. Res.***46**, 1942 (2013).

Novel 1,3-diphosphapropenes. New unsaturated phosphorus containing derivatives.

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 173

Dr. Raluca Septelean¹, Ms. Alexandra Muresan¹, Dr. Gabriela Nemes¹

1. Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, 1 Mihail Kogălniceanu Street, 400084, Cluj-Napoca

The high diversity of unsaturated organophosphorus compounds is a consequence of the large number of stable oxidation states of the phosphorus atom. This leads not only to an impressive number of compounds but also to a multitude of possible applications. The advance of synthetic methods allowed the preparation of unsaturated species like phosphalkenes (containing the P=C backbone)¹, diphosphalkenes (P=P)², diphosphapropenes (P=C-P, C=P-P)³ as well as fewer and less stable allenic systems such as phosphallenes (P=C=C)⁴ diphosphallenes (P=C=P, P=P=C)⁵ and heterophosphallenes (P=C=E, E-heavier element for group 14 or 15)⁶. We focused our work on 1, 3-diphosphapropenes that, due to the multiple coordination centers, can be used as ligands to transition metals.

We present here the synthesis, characterization and reactivity study of a new 1,3-diphosphapropene Mes*P=C(Cl)-P(=S)(Cl)Tip (Mes* = 2,4,6-tri-tertbutylphenyl, Tip = 2,4,6-tri-isopropylphenyl) designed as precursor to diphosphallenes of P=C=P=S type. The full characterization of the new diphosphapropene was done in solution using multinuclear NMR spectroscopy and mass spectrometry. The structure in solid state was unambiguously elucidated through single crystal X-ray diffraction.

Figure 1. The X-ray crystal structure of Mes*P=C(Cl)-P(=S)(Cl)Tip (50% probability ellipsoids, hydrogen atoms were omitted for clarity).

The newly prepared Mes*P=C(Cl)-P(=S)(Cl)Tip exhibits a high stability towards air and oxygen. Its reactivity towards strong bases has been tested as well as its use as ligand to metal fragments (Pd, Au, Pt). The dichloro-diphosphapropene shows encouraging results for the preparation of the corresponding allene which was evidenced at low temperature.

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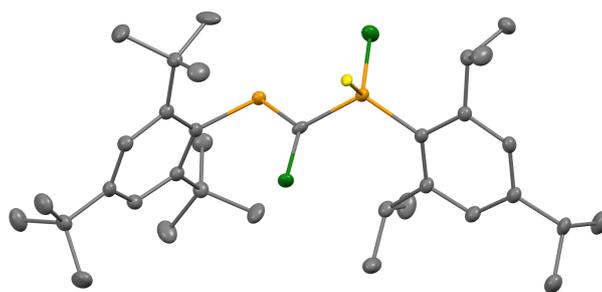


Figure 1.png

Oxidation of hydride and *p*-tolylsiloxanes: development of catalytic approaches

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 135

***Ms. Irina Goncharova*¹, *Dr. Ashot Arzumanyan*¹, *Dr. Sergey Milenin*², *Prof. Aziz Muzafarov*³**

1. A.N.Nesmeyanov Institute of Organoelement Compounds, RAS, 2. Enikolopov Institute of Synthetic Polymeric Materials, 3. N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences

Organosilicon chemistry was the slower developing field of chemistry compared to organic chemistry. So, many methods for obtaining [Si]-derivatives, functionalized ones, in particular, still are time-consuming, require harsh conditions, stoichiometric amounts of toxic and expensive reagents producing waste (some of them are commercially unavailable) which provokes Si–O-, Si–C- and other bonds destruction. Also these methods usually are of low functional group tolerance.¹

Functionalized siloxanes, on the other side, are believed to expand the fields of applicability of such compounds. So, developing of “green” and commercially available systems for functionalization of siloxanes is an actual task. Green chemistry is thought, will became the only suitable approach for selective synthesis of siloxanes with complex structures.

Two target types of compounds were chosen for elaboration of suitable method: siloxanols and *p*-carboxyphenylsiloxanes. They can be obtained *via* oxidation of easily accessible hydride siloxanes and *p*-tolylsiloxanes.

Well proven peroxide and metal combination was the first system to be tried for these oxidations (Scheme 1, *route A*).^{2,3} After optimizing the conditions we concluded, that this system allows simple compounds to be rather easy oxidized (such as triethylsilane and *p*-tolylpentamethyldisiloxane), but requires more harsh conditions for more complex ones.

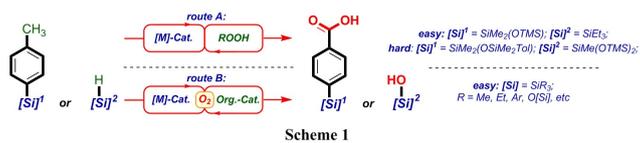
In the next stage of our study O₂ was chosen as the most abundant, eco-friendly and mild oxidant in combination with transition metal and organic catalyst. After optimizing the conditions we found out that this approach is applicable for oxidation of both hydride and *p*-tolylsiloxanes of various structures in high conversions and yields (Scheme 1, *route B*).^{4,5} This method is scalable and allows to synthesize target products in gram quantities.

Thus, we proposed a highly effective preparative method for the preparation of functionalized organosilicon compounds based on the catalytic aerobic oxidation of Si–H- and C–H-bond. This approach is based on “green”, commercially available, simple, and inexpensive reagents and employs mild reaction conditions: Co(OAc)₂ or Cu(OAc)₂/NHPI or NHSI catalytic system, O₂ as the oxidant, process temperature from 30 to 60 °C, atmospheric pressure.

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This work was supported by the RFBR project № 18-29-04060



Scheme 1.jpg

Tuning the toxicity of phosphonium based biocides using the bioisosteric fluoromethyl moiety

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 127

Mr. Marco Reichel¹, **Prof. Konstantin Karaghiosoff**¹, **Ms. Svetlana Dubrovnik**¹, **Ms. Cornelia Unger**¹,
Dr. Andreas Roidl¹

¹. Ludwig-Maximilian-University

Phosphonium salts are a long known substance class mainly used in Wittig reactions.^[1] Further, it is known that -CH₂OH containing phosphonium salts can have a biocidal effect on biofilms and especially the tetrakis hydroxymethyl phosphonium sulfate (THPS) is widely used as biocide in oil pipelines / oil fields and in the paper making industry against gram negative bacteria.^[2] The action of mode can be described in such a way that the proteins of the membrane wall react with the -CH₂OH groups of THPS to form -CH₂NR₂ with elimination of water (Figure 1).

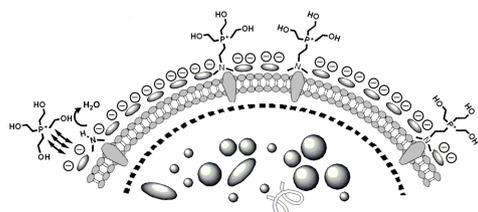
Figure 1. Mechanism of interaction and mode of action of THPS on the cell wall of gram negative bacteria (left), fluoromethylated phosphonium salt (right).

It is already known from warfare agents of the G series (sarin, cylosarin, soman), that also strong elemental fluorine bonds can be cleaved by organisms under HF formation.^[3] Thus the question arises whether the substitution of a -CH₂OH group by the bioisosteric -CH₂F group makes phosphonium salts more stable and thus less toxic, or whether the higher enthalpy of formation of HF causes such a cell wall reaction to occur more quickly and thus makes the compound more toxic. Various fluoromethylated phosphonium salts were synthesized and structurally characterized and their toxicity towards gram negative bacteria was determined and compared to that of THPS. The results provide information on how the toxicity of -CH₂OH phosphonium based biocides can be tuned with the help of the bioisosteric -CH₂F group.

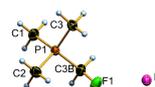
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Bakterium 3.png



Mx014-1.png

Efficient organocatalytic dehydrogenation of ammonia borane

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 230

Mr. Max Hasenbeck¹, Dr. Jonathan Becker¹, Dr. Urs Gellrich¹

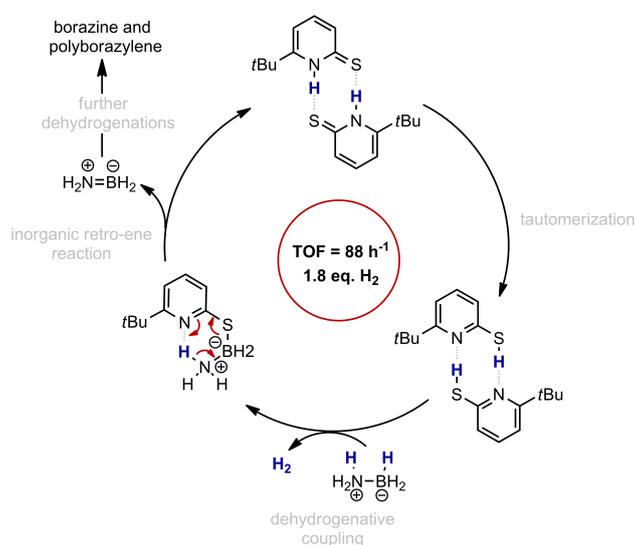
1. Justus-Liebig-Universität Giessen

Dehydrogenation of ammonia borane (AB) for hydrogen storage applications by main-group catalysts achieved considerable attention in recent years.^[1] We report the first example of an organocatalytic dehydrogenation of AB by sterically encumbered 6-*tert*-butyl-thiopyridone.^[2] With 1 mol% catalyst loading in refluxing THF 1.8 eq. H₂ per molecule ammonia borane are released within 2 h, corresponding to a turn over frequency (TOF) of 88 h⁻¹. This is, to our knowledge, the highest TOF reported for a metal-free catalyst hitherto.

The reaction mechanism was investigated experimentally and by DFT and accurate DLPNO-CCSD(T) computations. The first equivalent of H₂ is released by the protonation of the hydridic BH₃-group of AB by the S-H group of the mercaptopyridine form of the catalyst yielding a mercaptopyridine-borane complex. An intramolecular proton transfer of the NH₃ to the basic pyridine moiety releases H₂NBH₂ and regenerates the catalyst. Regarding the reorganization p-electron density, this reaction can be described as an inorganic retro-ene reaction. The mechanism reveals three important features of the catalyst responsible for its comparatively high activity: the bifunctionality by possessing an acidic and basic group, the sterically demanding *tert*-butyl group facilitating the formation of the active catalyst via monomerization, and that both tautomers are nearly isoenergetic.

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Organocatalytic dehydrogenation of ammonia borane.png

Efficient, non-empirical algorithm for the black-box computation of solvation entropies

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 231

Mr. Jama Ariai¹, Dr. Urs Gellrich¹

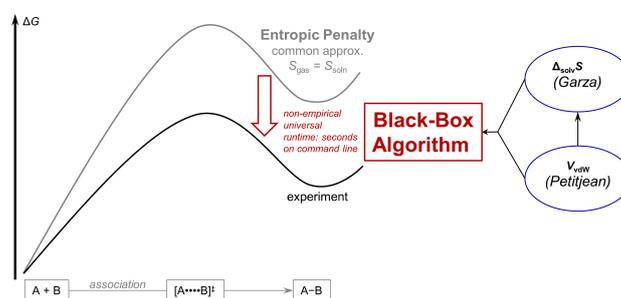
1. Justus-Liebig-Universität Giessen

Accurate computations of solution-phase entropies ΔS_{solv} are mandatory for the prediction of reaction rates/thermodynamics involving changes in molecularity. In common praxis, solution-phase free energies G_{solv} are obtained by summing up the gas-phase free energies G_{g} (from QM computations) and solvation free energies $\Delta_{\text{solv}}G$. The latter are often derived from additional computations using continuum solvation models. Due to their fitting parameters, however, the change of molecularity is not covered. Thus, this approach systematically penalizes bimolecular reaction pathways, such as $S_{\text{N}}2$ reactions and dimerizations. This error makes up to several kcal mol⁻¹ and thereby hinders drastically the predictive power of computationally investigated reaction mechanisms.

Herein we present a non-empirical, universal black-box algorithm to compute the solvation entropy with chemical accuracy within seconds on the command line. Universal denotes that this method is applicable to any solvent for minima and transition state structures and requires only the atomic coordinates. The formalism of the solvation entropy is taken from Garza and is physically sound.^[1] In contrast to implicit solvent models, no parametrization/fitting is necessary to account for bulk solvation but instead, tabulated physical parameters (solvent density, permittivity and molar mass) serve as arguments. Besides, the algorithm for the analytical calculation of van der Waals volumes developed by Petitjean provides the required molecular volume of the solute and solvent.^[2] Embedded all together into a single script, this procedure benefits from its efficiency as it is executable on a desktop machine without the need of high-performance computing (HPC) clusters. We present a case study in which experimental entropies are compared with entropies obtained by the conventional protocol and this new algorithm, rendering it a powerful tool in computational chemistry, especially for mechanistic investigations.

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Black-box algorithm for the computation of solvation entropies.png

Synthesis and application of anthraquinone derivatives on polyester matrix with supercritical carbon dioxide system

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 232

Prof. Young-A Son¹, Dr. Pentala Raju¹

1. Chungnam National University

Two series of anthraquinone dye derivatives have been successfully synthesized from commercially inexpensive and readily available starting materials. All synthesized anthraquinone molecules were characterized by ¹H NMR, ¹³C NMR, and UV-Vis spectroscopy and HRMS. The UV-Vis spectra of the compounds indicated that the absorption wavelengths of spectra were approximately 590 - 655 nm. Polyester polymer matrix were dyed with these compounds using supercritical carbon dioxide as a green medium. All the compounds displayed deep fixation properties and excellent color intensities even at low concentrations (0.5%). In the fastness experiments, all of compounds exhibited excellent results in washing, sweat and lightfastness. Hence, our results revealed that these types of anthraquinones are commercially most acceptable, and they practically exhibited satisfactory reaction uniformity.

Synthesis of monolithic polyurethane/methyltrimethoxysilane hybrid aerogels via ambient pressure drying

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 235

*Mr. Jinkyu Choi*¹, *Mr. Myeong Yeon Lee*¹, *Prof. Sang Eun Shim*¹

1. Inha university

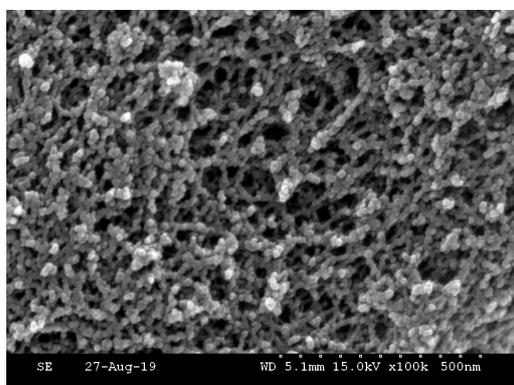
Polyurethane (PU) has excellent elasticity as an organic material. However, the nature of thermal insulation is limited. On the other hand, the silica aerogel as an inorganic material presents lower thermal conductivity than PU. Because it attributes superb insulation to high porosity (>95 %), large surface area (500-2000 m²/g) by mesopores of silica networks. A disadvantage of silica aerogel is brittle with low mechanical strength while the insulation property is worthy of notice.

In this research, silica aerogel was synthesized chemically by two other types of sol-gel methods on the surface of flexible PU foam as a base template. Methyltrimethoxysilane (MTMS) reacted as silica precursor in the presence of methanol, DI water, oxalic acid, and ammonium hydroxide catalysis. The final reactant was hydrophobic for the methyl group of MTMS without surface modification. A second chemical method added additional hydrophobic silica aerogel powders by different ratio to the previous experiment, when the condensation reaction occurs. These syntheses were followed by ambient pressure drying (APD). The inherent fragility of networks of silica aerogel was reinforced by the PU template. Another physical method adopted by filling silica aerogel powders into the PU pores up to 46% of weight percentage to PU before the coating of polyurethane adhesive on the surface of PU foam. The research analyzed the thermal conductivity and mechanical properties of inorganic/organic hybrid composites.

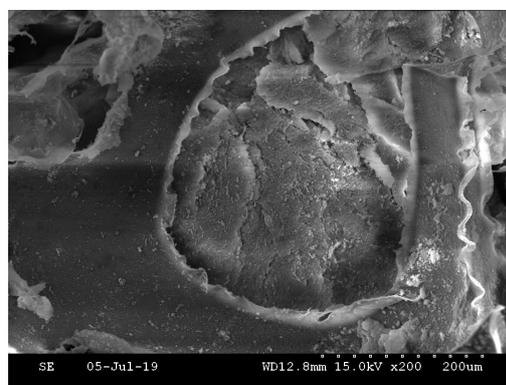
The hybrid PU/silica aerogel of 209 wt% of silica content resulted in 36.00 mW/mK thermal conductivity. This result shows reinforced thermal insulation property after the synthesis of silica aerogel compares to the raw PU foam of 41.48 mW/mK. The second chemical method obtained 40.48 mW/mK from 4.07 wt% of silica aerogel powder. The lowest 34.67 mW/mK result observed in 35.69 wt% of silica by physical method. Silica aerogel effects as thermal insulation material in the pores of PU foam. PU foam reduces external impact like a shock absorber to cover the mechanical defect of the composite.

Acknowledgments

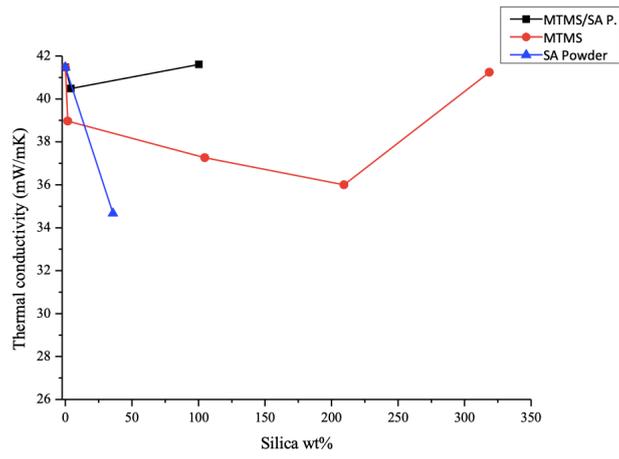
This work was supported by a grant (10080492) from Korea Evaluation Institute of Industrial Technology under Ministry of Trade, Industry and Energy (MOTIE), Republic of Korea.



Raw silica aerogel mtms .jpg



Silica aerogel pu foam.jpg



Thermal conductivity.png

Organic and nanoparticle derived composites and their potential application as antimicrobials and antifungals.

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 95

Mr. Mpholeki Lupiwana¹, Dr. Natasha October¹, Dr. Mohammed Balogun²

1. University of Pretoria, 2. Council for Scientific and Industrial Research, South Africa

The demand of new antimicrobial based products is mounting due to the increase in spread of infections and lack of effectiveness of the existing industrial products. Even though extensive advances have been made in the development of new antimicrobials, antimicrobial resistance (AMR) threatens this progress and presents major risks to human health. Another great concern, is the control, prevention and treatment of hospital acquired infections (HAI), which tend to be a global dilemma due to the overwhelming task of ensuring that the hospital environment is free of harmful bacteria[1].

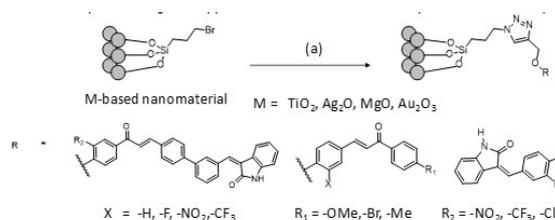
Although chemical antimicrobial agents have shown promise as antimicrobials, nanotechnology has gained significant importance due to their potent inhibitory capacity against microbes. More recently, the metallic nanoparticles have been explored and extensively investigated as potential antimicrobials. Metal oxide nanoparticles like TiO₂, Ag₂O and Au₂O₃ with antimicrobial activity when embedded or coated onto the surfaces of industrial products can find broad applications in water treatment, synthetic textiles, biomedical and surgical devices [2]. Moreover, composites prepared using metal nanoparticles and chemical antimicrobial agents may be employed as an alternative strategy to enhance the antimicrobial inhibitory activity. Derivatives containing indolone and chalcone as their core scaffolds have shown to exhibit excellent antimicrobial and antifungal activities [3]. Therefore, in this current research we have designed and synthesized a series of antimicrobial compounds, conjugated to a nano-substrate such as TiO₂, Ag₂O, MgO or Au₂O₃ respectively using a silicon-based linker to form a durable bond and click chemistry and key organic reactions (Scheme 1). The synthesized antimicrobial agents and nano-based composites will be assessed for their antimicrobial inhibitory activity and will be embedded or coated onto the surfaces of biomedical and surgical devices and may also be incorporated into disinfectants and synthetic paints with the hope of finding their application as antimicrobials in hospitals and industrial products.

Scheme 1: Incorporation of the synthesized antimicrobial organic compounds functionalised onto the nano-material, Reagent and Conditions: (a) NaN₃ in DMSO/ H₂O (1:9), C₆H₇NaO₆, CuSO₄.5H₂O, L-proline and various alkyne derivatives

Selected references:

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Scheme.jpg

Enhancing structural properties of PZT nano-powders for piezoelectric applications

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 111

Dr. Amina Kermad¹, **Dr. Sanaa El Korso**², **Prof. Abderrahim Choukchou Braham**², **Ms. Hidayet Kaouadji**², **Dr. Amine Brix Negassa**³, **Dr. Sofiane Soulimane**³, **Prof. Amel Boudjema**¹

1. Center for Scientific and Technical Research in Physico-Chemical Analysis, 2. Laboratory of Catalysis and Synthesis in Organic Chemistry, Department of Chemistry, Faculty of Science-tlemcen university, 3. Department of Biomedical Engineering, Faculty of Technology- Tlemcen University

Introduction

Piezoelectric materials are one of the best candidates for many applications, such as medical, mechanical or electronic applications. Among the piezoelectric materials, there is lead zirconate titanate $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, more commonly known as PZT [1].

The objective here is to study the influence of calcination temperature and lead content on the perovskite structural properties of PZT.

The samples were analyzed by X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The results obtained showed the formation of the perovskite structure for a temperature above 450 °C, this result is in agreement with the ATG.

Methods

The preparation of the PZT without lead excess and with a lead excess of 10 % and 15 % is carried out using the sol-gel method. This preparation was carried out with lead acetate, zirconium propoxide and titanium isopropoxide. The resulting dried gel was calcined at different temperatures. Table (1) summarizes the different calcination conditions.

Table. 1. Different conditions of calcination

Results and Discussion

Figure (1) shows the XRD diffraction pattern of the synthesized powders of PZT with a 10 % Pb excess calcined at different temperatures. The perovskite structure begins to settle between 500 and 600 °C. However, we notice the presence of the pyrochlore phase at $2\theta \sim 29^\circ$.

Similar studies [2, 3] reveal that the presence of excess lead reduces the formation of the pyrochlore phase. In our case, the formation of the pyrochlore phase may be caused by slow cooling [4].

Figure. 1. XRD patterns of prepared PZT at different calcinations temperatures

The TGA curve (Figure 2), shows three significant mass losses. The first two losses, between 25 and 300 °C, contribute to losses of water and organics [2]. The loss between 300 and 500 °C corresponds to evaporation of lead acetate oxide [3].

Figure. 2. Thermal gravity analysis (TGA) of dried gel of PZT.

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- [4] Z.-G. Ye, Handbook of advanced dielectric, piezoelectric and ferroelectric materials: Synthesis, properties and applications, Elsevier, 2008.

Temperature (°C)	Time (h)	Rate (°C/min)
500	1	5
600	1	5
700	1	5
800	1	5

Table. 1. different conditions of calcination.png

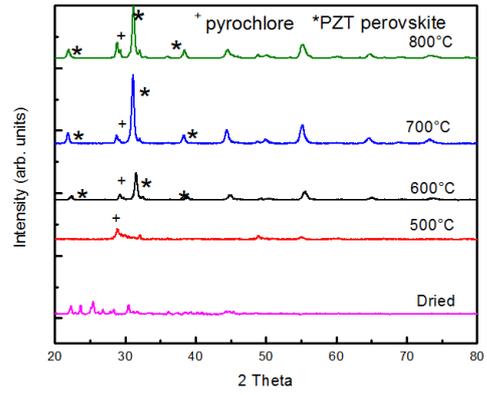


Figure. 1. xrd patterns of prepared pzt at different calcinations temperatures.png

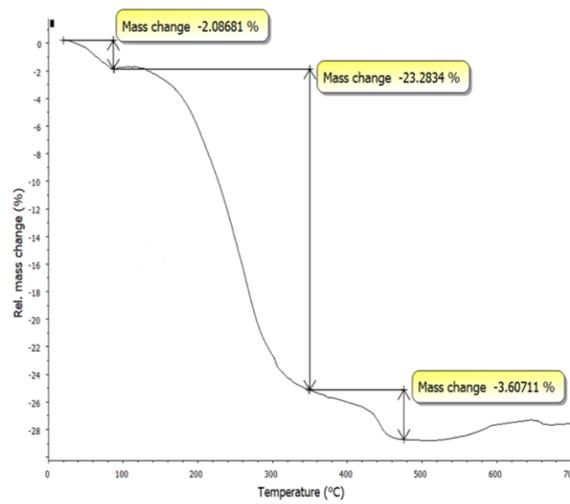


Figure. 2. thermal gravity analysis tga of dried gel of pzt..png

Highly efficient method for producing transparent and hydrophobic silica aerogels

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 146

***Mr. Dmitry Kholodkov*¹, *Dr. Ashot Arzumanyan*¹, *Prof. Aziz Muzafarov*¹**

1. A.N.Nesmeyanov Institute of Organoelement Compounds, RAS

In recent years, there has been an increased interest in porous materials, which is related to their applicability in different areas of science, medicine and technology. Aerogels, silica aerogels in particular, have special abilities: (1) high specific surface area and porosity, with a low density; (2) high insulation and soundproof rates; (3) optical transparency; (4) low permittivity; (5) low Young's modulus; (6) thermostability and other.

There are several successive stages that are carried out when obtaining silica aerogels: (1) sol-gel synthesis - wet gel forming; (2) aging and the formation of a lasting gel; (3) workup - preparing the gel for drying (including replacement one solvent with another, the catalyst and byproducts removal etc.); (4) drying - manufacturing an aerogel from the wet gel.

At the same time, we can highlight a number of critical technological problems, that are cost- and time-consuming, in the production of silica aerogels: duration of formation (1) and aging (2) of the gel (one to several days); use of excess amounts of acidic and/or alkaline catalysts/reagents; need to change one solvent in the gel pores to another and other stages of drying preparation (3); duration and high cost of the drying stage.

This work is aimed to solving these problems - developing a new method for obtaining aerogels, based on highly efficient, simple, commercially available and cheap catalytic system. This system will reduce the number and duration of technological stages of the process and will allow for preparing aerogels with tunable transparency, hydrophobicity and mechanical strength (Figure 1).

This work was supported by the Russian Foundation for Basic Research № 20-33-70051.

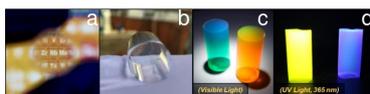


Figure 1. Transparent (a, b) and fluorescent (c, d) aerogels.

Puctire.jpeg

Synthesis of siloxane nanogel with phenylboronic functional groups

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 130

***Dr. Sergey Milenin*¹, *Dr. Fedor Drozdov*², *Mr. Ivan Meshkov*², *Prof. Aziz Muzafarov*²**

1. Enikolopov Institute of Synthetic Polymeric Materials, 2. N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences

Nanogels and similar hyperbranched siloxane structures are of great interest due to their unique properties: high adsorption capacity and gas permeability, separation ability, chemical stability. Siloxane nanogels can be obtained from commercially available starting organotrialkoxysilanes using simple polycondensation methods, which also contributes to their wide distribution [1, 2].

In this work, a siloxane nanogel containing phenyl borate functional groups was obtained. It is assumed that the presence of available phenylborate groups will allow further modification of the nanogel's surface using various reactions: Suzuki cross-coupling, Petasis reaction, Chan-Lam coupling and others. Using this approach, it is possible to obtain nanosized organosiloxane particles grafted with organic molecules: dyes, phosphors, drugs, etc.

First, a siloxane hyperbranched polymer was obtained by condensation of the sodium salt of methyltriethoxysilane in acetic acid. Second, the resulting silicate was modified with hydridysilyl groups by rearrangement with tetramethyldisiloxane in the presence of acetyl chloride. Finally, the hydride nanogel was hydrosilylated with 4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (St-BPin) obtained by the previously published method [3]. The reaction was carried out in toluene in the presence of a Karstedt's catalyst. The final product was a transparent, highly viscous liquid soluble in organic solvents. The structure of the nanogel was confirmed by NMR and IR spectroscopy, element analysis and GPC.

This work was supported by the Russian Foundation for Basic Research (Grant No. 19-29-05227 МК). Investigation of molecular-weight characteristics of polymers was made using the equipment of the Collaborative Access Center "Center for Polymer Research" of ISPM RAS.

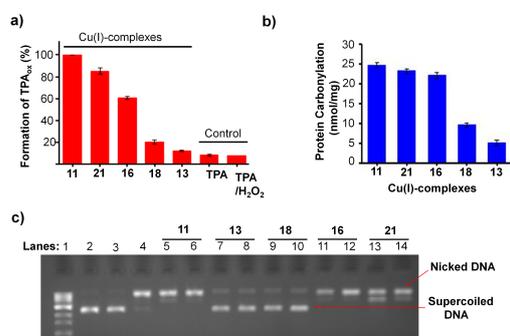
Role of hydrogen bonding by thiones in protecting biomolecules from copper(I)-mediated oxidative damage

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 22

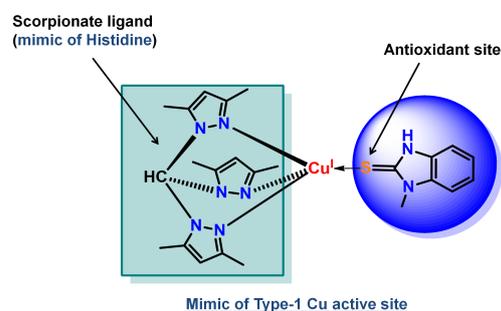
Mr. Rakesh Kumar Rai¹, Dr. Gouriprasanna Roy¹

¹. Shiv Nadar University

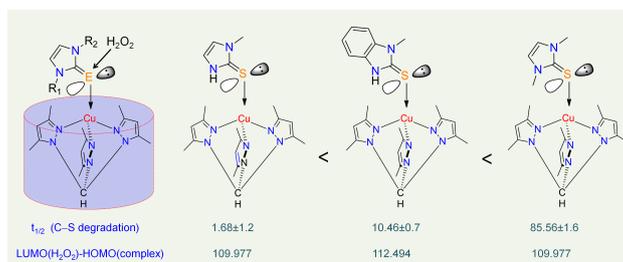
Reactive oxygen species (ROS) are involved in the oxidative damage to lipids, proteins and DNA. Hydrogen peroxide (H_2O_2), a prime member of ROS is produced in vivo due to various cell functions and its rapid increase results in the generation of hydroxyl radicals ($\cdot OH$) by reacting with free copper ions (Cu^{2+} or Cu^+) via Fenton-type reaction. This copper mediated generation of hydroxyl radical has been reported to cause Alzheimer's disease, cardiovascular disease and cancer. The sulfur containing small molecule including GSH, ergothioneine have evolved to protect cells from copper-mediated oxidative stress. L-ergothioneine (Erg) is well-known naturally occurring antioxidant small molecule, mainly synthesized in fungi, and bacteria, and present in large amount in various organs of human. In human blood, mostly in red blood cell (RBC), Erg is estimated to be present in the range of 1-4 mg/100 ml (approximately 46–183 mM) and has an excellent ability to scavenge many free radicals and protect metalloenzymes including haemoglobin from ROS. Herein, we describe the mechanism of reactivity of various derivatives of ergothioneine, imidazole and benzimidazole-based thiones with different electron donating or electron withdrawing substituents at the 5-membered heterocyclic ring, towards H_2O_2 and demonstrated the role of substituents on the kinetics of thione oxygenation and in protecting copper(I) mediated oxidative damage of DNA and protein.



Application.png



Theme.png



Toc.png

Ultra-Fast Surface Hardening and Strengthening of Low Alloy Steel For Thermal and Radiation Shielding

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 227

Ms. Lina Enan¹

1. Masters Student, Cairo University.

The development of modern technologies in the field of engineered materials has increased the interest towards the surface and bulk material improvements with physical, chemical and mechanical properties. However, there is a need to explore a new non-traditional processing for ultra-fast coating and surface hardening. Powder pack processing is introduced to low alloy steel and induced Intermetallic and/or ceramic borate whiskers for thermally resistant strengthened steel. Low alloy steel class A333 Grade-6 as well as ferritic heat resistant boron alloyed steels are boronized, compared and mechanically (3-point bending tests) and microstructurally studied. Powder pack is conducted at 950°C for 30 minutes. Boron is added in the form of a mixture of borax and boric acid in a crucible at induction furnace. Flexural strength increased from 450 MPa to 1921 MPa. The application of ammonia bicarbonate with powder pack enhance flexural strength to 2301 MPa. Ultra-fast boronizing along with ammonia induce both surface and bulk hardening that increase flexural strength for both thermal resistant and neutron shielding.

Power splitter and TE-TM Polarization separator based on magneto-photonic crystal fiber

Wednesday, 4th December - 13:30: Poster session (Hall) - Poster - Abstract ID: 259

Dr. Mohamed Redha Lebbal¹, Dr. larioui fateh Larioui¹, Prof. Touraya Bouchemat¹, Prof. Mohamed Bouchemat¹, Prof. Fouad Kerrou²

1. Department of Electronics, Laboratory L.M.I., University of Constantine 1, Constantine, Algeria, 2. laboratoire de Modélisation des dispositifs a énergies renouvelables et nanométrie, Université Frères Mentouri de Constantine1

Specifically, this work aims to achieve a power splitter and polarization separator of a guided light, basing on magnetic properties such as gyrotropy, mode coupling and optimization of geometric parameters of a magneto-photonic fiber. This fiber which makes it possible to split and separate the polarizations is characterized by the opto-geometric optimization of an Y junction based on anisotropic magnetic fluid in magneto-photonic crystal fiber, with one input and two outputs, able to separate combination of two guided modes TE/TM, into two waves of the same amplitude and in phase between them, an incoming light wave which arrives at the Y-branch input of the fiber.

Phosphorus-containing cations partnered by WCAs

Wednesday, 4th December - 14:30: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 142

Prof. Ingo Crossing¹

1. Albert-Ludwigs-Universität Freiburg

Weakly Coordinating Anions (WCAs) allow for the preparation of unusual reactive cations. Inter alia we have shown 2012 that the first homopolyatomic phosphorus cation P_9^+ is available, if partnered with the $[Al(OR^F)_4]^-$ WCA ($R^F = C(CF_3)_3$).

Here we report on our efforts to complex P_4 and other cages to electron poor $[CpFe(CO)_2]^+$ as well as directly prepare the first cation-tetrahedron $[P_3E]^+$ ($E = S, Se, Te$) partnered by suitable WCA counteranions.

References:

“From Phosphidic to Phosphonium? Umpolung of the P_4 -Bonding Situation in $[CpFe(CO)(L)(h^1-P_4)]^+$ Cations ($L = CO$ or PPh_3).”

I. M. Riddlestone, P. Weis, A. Martens, M. Schorpp, H. Scherer and I. Crossing*, ahead of print with *Chem. Eur. J.* **2019**. <https://dx.doi.org/10.1002/chem.201902075>

“Coordination Chemistry of P_4S_3 and P_4Se_3 towards the Iron Fragments $[Fe(Cp)(CO)_2]^+$ and $[Fe(Cp)(PPh_3)(CO)]^+$.”

P. Weis, I. M. Riddlestone, H. Scherer and I. Crossing*, online with *Chem. Eur. J.* **2019**. <http://dx.doi.org/10.1002/chem.201902339>

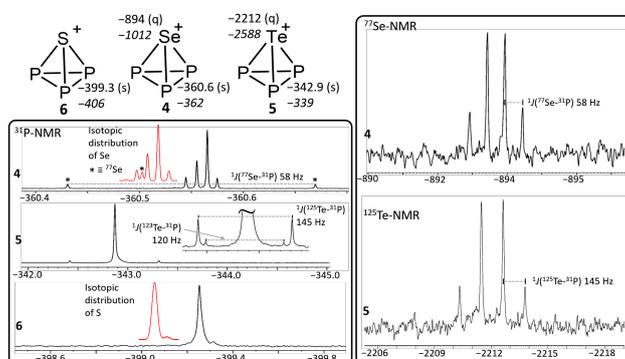


Figure 1.png

Si(II)/NHC supported Cu(I)- and Au(I)-benzene complexes and their application in glycoside synthesis

Wednesday, 4th December - 15:04: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 114

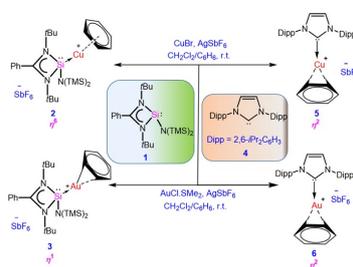
Ms. Nasrina Parvin¹, Prof. Shabana Khan¹

1. Indian Institute of Science Education and Research (IISER), Pune

Synthetic chemists often find fascination in isolating a compound that has been theoretically predicted as well as observed in the gas phase but never realized under laboratory conditions.¹ $[\text{Cu}(\text{C}_6\text{H}_6)]^+$ is such a compound that prefers the η^1/η^2 mode over the η^6 mode due to the augmented repulsion between the benzene ring and metal d-electrons. Nevertheless, the use of silylene as a neutral ligand² has led to the isolation of the first monomeric $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$ complex, whereas the analogous reaction with NHC led to the corresponding complex $[\text{Cu}(\eta^2\text{-C}_6\text{H}_6)]^+$.³ Greater π -acceptor behaviour of silylene stabilizes the $[\text{Cu}(\eta^6\text{-C}_6\text{H}_6)]^+$ complex. Furthermore, when we employed Au(I) instead of Cu(I), silylene and NHC forms $[\text{Au}(\eta^1\text{-C}_6\text{H}_6)]^+$ and $[\text{Au}(\eta^2\text{-C}_6\text{H}_6)]^+$ complexes, respectively. Both the silylene and NHC supported $[\text{Au-C}_6\text{H}_6]^+$ complexes were demonstrated as very good catalysts in glycoside synthesis. $[\text{Si}(\text{II})\text{-Au}(\eta^1\text{-C}_6\text{H}_6)]^+$ was found superior over $[\text{IPr}\cdot\text{Au}(\eta^2\text{-C}_6\text{H}_6)]^+$ complex when employing propargyl 1,2-*o*-orthoesters as donors. $[\text{Si}(\text{II})\text{-Au}(\eta^1\text{-C}_6\text{H}_6)]^+$ was further employed efficiently in the synthesis of branched pentamannan core of the HIV1-gp120.

References:

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3. N. Parvin, S. Pal, J. Echeverría, S. Alvarez and S. Khan, *Chem. Sci.*, 2018, **9**, 4333-4337.
4. N. Parvin and S. Khan (*unpublished result*).



Pbsi si cu complex.jpg

Poly(iminoborane)s: the missing link in inorganic main-group macromolecular chemistry

Wednesday, 4th December - 15:21: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 61

Mr. Nicolas Riensch¹, Dr. Ozan Ayhan², Dr. Holger Helten¹

1. Julius-Maximilians-Universität Würzburg, 2. RWTH Aachen University

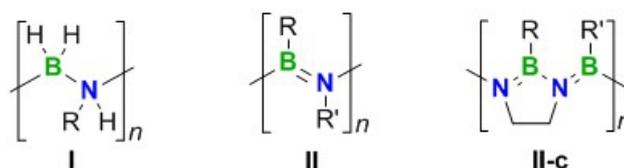
Polymers with a backbone composed of inorganic main group elements are of considerable interest as they often exhibit useful properties and functions that complement those of classical organic macromolecular materials. This is most clearly demonstrated by the commercial relevance of the well-known polysiloxanes (silicones). Organoboron-based materials such as π -conjugated organoborane polymers and BN-doped inorganic-organic hybrid polymers are currently attracting special attention.^[1] Surprisingly, well-defined poly(aminoborane)s (PABs, **I**; see Figure “BN-polymers”), i.e., inorganic B-N polymers, became accessible only quite recently through work by Manners and co-workers.^[2] Moreover, their unsaturated B=N congeners, poly(iminoborane)s (PIBs, **II**), have never been convincingly characterized previously. We recently achieved the synthesis of the first derivatives of this class of compounds from cyclic monomers (**II-c**).^[3] Synthesis routes to these new inorganic main group materials as well as studies of their properties will be presented. Furthermore, we have developed novel borazine-based hybrid cyclomatrix network polymers, which form spherical nanoparticles under precipitation polycondensation conditions. Using our Si/B exchange polycondensation approach the fully crosslinked polymer networks formed microspheres of about 900 nm on average with remarkable stability.^[4]

[1] a) H. Helten, *Chem. Asian J.* **2019**, *14*, 919; b) A. Lik, L. Fritze, L. Müller, H. Helten, *J. Am. Chem. Soc.* **2017**, *139*, 5692; c) A. Lik, S. Jenthra, L. Fritze, L. Müller, K.-N. Truong, H. Helten, *Chem. Eur. J.* **2018**, *24*, 11961; d) T. Lorenz, A. Lik, F. A. Plamper, H. Helten, *Angew. Chem. Int. Ed.* **2016**, *55*, 7236; e) T. Lorenz, M. Crumbach, T. Eckert, A. Lik, H. Helten, *Angew. Chem. Int. Ed.* **2017**, *56*, 2780.

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Bn-polymers.jpg

Aldol reaction of the heavier carbon homologues

Wednesday, 4th December - 15:38: Advanced synthesis and characterization (Auditorium) - Oral - Abstract ID: 82

Dr. Michael Haas¹

1. Technische Universität Graz

The classical aldol reaction and in particular its power in the reversible formation and breaking of carbon-carbon bonds is one of the most important biosynthetic tools for the evolution of life on earth.[1] For silicon-based compounds, however, this type of silicon-carbon bond formation was previously unknown, although it must be considered as a powerful alternative to the standard coupling techniques, such as Wurtz reaction and related methods,[2] hydrosilylation[3] as well as transition metal catalyzed silicon-carbon coupling reactions.[4] We considered the intramolecular sila-aldol reaction as an optimal starting point for the development of this transformation, as it should be entropically favored and should provide highly symmetric starting materials. Therefore, α,ω -bisacylsilanes were synthesized and reacted with equimolar amounts of KOtBu. In contrast to the classical carbon-based aldol reaction, no stable addition products could be isolated yet. However, in the case of the bisacylsilanes, the sila-aldol product reacted further in a highly selective rearrangement cascade by a directed breakup of the cyclohexasilane backbone and the insertion of an oxygen atom into the ring to give **1**. This novel transformation introduces a pioneering strategy for the formation of silicon-carbon bonds by establishing a further link between the two related fields of silicon- and carbon-Chemistry.

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[3] for example: Y. Liu, L. Deng, *J. Am. Chem. Soc.*, **2017**, *139*, 1798.

[4] for example: Y. Hua, P. Asgari, T. Avullala, J. Jeon, *J. Am. Chem. Soc.*, **2016**, *138*, 7982.

News from the chemistry of functionalized phosphabenzenes

Wednesday, 4th December - 14:30: Reactions of coordination compounds (Room 1) - Oral - Abstract ID: 244

Prof. Christian Müller¹

1. Freie Universität Berlin

Low-coordinate phosphorus(III) compounds have recently re-gained noticeable interest as the very peculiar stereoelectronic and coordination properties of such $\lambda^3\sigma^2$ -species differ significantly from classical trivalent $\lambda^3\sigma^3$ -phosphanes. These special characteristics can lead to interesting effects in more applied research fields, such as homogeneous catalysis and material science.

We recently found a facile synthetic access to the $\text{Si}(\text{CH}_3)_3$ -substituted phosphinine **II**, from which the parent compound $\text{C}_5\text{H}_5\text{P}$ (**I**) can be prepared by means of protodesilylation reaction (Figure 1).^[1,2] Interestingly we noticed, that the $\text{Si}(\text{CH}_3)_3$ -group in β -position of the phosphorus atom has a significant influence on the electronic properties of **II**, which can be attributed to the β -silyl effect. DFT calculations are in agreement with an increased nucleophilicity and basicity of the phosphorus atom in **I**, while a considerable increase in the gas phase basicities of various $\text{Si}(\text{CH}_3)_3$ -substituted phosphinines was noticed. As a result, $\text{Si}(\text{CH}_3)_3$ -substituted phosphinines show a distinct reactivity towards certain main group elements and main group compounds and unprecedented reactivities, particularly in E-H-activation reactions, were observed.

This lecture will focus on the design and preparation of novel, functionalized phosphinines (Figure 1), the higher homologs of pyridines. Special emphasis will be paid to the modification of their electronic properties, their coordination chemistry and reactivity.^[3]

Our recent results open up the opportunity to develop a new chemistry for phosphinines, complementary to the already established one.

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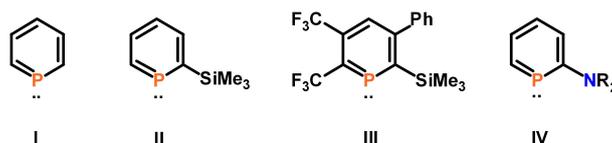


Figure 1.jpg

Nonspectator phosphorus ligands: formation of metallophosphorane by insertion of P into M–H and M–C bonds

Wednesday, 4th December - 15:04: Reactions of coordination compounds (Room 1) - Oral - Abstract ID: 226

Mr. Akira Tanushi¹, Dr. Seung Jun Hwang², Prof. Alex T. Radosevich¹

1. Massachusetts Institute of Technology, 2. Pohang University of Science and Technology

While phosphines (PR₃) are one of the most important class of ligands in transition metal catalysis, they are not actively involved in bond activation processes in most cases and often regarded as ‘spectator’ ligands. On the other hand, our group has developed various bond activation and catalytic transformation methods by enforcing nontrigonal geometry on tricoordinate phosphorus compounds. Based on the enhanced electrophilicity of the P(III) center, we anticipated such an unusual reactivity can also be observed when the nontrigonal P(III) compounds are ligated to transition metal centers as ligands. Herein we report the discovery of unprecedented insertion reactions of a nontrigonal phosphorus center into metal–hydride and metal–carbon bonds to result in metallophosphoranes, pentacoordinate phosphorus compounds with transition metal substituents. These results demonstrate fundamentally new reactivities of nontrigonal tricoordinate phosphorus ligands that diverge from a traditional view of phosphine ligands as ‘spectator’.

A novel phosphorus triamide **L1** was designed, synthesized and characterized. While a reaction of **L1** with RuCl₂(PPh₃)₃ yields a metal-phosphine type complex **1** in a similar manner with classic phosphines, a metallophosphorane **2** was formed via net insertion of P center into the Ru–H bond when **L1** was treated with RuHCl(CO)(PPh₃)₃ (Figure 1). The structures of the compounds have been crystallographically determined and the Ru complex **2** was found to be the first example of metalhydrophosphorane. Furthermore, the net insertion of distorted phosphorus ligand is not limited to Ru–H, but observed for organometallic compounds. Another phosphorus triamide ligand **L2** was synthesized and treated with Group 10 precursors. While a reaction with PtClMe(cod) yielded a metal-phosphine complex **3**, in reactions with Ni and Pd analogues, metallophosphoranes **4** and **5** were formed respectively by the migration of methyl groups from metal to phosphorus (Figure 2). The synthesis, structural and electronic aspects of these compounds and reactions will be described in the talk.

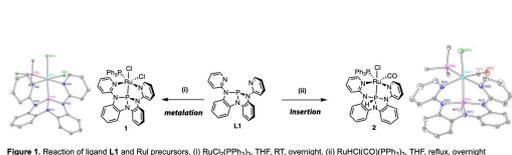


Figure 1. Reaction of ligand **L1** and RuI precursors. (i) RuCl₂(PPh₃)₃, THF, RT, overnight. (ii) RuHCl(CO)(PPh₃)₃, THF, reflux, overnight

Figure1.jpeg

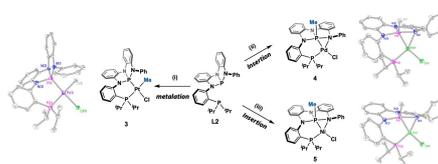


Figure 2. Reaction of ligand **L2** and Group 10 methyl precursors. (i) (cod)PtClMe, benzene, RT, 2h. (ii) (cod)PdClMe, benzene, RT, 2h. (iii) NiClMe(PPh₃)₃, benzene, RT, 2h.

Figure2.jpeg

Polyoxidoborate chemistry: coordination (1-D chain) polymers with Zn(II) borates

Wednesday, 4th December - 15:21: Reactions of coordination compounds (Room 1) - Oral - Abstract ID: 21

***Prof. Michael Beckett*¹, *Dr. Mohammed Altahan*¹, *Dr. Peter Horton*²**

1. Bangor University, 2. University of Southampton

Polyborate (polyoxidoborate) anions are readily self-assembled and templated by suitable cations from $B(OH)_3$ in alkaline aqueous solution. This is because in basic aqueous solution $B(OH)_3$ exists as a Dynamic Combinatorial Library (DCL) of numerous anionic polyborate species [1]. Stoichiometry, steric effects and H-bonding interactions all play important roles in the energetics of engineering these crystalline products [2,3]. Often, salts containing insular (or isolated) polyborate anions are formed and this is particularly the case if the templating cations are organic or are inert transition-metal complexes. The use of labile transition-metal cations results in an additional DCL to interact with the polyborate anions. This allows for the possibility of the polyborate anion entering the primary coordination sphere of the metal with formation of O-M coordinate bonds and polyborate transition-metal complexes. This lecture describes some new aspects of Zn(II) coordination chemistry focusing on two examples, $[Zn(en)\{B_6O_7(OH)_6\}]\cdot 2H_2O$ (en = 1,2-diaminoethane) and $[Zn(pn)\{B_6O_7(OH)_6\}]\cdot 1.5H_2O$ (pn = 1,2-diaminopropane), which feature the the hexaborate(2-) anion [4]. A structurally similar Cu(II) complex, $[Cu(en)\{B_6O_7(OH)_6\}]\cdot 3H_2O$ will also be briefly described.

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Biphilic [1,4]-additions to geometrically distorted NNNP

Wednesday, 4th December - 15:38: Reactions of coordination compounds (Room 1) - Oral - Abstract ID: 88

*Dr. Colet te Grotenhuis*¹, *Mr. Jared T. Mattos*¹, *Prof. Alex T. Radosevich*¹

1. Massachusetts Institute of Technology

Introduction

Neutral tricoordinate phosphorus (σ^3 -P) compounds commonly exhibit pyramidal structures with local 3-fold (C_{3v}) symmetry about phosphorus. The electronic structure instilled by this geometry is associated with Lewis basicity and nucleophilicity which underpin essentially all of their applications in modern synthesis, coordination chemistry, and catalysis. We have previously shown that severe geometric distortion to C_{2v} symmetry imparts significant electrophilic character at phosphorus as opposed to the typical Lewis basicity of σ^3 -P compounds (Figure 1). Consequently, this new biphilic (both nucleophilic and electrophilic) character opens up the potential to develop novel transformations.

Methods

The compounds are synthesized air and moisture free in a glovebox and studied by 1D- and 2D-NMR spectroscopy as well as X-ray crystallography and HRMS. Product selectivity and the reaction mechanism are investigated by DFT calculations.

Results

The reaction of geometrically distorted NNNP (**1**) with dienes results in the formation of Kukhtin-Ramirez type adducts as proven by crystallography (Figure 2). These oxazaphospholenes (**2**) are formed by [1,4]-addition and when one of the double bonds is part of an aromatic ring, that ring is dearomatized. The formation of these new compounds is studied with DFT and their properties are tested through follow-up chemistry.

Discussion

The geometry around phosphorus in NNNP (**1**), enforced by the triamide ligand, leads to biphilic reactivity whereas classically tricoordinate phosphorus compounds react as nucleophiles. In contrast to canonical 3-fold symmetric σ^3 -P structures, the phosphorus center undergoes [1,4]-addition to (aromatic) dienes to give stable σ^5 -P compounds (Figure 2). DFT calculations confirm that concerted push-pull interactions with a diene result in the formation of oxazaphospholenes (**2**). We were able to exploit this reactivity in the dearomatization of benzene and pyridine rings, of which the resulting diene could be further derivatized. Release of the modified fragments leads to the release of modified organic heterocycles, which are important in the pharmaceutical industry. The work presented here displays a novel mode of reactivity achieved by the biphilic character of phosphorus which is enforced by ligand design. A new metal-free reaction is presented for the modification of heterocycles without pre-functionalization of the substrate.

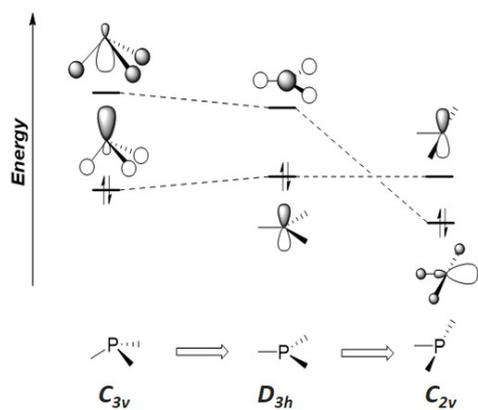


Figure 1.jpg

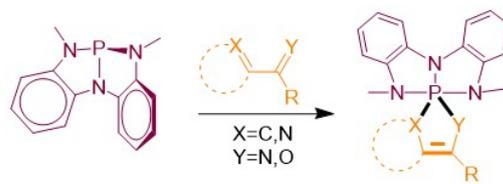


Figure 2.jpg

Push-pull stabilized P₂ and As₂ derived by oxidative coupling of heavy rhenium pnictides

Wednesday, 4th December - 15:55: Reactions of coordination compounds (Room 1) - Oral - Abstract ID: 143

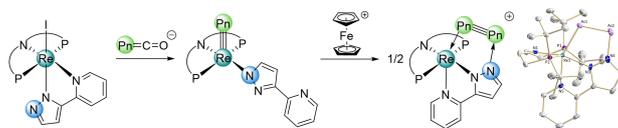
Dr. Josh Abbenseth¹, **Dr. Martin Diefenbach**², **Dr. Alexander Hinz**³, **Prof. Jose Goicoechea**⁴, **Prof. Max Holthausen**², **Prof. Sven Schneider**¹

1. Georg-August-Universität Göttingen, 2. Goethe Universität Frankfurt am Main, 3. Karlsruher Institute für Technologie, 4. University of Oxford

While dinitrogen is ubiquitous in nature the heavier homologues diphosphorus and diarsenic are only encountered as highly reactive intermediates due to their significant lower bond strength. Multiple reports feature reduced P₂ⁿ⁻ and As₂ⁿ⁻ moieties bound between metal centers or organic residues but stabilization of the neutral congeners at ambient conditions remains challenging.^[1]

We aimed to generate terminal heavy pnictide complexes to investigate the possibility of pnictide radical coupling to give diatomic species. Herein, we report the first terminal heavy pnictide complexes beyond group 6. Reaction of the octahedral Re(III) complex (PNP)ReI(PyrPz) (PNP = N{CH₂CH₂P^tBu₂}₂, PyrPz = C₈H₆N₃) with [Na(dioxane)_x][PnCO] (Pn = P, As) leads to the clean formation of the Re(V) pnictides (PNP)Re(Pn)(PyrPz). One electron oxidation results in radical coupling to give (PNP)Re(Pn₂-PyrPz) complexes featuring five membered metallacycles as the main reaction products. Theoretical computations suggest that a push-pull interaction of the metal center and the PyrPz ligand stabilizes the neutral Pn₂ fragments, which are best described as neutral diphosphorus and diarsenic.

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Generation and oxidative coupling of heavy rhenium pnictides.jpg

Green approaches for the synthesis of nucleotides, their conjugates and analogues

Wednesday, 4th December - 16:40: Multiple topics (Auditorium) - Oral - Abstract ID: 12

Ms. Lucie Appy¹, Dr. Anaïs Depaix¹, Dr. Xavier Bantreil¹, Dr. Frédéric Lamaty¹, Dr. Suzanne Peyrottes¹, Dr. Béatrice ROY¹

1. University of Montpellier

Introduction: Given the importance of nucleotides and their derivatives in biological processes, numerous methods have been developed to access these compounds and their structural analogues.^[1] Their scope ranges from mechanistic probes to versatile chemical tools for assay development and biomedical applications. Most of these syntheses present important drawbacks, such as the use of non-volatile and harmful solvents (DMF, pyridine), preparation of substrates or phosphorus reagents in their alkylammonium form due to solubility issues, anhydrous conditions, and fastidious purifications.

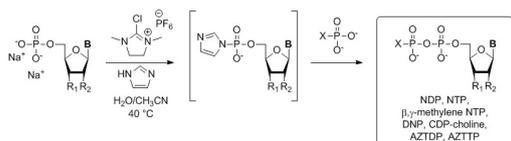
Methods: We have developed original one-pot, protecting-group free approaches, which are user-friendly and reliable, for nucleotides starting from nucleoside 5'-monophosphates and through phosphorimidazolid intermediates. Both methods present convenient set-up, i.e. non-dry solvent and reagents, substrates in their sodium or acid form, and commercially available and cheap phosphorus reagents as sodium or potassium salts.

Results & Discussion: The first strategy uses 2-chloro-1,3-dimethylimidazolium hexafluorophosphate and imidazole as activating agents in a water medium, and allows to access a variety of nucleosides 5'-polyphosphates, as well as conjugates and analogues (Scheme 1).^[2]

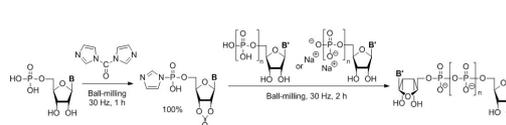
The second strategy is a solvent-assisted mechanochemical approach, which allows to prepare symmetrical and mixed dinucleoside 5,5'-polyphosphates.^[3] Under ball-milling conditions, nucleoside 5'-monophosphates are quantitatively activated using the eco-friendly *N,N'*-carbonyldiimidazole into their phosphorimidazolid derivatives. The addition of a nucleoside 5'-mono, di or triphosphate directly leads to the formation of the corresponding dinucleotides. Other benefits of this one-pot method include short reaction time, high conversion rates and easy set-up and purification. This work offers new perspectives for the synthesis of nucleotide conjugates and analogues, combining the phosphorimidazolid approach and milling conditions (Scheme 2).

Since phosphorimidazolides are essential intermediates for pyrophosphate bond formation, our studies offer new perspectives for the development of greener methods to access a wide range of nucleotide derivatives and analogues.

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Scheme 1.jpg



Scheme 2.jpg

Attractive new boron, phosphorus and silicon chemistry

Wednesday, 4th December - 16:57: Multiple topics (Auditorium) - Oral - Abstract ID: 33

Dr. Herbert Roesky¹

1. Göttingen

In the year of celebrating the 150th anniversary of the Periodic Table it is time for reflecting the availability of certain elements. Aluminum and silicon are ubiquitous elements in the earth's crust and plentiful available. Therefore we started our investigations using these elements preferentially already a few years ago. In this lecture the preparation of compounds with boron, silicon and phosphorus with low oxidation states of these elements will be shown. BF an isoelectronic species to CO was prepared and stabilized with carbene. The properties of BF will be discussed. For the preparation of silicon and phosphorus compounds with low valent silicon and phosphorus we developed new synthetic methods without using alkaline metals for the reduction of the precursors with the common higher oxidation state. A phosphinidene- silylene compound with low valent silicon and low valent phosphorus reacts selectively with sulfur, selenium and tellurium, respectively, under oxidation of the silicon atom. The application of the boron and aluminum compounds as catalysts will be presented. Moreover, the formation of compounds with Si-Al bonds with the two positive polarized elements was a challenging task. Examples of compounds with Si-Al bonds will be reported. Furthermore the cyclohexane analogue with the elements of silicon and aluminum was for the first time successfully prepared.

Tethered η^5 -oxocyclohexadienyl piano-stool ruthenium(II) complexes: catalysts with metal–ligand cooperation for sustainable energy

Wednesday, 4th December - 17:14: Multiple topics (Auditorium) - Oral - Abstract ID: 196

Dr. Emmanuel Puig¹, **Dr. Manel Kechaou-Perrot**¹, **Dr. Jean-Marc Sotiropoulos**², **Dr. Karinne Miqueu**²,
Mr. Raphael Verron³, **Dr. Cédric Fischmeister**³, **Dr. Pierre Sutra**¹, **Dr. Alain Igau**¹

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Ruthenium is one of the most intensively used metals in catalysis, partly due to his lower price, but also, because a wide span of stable Ru-based catalysts can be prepared. The objective of our fundamental research studies is to develop efficient homogeneous ruthenium catalysts displaying metal-ligand cooperation for challenging transformations targeting sustainable sources of energy. A relevant example of “piano-stool” bifunctional complex displaying metal–ligand cooperation is the Shvo’s pre-catalyst **I**, a h^4 -cyclopentadienone-ligated diruthenium complex that efficiently promotes a number of chemical transformations.¹ Shvo *et al.* proposed that **I** thermally dissociates into two monoruthenium active species, the 18-e⁻ **II** species and the remaining elusive 16-e⁻ **III** complex (Figure 1a).

Following the Shvo-type catalysts in which the cyclopentadienone cyclic ligand act as an internal pendant basic site, we developed a straightforward synthesis of tethered η^5 -oxocyclohexadienyl half-sandwich ruthenium(II) complexes **A** (Figure 1b).² Since the first η^5 -oxocyclohexadienyl metal complex published in 1976 by Cole-Hamilton, Young and Wilkinson,³ half-sandwich related complexes are very scarce. Note that before our work, none of the reported η^5 -oxocyclohexadienyl transition metal complexes were tested in catalysis.⁴

Bifunctional complexes featuring metal acidic and ligand basic sites are associated to highly efficient (de)hydrogenation processes.^{5,6} In marked contrast the Shvo’s catalyst **I**, our tethered η^5 -oxocyclohexadienyl half-sandwich ruthenium(II) complexes **A** are structurally easily tunable. Hence, it is possible to exploit the large steric and electronic properties of our new tethered η^5 -oxocyclohexadienyl complexes **A** to improve and optimize the catalytic performances in the selected catalytic transformations.

The straightforward synthesis of tethered η^5 -oxocyclohexadienyl half-sandwich ruthenium(II) complexes, as well as selected catalytic activities including catalytic upgrade of (bio)-ethanol into higher alcohols such as n-butanol by the Guerbet reaction for the production of advanced biofuels will be presented.

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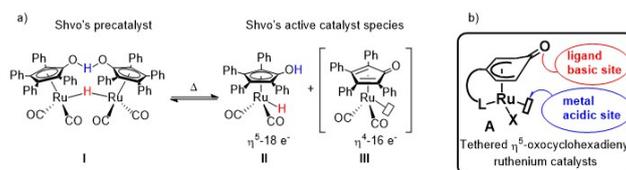


Figure 1: a) Representation of the precatalyst Shvo's reagent I. b) General structure of bifunctional tethered η^5 -oxocyclohexadienyl ruthenium catalysts A.

Figure abstract epuig.jpg

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