24.
NORD
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DOKTORANDEN
KOLLOQUIUM

24. Norddeutsches Doktorandenkolloquium

26.–27. September 2024 · Rostock

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WELCOME

Dear colleagues, dear PhD students,

On behalf of the Institute of Chemistry at the University of Rostock as well as the Leibniz Institute for Catalysis we would like to welcome you to the 24th North German Doctoral Student Colloquium (Norddeutsches Doktorandenkolloquium, NDDK).

The NDDK already has a long and successful history: Inspired by the Association of Northern German Universities (Verbund Norddeutscher Universitäten), the NDDK was founded in 1998 on the initiative of Prof. Dr. Jürgen Heck (University of Hamburg). Since its inception, the NDDK has offered PhD students in inorganic chemistry and related fields a platform to present their current research results in the form of talks and posters. The pleasant atmosphere of the NDDK also encourages personal conversations, so new contacts can be easily made and existing ones may be strengthened.

Traditionally, the universities of the northern German states of Bremen, Hamburg, Mecklenburg West-Pomerania, Lower Saxony, and Schleswig-Holstein participate in the NDDK. Since the 20th anniversary of the NDDK in 2018, Berlin and Brandenburg have also been represented. Like in previous years, we can look forward to exciting contributions from various research fields of inorganic chemistry, such as inorganic molecular and solid-state chemistry, homogeneous and heterogeneous catalysis, materials science, coordination chemistry, as well as organometallic and main group chemistry. With 99 registered participants, we eagerly await 17 exciting talks and 39 poster presentations this year.

Special thanks are due to our numerous sponsors and supporters, without whose generous contributions the 24th NDDK would not be possible. We would also like to extend our heartfelt thanks to the many helping hands from the inorganic chemistry research groups who are contributing to the success of the 24th NDDK.

We wish everyone two exciting days filled with fascinating chemistry and stimulating exchange of ideas!

The organizing committee: Axel Schulz, Torsten Beweries, Wolfram Seidel, Martin Köckerling, Jonas Bresien

THANKS!

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HISTORY

Previous conference locations: 1998–2024

NDDK	Year	Host
1	1998	Universität Hamburg
2	1999	Universität Hamburg
3	2000	Universität Hamburg
4	2001	Universität Hamburg
5	2002	Carl von Ossietzky Universität Oldenburg
6	2003	Christian-Albrechts-Universität Kiel
7	2004	Universität Hamburg
8	2005	Universität Rostock
9	2006	Universität Rostock
10	2007	Jacobs Universität Bremen
11	2008	Technische Universität Braunschweig
12	2009	Carl von Ossietzky Universität Oldenburg
13	2010	Universität Greifswald
14	2011	Leibniz Universität Hannover
15	2012	Christian-Albrechts-Universität Kiel
16	2013	Universität Bremen
17	2014	Leibniz-Institut für Katalyse Rostock
18	2015	Georg-August-Universität Göttingen
19	2016	Universität Hamburg
20	2017	Christian-Albrechts-Universität Kiel
21	2018	Technische Universität Braunschweig
22	2019	Carl von Ossietzky Universität Oldenburg
23	2023	Freie Universität Berlin
24	2024	Universität und Leibniz-Institut für Katalyse Rostock

VENUE

The NDDK is held at the lecture building of the **Institute of Chemistry** (Albert-Einstein-Str. 3a), located on Rostock's South City Campus.

Map adapted from osm.org

The Institute of Chemistry is easily accessed using public transport. Use the following tram or bus stops:

Joachim-Jungius-Str.	bus line 39
Erich-Schlesinger-Str.	tram lines 4,5,6
Bei der Tweel	bus line 27

Public transport itineraries can be found via Google Maps or the DB Navigator app. The latter also allows you to buy tickets for public transport.

Catering during the breaks and the barbecue are free of charge. Snacks and drinks will be available during all coffee breaks as well as the poster session.

Lunches are not included and are at each participant's own discretion. The Mensa offers reasonably priced menus. Alternatively, you may find a variety of restaurants in the city centre, which is only a couple of minutes away by tram.

Locations

Talks
Lecture Hall 001

Poster Session
Foyer / SR 203

Barbecue
Courtyard

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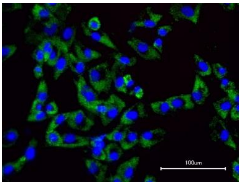

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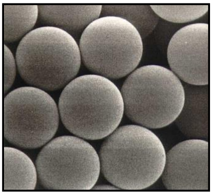

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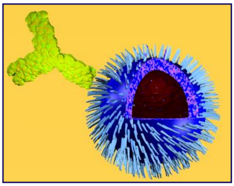

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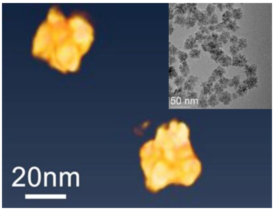

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References:

[1] Labeling of hMSC with fluorescent perimag® (nucleus: blue; perimag® in cytoplasm: green) , T. Kilian *et al. Nanomedicine* **2016**, 11 (*15*) 1957-1970.
[2] Viability assessment of Salmonella cells with nanomag®-D particles, E. Fernandez *et al. Biosensors and Bioelectronics* **2014**, (*52*) 239-246.
[3] TEM tomography image of synomag®-D, L.J. Zeng, Chalmers University of Technology, Göteborg.

PROGRAMME

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	Thursday 26 Sep 2024	**Friday** 27 Sep 2024
08:00	*Arrival*	
20		
40		*Registration*
09:00		O9 Moritz Ernst
20		O10 Dustin Bockhardt
40		O11 Mirko Rippke
10:00		*Coffee break*
20		O12 Chiara Looks
40		O13 Sahar Khandan
11:00		O14 Bastian Achenbach
20		*Coffee break*
40		O15 Marcel Eilers
12:00	*Registration & Exhibition* *(continuous)*	O16 Nadeschda Geibel
20		O17 Kushik
40		*Awards + Closing*
13:00		*Depature*
20		
40		
14:00	*Welcome*	
20	O1 Jonas Surkau	
40	O2 Pablo Cortés Soláns	
15:00	O3 Henner Pesch	
20	O4 Sanel Suljić · How-to	
40	Poster session	
16:00	*Cake buffet*	
20	*15:40–16:30 odd poster numbers*	
40	*16:30–17:20 even poster numbers*	
17:00		
20	O5 Christian Urbank · How-to	
40	O6 Ciara Isabel Kiene	
18:00	O7 Gesa Dreyhsig	
20	O8 Friederike Marie Hamann	
40	*Coffee break / Group leaders' meeting*	
19:00	*BBQ*	
20		
40		
20:00		
20		
40	*until 22:00*	

TALKS

Thursday 26 Sep 2024

12:00		Registration
14:00-15:40		*Session 1* *Chair: Samantha Frank*
14:00		Welcome to the 24th NDDK
14:20	O1	**Jonas Surkau** | Universität Rostock | Schulz *Tricyanomethane or Dicyanoketenimine – Silylation makes the Difference*
14:40	O2	**Pablo Cortés Soláns** | Humboldt-Universität zu Berlin | Pérez-Bitrián *Organoxenonium(II) Salts in Transition Metal Chemistry*
15:00	O3	**Henner Pesch** | Georg-August-Univerität Göttingen | Siewert *Mechanistic Studies on the Electrochemical Functionalization of Alkenes Enabled by (Inter)Chalcogen-Catalysis*
15:20	O4	**Sanel Suljić** | Magritek *How-to lecture: Ultra-high resolution 90 MHz Spinsolve MultiX NMR for simultaneous on-line analysis of biphasic Suzuki coupling*
15:40-17:20		*Poster session + cake buffet*
15:40		odd poster numbers
16:30		even poster numbers
17:20-18:40		*Session 2* *Chair: Ayu Afiqah Nasrullah*
17:20	O5	**Christian Urbank** | Universität Hamburg | Vondung *How-to lecture: What to do with DOSY-Spectra*
17:40	O6	**Ciara Isabel Kiene** | Georg-August-Univerität Göttingen | Schneider *Electrochemical Acetonitrile Synthesis from N_2*
18:00	O7	**Gesa Dreyhsig** | Freie Universität Berlin | Hasenstab-Riedel *Bichloride-Based Ionic Liquids of the Merged Storage, Processing, and Electrolysis of Hydrogen Chloride*
18:20	O8	**Friederike Marie Hamann** | Universität Rostock | Seidel *Heterobimetallic mediators for electrocatalytical hydrogenation*
18:40		Coffee break
18:40-19:00		*Group Leaders' Meeting* Lecture Hall 002
19:00-22:00		*Barbecue* Courtyard

TALKS

Friday 27 Sep 2024

08:40		Registration	
09:00-10:00		*Session 3*	*Chair: Kevin Schwitalla*
09:00	O9	**Moritz Ernst** | Freie Universität Berlin | C. Müller *Investigations of novel Synthetic Pathways towards Phosphorus Heterocycles*	
09:20	O10	**Dustin Bockhardt** | TU Braunschweig | Tamm *N-Heterocyclic Carbene-Phosphinidene Manganese Carbonyls*	
09:40	O11	**Mirko Rippke** | Leibniz-Institut für Katalyse | Beweries *Late transition metal PN(H)N complexes for the dehydrocoupling of amine borane adducts*	
10:00		Coffee break	
10:20-11:20		*Session 4*	*Chair: Zeinab Hosseinpour*
10:20	O12	**Chiara Looks** | Universität Hamburg | Jacobi von Wangelin *Nanoclusters of 3d Transition Metals: Synthesis, Characterization and Catalysis*	
10:40	O13	**Sahar Khandan** | Constructor University | Kortz *Synthesis and Structural Characterization of Peroxo-Containing Polyoxotungstates*	
11:00	O14	**Bastian Achenbach** | Christian-Albrechts-Universität zu Kiel | Stock *High-Throughput Based Discovery and Characterization of Porous Al-Carboxylates*	
11:20		Coffee break	
11:40-13:00		*Session 5*	*Chair: Marvin Janssen*
11:40	O15	**Marcel Eilers** | Carl von Ossietzky Universität Oldenburg | Beckhaus *Reactions of Cumulenes with Bis(pentafulvene)titanium complexes*	
12:00	O16	**Nadeschda Geibel** | Carl von Ossietzky Universität Oldenburg | T. Müller *Germaaluminocenes – Masked Heterofulvenes*	
12:20	O17	**Kushik** | Leibniz-Institut für Katalyse | Hering-Junghans *The Azide-Wittig Reaction*	
12:40		Awards + Closing	

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POSTERS

P1 **Sotirios Pavlidis** | Humboldt-Universität zu Berlin | Abbenseth

Two-fold proton coupled electron transfer at a Ta(V) aniline complex mediated by a redox-active NNN pincer ligand

P2 **Anupam Sarkar** | Constructor University | Kortz

Host-Guest Chemistry in Polyoxo-Noble-Metalate Metal-Organic Frameworks

P3 **Rupesh** | Universität Hamburg | Vondung

Hybrid O/P-Donor Ligands for F-Element Chemistry

P4 **Yannic Pilopp** | Universität Rostock | Schulz

Reactivity of azides towards five-membered biradicals

P5 **Samantha Frank** | Freie Universität Berlin | C. Müller

A Phosphinine-Borane Adduct activates Water

P6 **Kevin Schwitalla** | Carl von Ossietzky Universität Oldenburg | Beckhaus

From Coordination to Noncoordination: Substitution Lability of Titanium Triflato Complexes

POSTERS

P7 **Shubham Goel** | Leibniz-Institut für Katalyse | Beweries

Development of cooperative late transition metal complexes for dehydrocoupling of amine boranes

P8 **Marvin Janssen** | Universität Bremen | Beckmann

Advances in the Kinetic Stabilization of p-Block Elements

P9 **M. Elcheikh Mahmoud** | Constructor University | Kortz

Synthesis and Characterization of Lanthanide-Containing Asymmetric Wells-Dawson Ion

P10 **Moritz L. Bubenik** | Humboldt-Universität zu Berlin | Pérez-Bitrián

Unlocking the Lewis Acidity of Arylxenonium(II) Ions

P11 **Olga Verbitsky** | Universität Potsdam | Kulak

Interaction of DNA with Cu(II) complexes of monoalkylated oxacyclen derivatives

P12 **Zeinab Hosseinpour** | TU Braunschweig | Tamm

Zinc Hydride Complexes Stabilized by Anionic N-Heterocyclic Carbenes: Application in the Hydrosilylation of Ketones, Aldehyde and CO_2

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P13 **Ayu Afiqah Nasrullah** | Leibniz-Institut für Katalyse | Hering-Junghans
Diverse Reactivity of Cyanophosphide

P14 **Corinna Girschik** | Carl von Ossietzky Universität Oldenburg | T. Müller
Syntheses of Pyridine-Stabilised Silyl Borates

P15 **Simon Hansen** | TU Braunschweig | Bröring
Lithium corroles – Synthesis and application for metathesis with early transition metal precursors

P16 **Arun Pal** | Constructor University | Kortz
Fluorinated Arylarsonate-Containing Polyoxomolybdates: pH-dependent Formation of Mo_6 *vs* Mo_{12} *Species and Their Solution Properties*

P17 **Kai-Thorben Kuessner** | Georg-August-Universität Göttingen | Siewert
Electrochemical Hydrogenation of carbonyl compounds with a Manganese Catalyst

P18 **Lukas Fischer** | Freie Univeristät Berlin | Hasenstab-Riedel
The Diverse Chemistry of Antimony Teflates: Superacids, Strong Oxidizers and Weakly Coordinating Anions

POSTERS

P19 **León Hillers** | Universität Hamburg | Vondung

Synthesis of Hemilabile Cyclopentadienyl Phosphine Ligands and their Uranium Complexes for Small Molecule Activation

P20 **Leon Ohms** | Universität Rostock | Schulz

Pacman Phosphanes as Macrocyclic Ligands in Main-Group and Transition Metal Complexes

P21 **Andrey Petrov** | Leibniz-Institut für Katalyse | Hering-Junghans

Chemistry of η^2-dipnictene-titanocene complexes

P22 **Pascal Komorr** | Universität Bremen | Beckmann

Kinetic Stabilization of Chalcogen Radical Cations

P23 **Lene Zabojnik** | Universität Rostock | Seidel

Polynuclear complexes with a triazole dithiolate ligand

P24 **Erik Torsten Sanner** | Freie Universität Berlin | C. Müller

Synthesis and Coordination Chemistry of a Ferrocenyl substituted Phosphinine

P25 **Pascal Kramer** | Universität Rostock | Schulz

Synthesis of Pacman pnictides

P26 **Vinaya Siby** | Constructor University | Kortz

Synthesis and Characterization of Dimethylarsinate- and Organoarsonate-Functionalized Polyoxomolybdates

P27 **Hendrik Peters** | TU Braunschweig | Bröring

Arsenic Corroles

P28 **Max Neubauer** | Leibniz-Institut für Katalyse | Hering-Junghans

Bisimonophosphoranes as Synthetic Building Blocks

P29 **Lukas Jacobsen** | Universität Greifswald | Schulzke

Molybdenum mediated synthesis of bio-active indolizine-based pentathiepines: Synthesis and late-stage modification

P30 **Yannis Höhle** | Georg-August-Universität Göttingen | Schneider

Photoinduced hydrogenation of a N_2-derived Re-Imido complex

P31 **Leo Wessel** | TU Braunschweig | Frank/Tamm

Imidazoline-2-imine Iron(I) Complexes with Spin-Crossover Behaviour

P32 **Isabell Prediger** | Universität Potsdam | Kulak

Oxidation of acetol with earth-abundant metal salts

P33 **Pooja Kulashri** | Constructor University | Kortz

Palladium(IV)-Containing Polyoxotungstate

POSTERS

P34 **Simon Richter** | Georg-August-Universität Göttingen | Schneider

Synthesis and Reactivity of a square-planar Osmium(II) Complex

P35 **Sebastian Günther** | TU Braunschweig | Bröring

Influence of Supersaddling Modes on Copper Corroles: Studying Reactivity in Regioselective ß-ß'-Coupling

P36 **Lakita Khidtta** | Constructor University | Kortz

Palladium(II)-Containing Tungstophosphate

P37 **Karsten Paul Lüdtke** | Universität Rostock | Schulz

Imidazolium-substituted diphosphaindenylides – synthesis, biradical character and reactivity

P38 **Thomas Marx** | Universität Hamburg | Burger

Antiferromagnetic Coupling of Dimeric Iridium PDI Complexes

P39 **Chenghuan Liu** | Carl von Ossietzky University Oldenburg | T. Müller

Anionic 1H-/2H-tetrolide rearrangement: a computational investigation

ORAL PRESENTATIONS

Tricyanomethane or Dicyanoketenimine – Silylation makes the Difference

Jonas Surkau,[a] Jonas Bresien,[a] Dirk Michalik,[a] Axel Schulz*[a]

[a] *Institute of Chemistry, University of Rostock, Germany.*

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The concept of pseudohalides has been established in 1923, whereby tricyanomethanide $[C(CN)_3]^-$ is one of two planare pseudohalide anions. The protonation occurs at the central carbon atom leading to the strong Brønsted acid $HC(CN)_3$ (pKa = −5). The imine tautomer is not preferred in solution just as in solid state.[1]

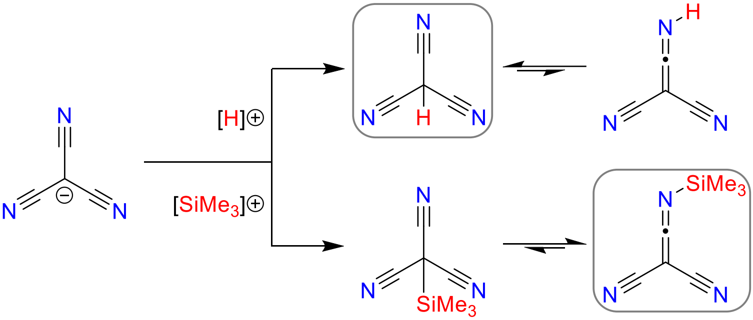

Figure 1: $[C(CN)_3]^-$ is protonated at the central C atom (top), but silylated at the terminal N atom (bottom).

In the past, several silylated, linear pseudohalides (Me_3Si-CN, Me_3Si-N_3,…) have been synthesized. In terms of $[C(CN)_3]^-$, silylation occurs at the terminal nitrogen atom, which is in contrast to the protonation and the concept of the “heavy proton”. The reaction is performed by addition of Me_3Si-I to a suspension of $Ag[C(CN)_3]$ in diethyl ether forming silver iodide as side product. This uncharged product compound has been described in detail by analytical and computational studies, e.g. illustrating the dominance of deformation energy instead of hyperconjugation. The addition of two more trimethylsilyl cations leads to the highly symmetric, persilylated dication $[C(CN\cdot SiMe_3)_3]^{2+}$ with two equivalents of $[B(C_6F_5)_4]^-$ as counterions extending the group of persilylated, linear pseudohalides ($[Me_3Si\text{-}Y\text{-}SiMe_3]^+$, Y = CN, OCN, SCN, NNN).[2]

[1] [a] K. Banert, M. Chityala, M. Hagedorn, H. Beckers, T. Stüker, S. Riedel, T. Rüffer, H. Lang, *Angew. Chem. Int. Ed.* **2017**, *56*, 9582−9586; [b] J. Surkau, K. Bläsing, J. Bresien, D. Michalik, A. Villinger, A. Schulz, *Chem. Eur. J.* **2022**, *28*, e202201905.

[2] J. Surkau, J. Bresien, D. Michalik, A. Schulz, *Angew. Chem. Int. Ed., accepted*.

Organoxenonium(II) Salts in Transition Metal Chemistry

Pablo Cortés Soláns,[a] Alberto Pérez-Bitrián*[a]

[a] *Institut für Chemie, Humboldt-Universität zu Berlin, Germany.*

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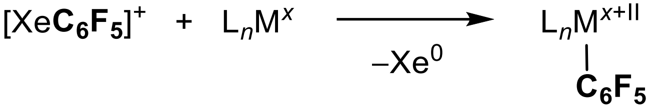
The current interest in high-oxidation-state metal complexes[1] is accelerating the development of suitable oxidizers, especially with ligand-transfer ability. Since the synthesis of the first organoxenon compound in 1989,[2] a number of species containing Xe−C bonds increased significantly.[3] Although their reactivity as electrophilic-transfer reagents has been demonstrated, their suitability as oxidizers in organotransition metal chemistry has not been explored yet. In this regard, we envisioned using such species for the synthesis of organometallic complexes, releasing only Xe as side-product, and thus resulting in an efficient alternative for the formation of metal−carbon bonds with a high atom economy.

A new methodology for the synthesis of high-oxidation-state metal complexes by means of organoxenonium(II) salts will be presented. It consists in the electrophilic transfer of an halogenated aryl group to the metal center, which is oxidized (see Figure 1). Our initial focus is set on the well-understood organoxenon compound $[XeC_6F_5]^+$. In relation to metal complexes, heavy metals (Au, Pt, Pd) provide a suitable platform to begin with, since the synthesis of Au(III), Pt(IV) and Pd(IV) complexes by using strong oxidizers is also well-established. The influence of a variety of ligands is also investigated to unravel the most suitable ones to withstand such strong oxidizing conditions, enabling the design of new appropriate precursors.



$$[Xe\mathbf{C_6F_5}]^+ + L_nM^x \xrightarrow[-Xe^0]{} L_nM^{x+II}(\mathbf{C_6F_5})$$

Figure 1: Synthetic strategy for the oxidation of transition metal complexes with organoxenonium(II) salts.

[1] M. Malischewski, in *Comprehensive Organometallic Chemistry IV, Vol. 1* (Ed.: P. L. Holland), Elsevier, Amsterdam, **2022**, pp. 109–134.

[2] a) D. Naumann, W. Tyrra, *J. Chem. Soc., Chem. Commun.* **1989**, 47–50. b) H.-J. Frohn, S. Jakobs, *J. Chem. Soc., Chem. Commun.* **1989**, 625–627.

[3] H.-J. Frohn, V. V. Bardin, *Organometallics* **2001**, *20*, 4750–4762.

Mechanistic Studies on the Electrochemical Functionalization of Alkenes Enabled by (Inter)Chalcogen-Catalysis

Henner Pesch,[a] Sebastian Graf,[b] Theresa Appleson,[b] Alexander Breder,[b] Inke Siewert [a]

[a] *Institute of Inorganic Chemistry, Georg-August-University Göttingen, Germany.*
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Alkenes are a readily available structural motif in organic synthesis, and therefore a common starting point for further functionalizations. Research has been to a large extent focused on transformations using transition metal catalysts, for instance, in allylic functionalizations.[1] Although tremendous progress has been made over the past decades, these protocols sometimes face selectivity issues concerning di-, tri-, and tetrasubstituted olefinic substrates. On the contrary, catalysts based on p-block elements such as iodine, sulfur, and selenium have been investigated as a complementary approach in such transformations and were successfully applied to multisubstituted internal alkenes. For example, selenium catalysts have been introduced to catalyse a multitude of oxidative reactions, including the allylic functionalization. These reactions, however, necessitate the use of strong oxidants such as *N*-haloamides and -imides, hypervalent iodine compounds or peroxides, which leads to poor redox and atom economy and sometimes low chemoselectivity.[2,3] Electrochemistry circumvents this, as reactive species can be generated at mild conditions with a fine tuneable oxidation potential.

Herein, we report an electrochemical protocol utilizing organic diselenides for the anodic allylic functionalization of alkenes. The mechanism of this reaction with and without disulfides as co-catalysts is elucidated and a variety of allylic aminations using internal *N*-based nucleophiles are presented.[4]

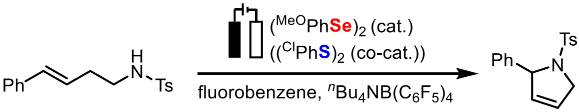

Figure 1: Electrochemical intramolecular amination reaction catalyzed by a diselenide for which the mechanism, with and without a disulfide, was investigated.

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Ultra-high resolution 90 MHz Spinsolve MultiX NMR for simultaneous on-line analysis of biphasic Suzuki coupling

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With the launching of the Spinsolve 90 ULTRA MultiX, Magritek has taken another step towards achieving even higher resolution, versatility, and sensitivity on the bench. These powerful magnets are now available with automatic multinuclear probes which make it possible to measure multiple nuclei on the same instrument. The Spinsolve 90 has the highest sensitivity that enables advanced experiments, such as HSQC-ME, to be acquired in just 2 minutes. It´s unparalleled magnet design enables highly efficient solvent suppression performance making it possible to measure samples in protonated solvents as they come from the reactor. The versatility of the Spinsolve MultiX probes, which can automatically switch between several X-nuclei, like ^{13}C, ^{31}P, ^{7}Li, ^{29}Si, (among others) provides a convenient working environment without the need for user interference. Thanks to the compactness and portability of these systems, a wide range of applications e.g. on-line monitoring of chemical reactions or qNMR studies are possible as the NMR spectrometers can directly be installed next to the chemical reactors or in the production sites(1,2).

Within this presentation, a study of the well-known Suzuki coupling will be presented that contains simultaneous on-line monitorings of a biphasic set-up using Spinsolve 90 MHz benchtop NMR systems. For the first time, for each liquid phase one NMR system was detecting the outcome of the reaction via 1H, 19F, 11B, and 31P NMR. Such a set-up enables the user to deeply understand the mechanism behind this crucial C-C coupling reaction without leaving the lab by a direct NMR feedback. Consequently, this NMR feedback offers the option to intervene immediately optimizing the reaction steps at place if needed.

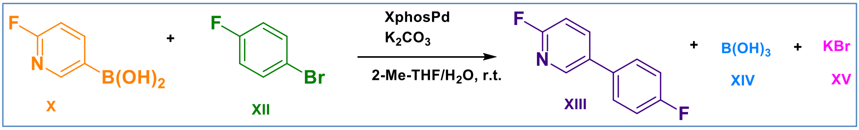

Figure 1: Biphasic Suzuki coupling reaction followed on-line with two Spinsolve NMR systems via 1H, 19F, 11B, and 31P NMR.

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What to do with DOSY-Spectra

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In the last few decades, the utilization of diffusion-ordered NMR spectroscopy (DOSY) has become an increasingly important component of the standard toolkit of coordination chemistry. Highly accurate spectra are readily available at most NMR departments, and as such, the correct analysis of the acquired results is the only hurdle for many researchers.

In this “How-to”, we want to show that diffusion is much more than just *Stokes-Einstein*. Using the relation between the diffusion coefficient (D) and the molecular weight (M), external calibration curves have been derived by *Stalke* and co-workers, allowing for the non-destructive approximation of M in solution.[1] But, next to the *Stalke*-method, there is a plethora of different models available, which might give contradicting results.[2]

In our work, we tested the accuracy of the most common DOSY interpretation methods and could show the limits in their general applicability. Subsequently, we developed an interpretation method, which is more generally applicable to a wide range of organometallic and organic molecules. In this how-to we will use the example of several uranyl-complexes for a step-by-step guide, introducing the audience to this field.

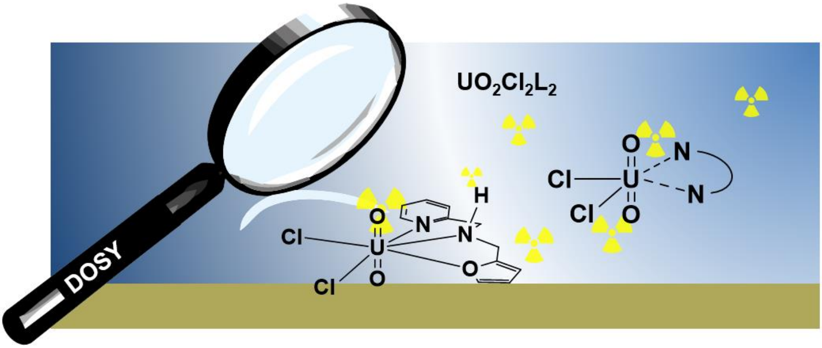

Figure 1: DOSY - more powerful than you think! (Graphic inspired by Stalke et al.).

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Electrochemical Acetonitrile Synthesis from N_2

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Reductive N_2 splitting into nitrido complexes is a promising strategy for nitrogen fixation beyond ammonia.[1,2] Electrochemically driven approaches are still in their infancy and recently gained more attention. In the last years, our group introduced rhenium pincer platforms that facilitate the electrochemically driven reductive splitting of dinitrogen.[3-6] In addition, synthetic strategies were developed to generate nitriles from N_2 through nitride alkylation and subsequent chemical redox steps.[7]

In this contribution, we present the transfer of this synthetic approach to the electrochemical redox regime. The formation of acetonitrile is demonstrated by electrolysis of an N_2 derived rhenium aldimido complex (Figure 1). The mechanism will be discussed based on electroanalytical examinations.

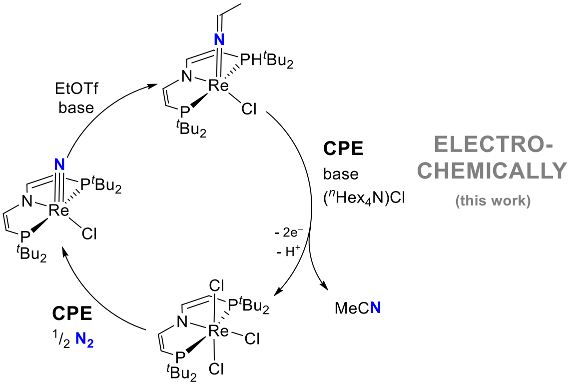

Figure 1: (Electro-)chemical conversion of Dinitrogen to Acetonitrile.

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Bichloride-Based Ionic Liquids of the Merged Storage, Processing, and Electrolysis of Hydrogen Chloride

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Hydrogen chloride (HCl) is produced as a by-product in industrial processes on a million-ton scale and is either dissolved in water to form hydrochloric acid or used directly as gaseous HCl.[1] Since HCl is inherently dangerous, its storage and transport in industrial plants are usually avoided, particularly on a large scale, but is produced on-site and directly utilized in further industrial processes.[2]

Herein, we report a complementary approach to safely store HCl forming the bichloride-based Ionic Liquid $[NEt_3Me][Cl(HCl)_n]$ (**Figure 1**). Although HCl release from this Ionic Liquid is possible through heating or vacuum application, the bichloride can be used also directly to produce industrially important chemicals like vinyl chloride or chloromethane. Alternatively, $[NEt_3Me][Cl(HCl)_n]$ can be electrolyzed under anhydrous conditions using a membrane-free cell to generate dry hydrogen and the corresponding chlorination agent $[NEt_3Me][Cl(Cl_2)_n]$, thus enabling the combination of these Ionic Liquids for the production of base chemicals.[4,5]

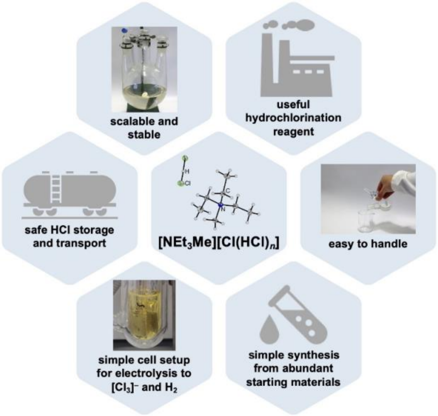

Figure 1 Bichloride-based Ionic Liquids complement the established systems of gaseous and aqueous HCl.

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Heterobimetallic mediators for electrocatalytical hydrogenation

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Phosphine ligands are widely used in homogeneous catalysis due to the tuneable donor strength and steric variability by the rich pool of possible substituents. Especially diphosphine ligands present the advantage of chelate ligands with potentially flexible bite angles. In addition, metal-ligand-cooperativity presents a field of interest because either redox-active ligands, acid/base behavior or potential H atom transfer might be involved. Recently, this cooperative behavior of ligands has risen in popularity for catalysts in electro-catalytical hydrogenation reactions as it potentially allows milder conditions and avoid the use of elemental dihydrogen.

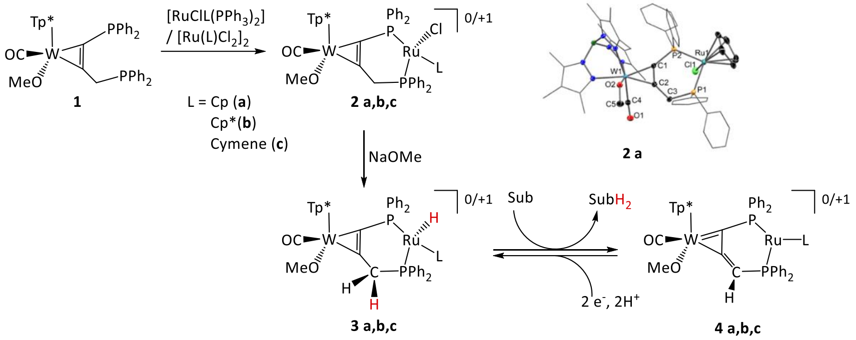

Figure 1: Reaction scheme of intended catalysed hydrogenation.

Air stable heterobimetallic W/Ru complexes, in which the metals are linked by an acetylenediphosphine bridging ligand, have previously been shown to be applicable as catalysts making use of the tunability of the phosphine ligands while also providing a potentially redox-active alkyne complex backbone.[1] In subsequent studies, a novel ligand on this base bearing a methylene spacer was developed. While these binuclear complexes show several interesting properties, the protic hydrogen at the propargylic position and a hydride at the metal are perfectly suited for polar hydrogen transfer. The investigations are devoted to the development of hydrogenation reactions driven by electrolysis. New complexes and advances in the conceptual realization are presented.

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Investigations of novel Synthetic Pathways towards Phosphorus Heterocycles

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Phosphaalkynes are starting materials for accessing different phosphorus heterocycles, such as *ortho*-substituted phosphinines by the pyrone route.[1]They can be used as well for the synthesis of phospholide-anions, the isolobal phosphorus analogues of the well-known cyclopentadienyl-anion.[2] In the last years it was shown that the reaction of alkynes and nitriles with both, the pentaphospholide- and the heptaphosphide-anion, yields 1,2,3-tri- and azatriphospholide-anions.[3,4] We present here that the reaction of phosphaalkynes with these polyphosphides gives 1,3,4-tri- and barely studied tetraphospholide-anions. Due to the limited amount of stable phosphaalkynes, we investigated the reactivity of the polyphosphides towards a trimethylsilyl substituted phosphaalkene, leading to the same aromatic heterocycles. This reactivity has been transferred to the pyrone route and thus, a ferrocenyl-substituted phosphinine could indeed be synthesized. Furthermore, in a direct reaction of white phosphorus (P_4) with sodium and carbonyl acid chlorides under certain conditions, tetraphospholide anions can be synthesized in one step from elemental phosphorus.

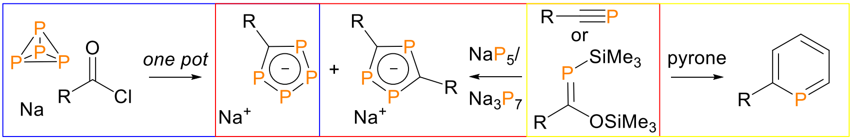

Figure 1: Intersecting novel synthetic pathways towards phosphorus heterocycles.

The novel phosphorus heterocycles were used as ligands for different metal complexes. These phosphinine and phosphaferrocenes complexes were further investigated for their structural and electrochemical properties.

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N-Heterocyclic Carbene-Phosphinidene Manganese Carbonyls

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Phosphorus chemistry mimicking the reactivity of carbenes is highly sought-after, due to the diagonal C-P relationship with phosphorus as a “carbon copy”.[1] While the quest for transition metal carbene complexes has been proven successful over the past decades, synthesis of phosphinidene complexes, especially including a 3d-transition metal, still remains a challenging task.[2,3]

Within our group, a new type of cationic, terminal phosphinidene ligand with a N-heterocyclic carbene (NHC) moiety has been established and employed in several 4d- and 5d-transition metal complexes of the type NHC-P=X (X = (*p*-cymene)MCl with M = Ru, Os; Cp*MCl with M = Rh, Ir);[4–6] the former have been successfully used as catalysts for the hydroboration of nitriles, esters and amides.[6]

Herein, we present the first series of Fischer-type 3d-transition metal complexes with a cationic NHC-phosphinidene ligand (IDippP)Mn(L)$(CO)_3$ (IDipp = 1,3-(diisopropylphenyl)imidazolin-2-ylidene; L = CO, PR_3 (R = Ph, Me), tetramethylimidazolin-2-ylidene, *o*-Xyl-NC). The reactivity of the unusual P=Mn double bond has been studied as well as substitution reactions at the metal center including kinetic investigations.

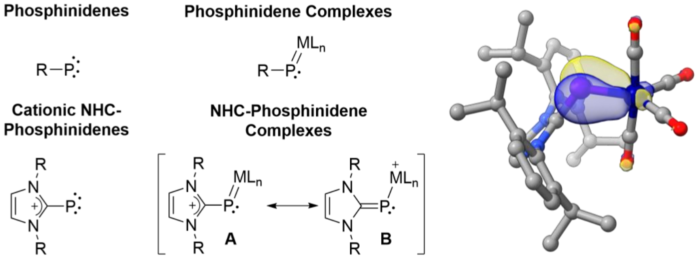

Figure 1: Comparison of different phosphinidenes and phosphinidene metal complexes (left) and display of the P=Mn double bond (HOMO-1) of (IDippP)Mn$(CO)_4$ (TPSSh/def2-TZVP) (right).

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Late transition metal PN(H)N complexes for the dehydrocoupling of amine borane adducts

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Poly(aminoboranes) are often discussed as precursors for BN-based ceramics and single-layer hexagonal BN thin films and are valence isoelectronic to polyolefins.[1] A clean and atom efficient method to form these materials is the catalytic dehydrocoupling of amine borane adducts ($H_3B{\cdot}NRH_2$, R = H, Me). So far, cooperative PNP complexes with an NH-functionality have shown the highest activity for these reactions.[2] We were interested whether this behaviour is exclusive to PNP ligands or can be transferred to other cooperative PNN systems. In a previous study, we investigated the coordination chemistry of pyrazole-based Rh(I) PNN(H) complexes and the catalytic dehydrocoupling of $H_3B{\cdot}NMeH_2$. We found an increased activity upon addition of base, likely forming a Rh hydride complex as the active catalyst.[3]

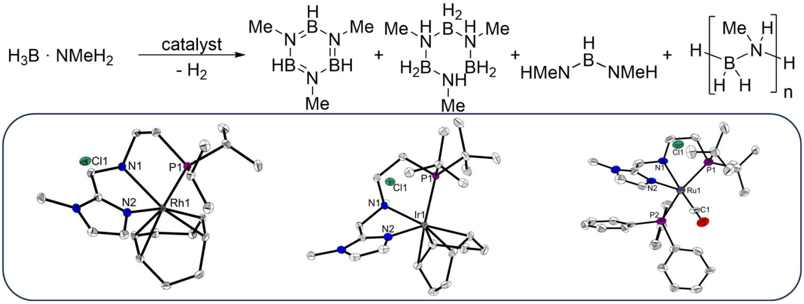

Figure 1: Dehydrocoupling of methylamine borane and molecular structure of some late transition metal complexes with imidazole based PN(H)N ligands.

For the synthesis of new imidazole-based PN(H)N complexes the corresponding metal precursors are added to the known PN(H)N ligand. Furthermore, in this presentation we will highlight the differences of these late transition metal complexes and show their application for the catalytic dehydrocoupling of amine borane adducts.

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Nanoclusters of 3d Transition Metals: Synthesis, Characterization and Catalysis

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Polynuclear metal clusters composed of 3d transition metals like manganese, iron and cobalt are defined as the aggregation of a finite number of atoms through metal-metal or metal-nonmetal bond interactions.[1] Early transition metals often form high-valent clusters, especially in combination with strong electron donating ligands such as CO or phosphines. Recently, our group has presented the synthesis of three-dimensional nanoclusters featuring μ_3-bridged organyl ligands, being characterized by unprecedented topologies and unique metal-ligand coordination interactions.[2]

The synthesis of these metal organyl clusters was enabled by the use of linear, reactive metal amides as precursors. This approach also allowed the generation of discrete Mn_6, Fe_4, Fe_6 and Fe_7 heteroleptic hydride clusters by the addition of a hydride source.[3] The μ_2/ μ_3 bridged hydrides exhibit a high catalytic activity in the hydrogenation reaction of olefins, alkynes and imines, while the μ_3 alkynyl bridged clusters may serve as catalysts in the trimerization of alkynes.[3]

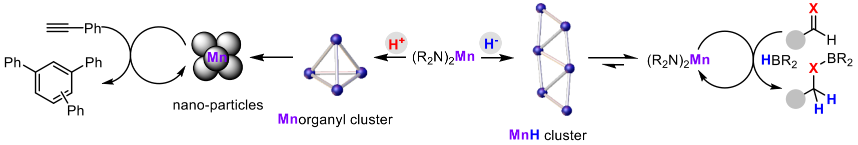

Figure 1: Catalytic activity of 2D and 3D nanoclusters of manganese and their synthetic pathways which involve the addition of a protic or hydridic hydrogen source.

The current focus is on the development of heterobimetallic clusters by doping the organomanganese structures with iron and by modifying the amide precursor with respect to their stability and pK_a value. On the other hand, structural diversity is induced by chelating ligands which extend the range of topologies and allow the tuning between 2D and 3D cluster architectures. The aim is also to broaden the scope of potential metals for the cluster synthesis to chromium, cobalt and nickel.

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Synthesis and Structural Characterization of Peroxo-Containing Polyoxotungstates

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Polyoxometalates (POMs) are a unique class of discrete, anionic, and soluble polynuclear metal oxides, which are generally constructed using early *d*-block metals in high oxidation states, and oxo or hydroxo-bridging ligands. The coordination flexibility and the ability to adopt several coordination geometries result in POMs exhibiting a diverse range of structural topologies and chemical compositions [1]. The incorporation of peroxo-containing metal-oxo clusters into POM structures represents a new subarea of POM chemistry. The class of peroxo-POMs has garnered attention due to their structural and compositional novelty, stability in solution, and promising applications in catalysis. In recent years, we have systematically explored the synthesis of various structures by integrating polyoxoanions with *3d*- and *4f*-block metal cations, including Zr^{4+}, Hf^{4+}, and Ce^{4+}, in the presence of hydrogen peroxide [2-4]. Herein, we present our latest discoveries on peroxo-containing polyoxotungstates, providing a detailed analysis of their molecular structure through various analytical methods.

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High-Throughput Based Discovery and Characterization of Porous Al-Carboxylates

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Aluminum carboxylates as a class of aluminum compounds have gained increasing interest in the last decades, especially with the use of polycarboxylic acids for the synthesis of porous metal-organic frameworks (MOFs).[1,2] The combination of high chemical and thermal stability, readily available and inexpensive starting materials, and permanent porosity makes Al-MOFs interesting candidates for a wide range of applications, including gas storage and separation.[1] While many polycarboxylic acids have been employed for the synthesis of Al-MOFs, only relatively few systematic studies have been reported with monocarboxylic acids.

Here we present the results of a systematic high-throughput investigation of the system Al^{3+} / NaOH / CH_3COOH / H_2O, that yielded four phase-pure compounds including a series of porous aluminum salts $[Al_{24}(OH)_{56}(CH_3COO)_{12}]X_4$ with X = Cl^-, Br^-, I^-, HSO_4^- denoted as CAU-55 containing a porous Al_{24} cluster cation $[Al_{24}(OH)_{56}(CH_3COO)_{12}]^{4+}$ (Fig. 1a).[3] The crystal structures of the aluminum acetates were elucidated by electron diffraction and single crystal X-ray diffraction and porosity of the CAU-55 compounds was confirmed by gas and vapor sorption measurements.

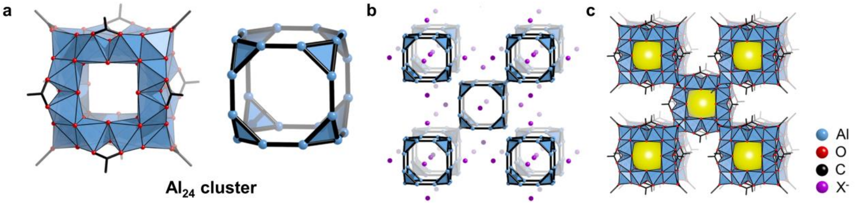

*Figure 1: Crystal structure of CAU-55. (**a**) Al_{24} ion {$[Al_{24}(OH)_{56}(CH_3COO)_{12}]^{4+}$} (**a**) built up from trimeric building units; (**b**) and (**c**) Body centered packing of Al_{24} cluster cations and anions (X^- = Cl^-, Br^-, I^-, HSO_4^-) occupying the octahedral voids and the cages being marked by a yellow sphere.*

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Reactions of Cumulenes with Bis(pentafulvene)titanium complexes

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Over the past 20 years, the frustrated system in pentafulvene complexes has been applied in effective activation reactions with various H–E bonds (E = H, C, N, O, Hal)[1] and multiple bond substrates[1,2] such as ketones or nitriles under mild conditions. Herein, we report selective reactions of bis(pentafulvene)titanium complexes **Ti1** with either one or two equivalents of cumulenes, leading to different coordination modes depending on the corresponding cumulene or the pentafulvene ligand used. Complexes resulting from reactions with one equivalent of cumulene still containing one remaining active fulvene function maintain the advantage of enabling additional substrate activation reactions with H–E bonds or multiple bond substrates, which was investigated with alcohols, amines, HCl, ketones and nitriles.

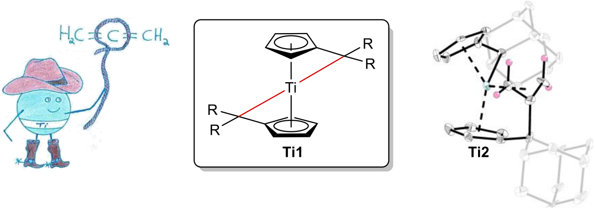

*Figure 1: Reaction of **Ti1** with propa-1,2-diene leads to the formation of Ti-allyl complex **Ti2**.*[3]

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Germaaluminocenes – Masked Heterofulvenes

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Germaaluminocenes **2** are formed by salt metathesis reactions of dipotassium germacyclopentadienediides K_2[**1**] with pentamethylcyclopentadienylaluminum dichloride followed by intramolecular rearrangement (Figure 1a).[1–2] The reactivity pattern of these sandwich complexes is determined by the electrophilic central aluminum atom and by the nucleophilic dicoordinated germanium center. Surprisingly, the products formed by reactions with Lewis acids, Lewis bases, amphiphiles and compounds with polar double bonds are those expected from the reaction of a hypothetical aluminagermapentafulvene with these types of reagents (Figure 1b). This suggests that germaaluminocenes are synthetic equivalents to these pentafulvenes.[2]

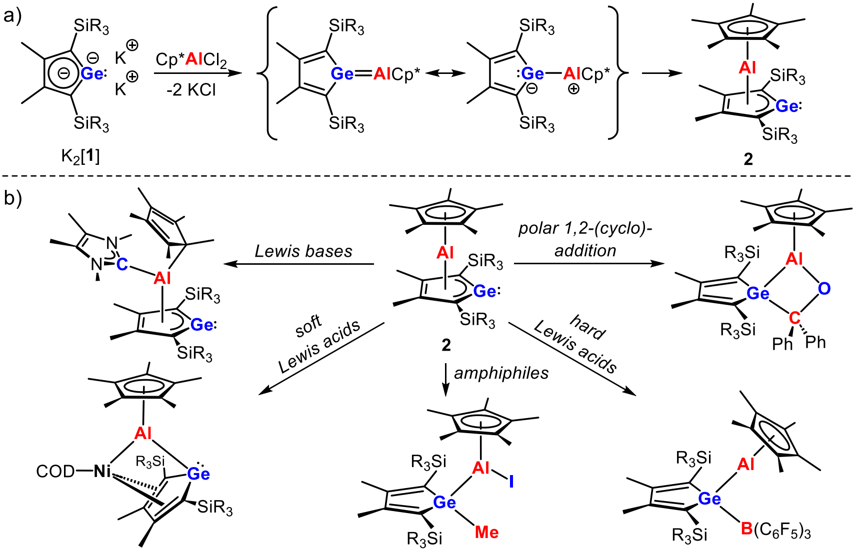

*Figure 1: a) Synthesis of germaaluminocenes **2** (SiR_3=$SiMe_3$, $SiMe_2{}^tBu$). b) Reactivity pattern of **2**.*

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The Azide-Wittig Reaction

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The construction of C=N and C=C double bonds serves as the foundation for organic synthesis in academia as well as in industry. In this context, the Wittig reaction is one of the most important reactions. In 1953, Wittig and Geissler showed that the reaction of methylene triphenylphosphorane with benzophenone gives 1,1-diphenyl-ethylene.[1] Prior to Wittig, Staudinger reported that the imine PhC(H)NPh can be formed efficiently by reacting iminophosphorane PhN=PPh$_3$ (generated from Ph−N$_3$ and PPh$_3$) with benzaldehyde.[2] This resulted in the development of aza-Wittig reactions where one of the key intermediates are so-called azidophoshphoranes, which are generally unstable and form iminophosphoranes upon N$_2$-extrusion. Furthermore, there is another significant class of compounds analogous to azidophosphoranes known as triazabutadienes (TBDs) or conjugated triazenes. In 1965, Winberg and Coffman reported the first synthetic route for TBDs by treating a bis(imidazolidine) with azides at 0 °C.[3] TBDs find wide range of applications such as diazotization reagents,[4] in metal-free cross-coupling,[5] as fluorescence sensors for Fe^{III} ions,[6] and in selective protein modification.[7]

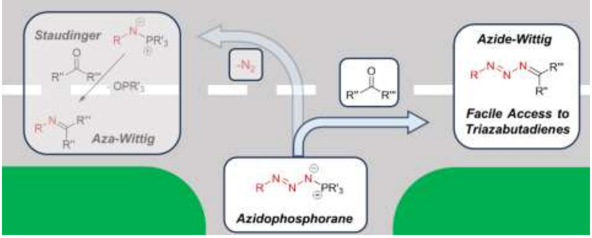

Figure 1: Wittig-type reactivity of azidophosphorane

Previously, our group has utilized phospha-Wittig reactions for the synthesis of phosphaalkene-based ligands containing P=C double bonds.[8] In our quest to synthesize bis-phosphaalkene ligands, we were only able to functionalise one arm of 2,2′-iminobisbenzaldehyde. To install an imine-unit we treated mono-functionalised 2,2′-iminobisbenzaldehyde with Mes*N$_3$ (Mes* = 2,4,6-tBu$_3$C$_6$H$_2$) and PMe$_3$. Crystal structure elucidation revealed an *E*-configured triazabutadiene unit is incorporated in place of the second aldehyde arm. This result uncovered the first Mes*N$_3$-transfer in a Wittig-type reaction. Based on this fortuitous discovery, representing that the sterically hindered azide Mes*N$_3$ and PMe$_3$ in the presence of an aromatic aldehyde yields a TBD, we now report on the "Azide-Wittig" reaction. This reaction tolerates a wide range of aldehydes and organic azides as coupling partners.

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POSTER PRESENTATIONS

Two-fold proton coupled electron transfer at a Ta(V) aniline complex mediated by a redox-active NNN pincer ligand

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Proton coupled electron transfer (PCET) reactions are of fundamental importance in catalytic applications such as CO_2 conversion, hydrogenation or ammonia oxidation reactions.[1] In transition metal complexes these concerted one electron/one proton transformations are usually associated with a change in oxidation state by the respective metal center. For these processes, the efficient weakening and control of the bond dissociation free energies (BDFEs) of the respective E–H bonds is of fundamental importance. We now show that a Ta(V) pincer complex[2] can facilitate aniline oxidation via PCET under retention of the metal oxidation state. For this a redox non-innocent pincer ligand, capable of two-electron oxidation, is utilized to mediate PCET from coordinated aniline to produce a Ta(V) imido complex.

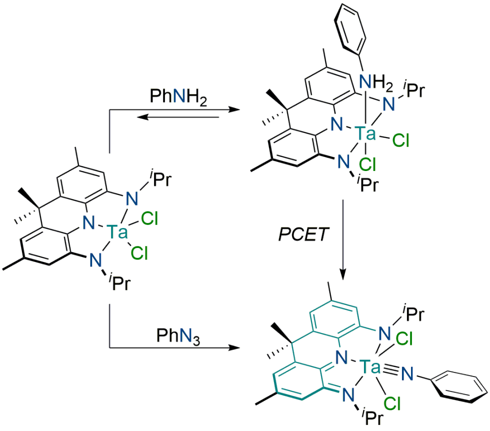

Figure 1: Synthesis of Ta(V) aniline and imido complexes and their interconversion via PCET.

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Host-Guest Chemistry in Polyoxo-Noble-Metalate Metal-Organic Frameworks

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Polyoxopalladates (POPs) are polyoxo-noble-metalates with Pd as the addenda atom and tetrahedral or tripodal oxoanions (e.g., PO_4^{3-}, AsO_4^{3-}, SeO_3^{2-}, and $PhAsO_3^{2-}$) or bidentate groups (e.g., acetate and dimethylarsinate).[1-2] On the other hand, metal-organic frameworks (MOFs) are formed by metal ions or clusters as building blocks connected by organic ligands leading to a three-dimensional structure.[3] Both classes of materials possess an enormous diversity in composition as well as structure, associated with diverse properties and applications in the areas of molecular recognition, biosensing, catalysis, and magnetism.[1-4]

In 2019, we have shown that an externally functionalized Pd_{13} POP can form a three-dimensional MOF framework, which represented the first POP-MOF, JUB-1.[5] In the present work, several derivatives of JUB-1 have been prepared via one-pot aqueous reactions and structurally characterized by single-crystal X-ray diffraction (XRD), infrared spectroscopy (FT-IR), and several other analytical techniques.

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Hybrid O/P-Donor Ligands for F-Element Chemistry

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Uranium is one of the most intriguing elements of the actinide series. It is known to exhibit multiple oxidation states and have a rich redox chemistry.[1] Uranium is well placed in the actinide series so it can involve its f-orbitals in partial covalent bonding while the U-L bonds remain quite polarized and hence reactive.[2] Low valent uranium species have been shown to activate small molecules like N_2, CO, CO_2 and H_2O.[3] Some of these reactivity patterns are not usually found with their d-block or p-block counterparts. Among various complexes with activated small molecules, there are only very few reports for catalytic reductive conversions of small molecules by uranium.[2]

To overcome the current limitations of catalytic small molecule activation with uranium, we are developing a class of hemilabile ligands based on well-established aryloxo ligands. Utilizing the mismatch between the hard Lewis acid uranium and the soft Lewis base phosphorous, we designed aryloxide-phosphine hemilabile ligands and investigated their coordination chemistry with f-elements. The insights into bonding and reactivity of the generated low valent uranium and lanthanum complexes will help to improve complex design criteria to facilitate the release of the reduced products.

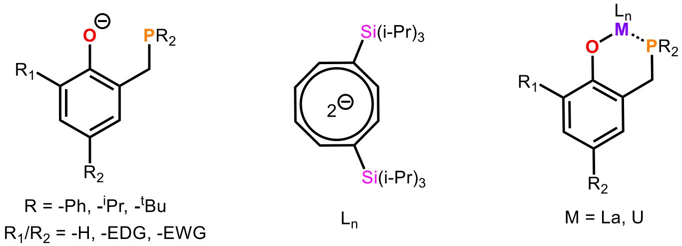

Figure 1: Synthesized ligands and the targeted lanthanide, actinide complexes.

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Reactivity of azides towards five-membered biradicals

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The reactivity of azides towards four-membered biradicals (**1**) leading to the formation of staudinger type reaction products **4** was already investigated a few years ago.[1] In this work we used an already established five-membered biradical for reactions with different types of azides.[2–3] When reacting **2** with Dipp- or Dbmp-azide (Dipp=diisopropylphenyl, Dbmp=dibromomethylphenyl), species **2**, **3** and **4** were detected in the reaction mixture. Especially the formerly unknown addition product **3** was of interest, as it is not stable in solution and slowly decomposes to form the staudinger type reaction product **4**.

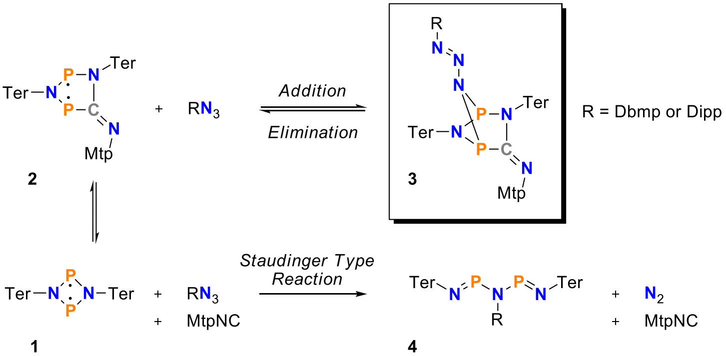

*Figure 1: Different reaction pathways when reacting five-membered biradical **2** with azides.*

Nevertheless, addition products **3** were able to be isolated as solids via selective crystallization from the reaction mixture after an exact amount of reaction time. Low temperature NMR experiments and quantum chemical calculations were performed to get further insights into the reaction mechanism as well as the properties and stability of **3**.

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A Phosphinine-Borane Adduct activates Water

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The interest in transition metal free activation of small molecules, such as H_2O, increased drastically in the past years. The ability of phosphinines to activate water is so far limited to *ortho*-donor functionalized phosphinines. Both, the SPS-phosphinine **A**[1] and the *tetra*-pyridyl phosphinine **B**[2] activate water selectively, while the PN-phosphinine **C**[3] activates water only upon coordination to a rhodium metal centre.

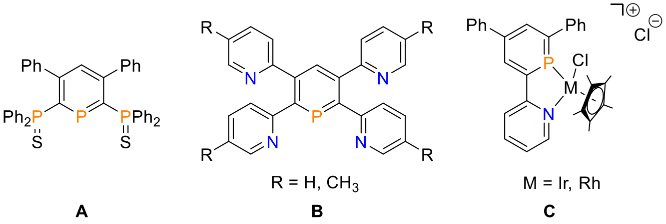

Figure 1: Literature known ortho-donor functionalized phosphinines for activation of water.[1-3]

We show here that the recently reported 3,5-bis(trimethylsilyl)-phosphinine-$B(C_6F_5)_3$ adduct (**1**) activates water in an equimolar reaction. Unlike the published examples, **1** activates water without cooperation with *ortho* functional groups in the phosphinine. In addition, the product shows a hitherto unknown keto-enol tautomerism (**2**) at the phosphinine moiety, that can be observed by means of NMR spectroscopy.

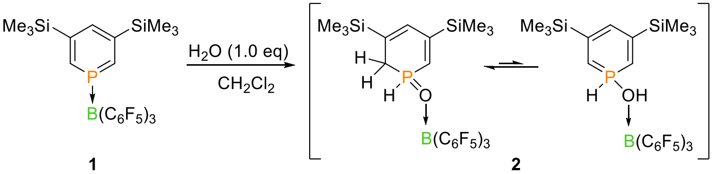

*Figure 2: Activation of water with phosphinine-borane adduct **1** and the keto-enol tautomerism (**2**).*

We investigated the reactivity of **2**, including deprotonation reactions. Further investigations in this direction are currently in process.

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From Coordination to Noncoordination: Substitution Lability of Titanium Triflato Complexes

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New concepts for obtaining cationic complexes with triflate anions from triflato ligands were developed. Various routes are leading to titanium(III) and titanium(IV) triflato complexes. The donor-free titanium(III) triflato complex is a Lewis acid and forms various adducts with monodentate Lewis bases. The reaction with bidentate ligands results in cationic titanium(III) complexes by displacement of the triflato ligand with bidentate ligands. The reactions of pentafulvene titanium complexes with either triflic acid or silver triflate give titanium(IV) triflato complexes in good yields. Hydrolysis of the titanium(IV) bistriflato complexes leads to cationic aqua complexes via displacement of the triflato ligand, which consequently acts as a non-coordinating anion (**Figure 1**).[1] Functionalized titanium(IV) triflato complexes were synthesized by insertion of pyridine-based aldehydes into the Ti–C bond. Depending on the donor strength, the triflato ligand is displaced by the pyridinyl ligand to produce a cationic complex with a triflate anion. The reactivity of those complexes was studied by reactions with an NHC and with HCl. The highly diagnostic ^{13}C NMR values of the trilate and ^{15}N NMR values of the pyridine-based ligand and UV/Vis spectra further support the coordination mode determination.[2]

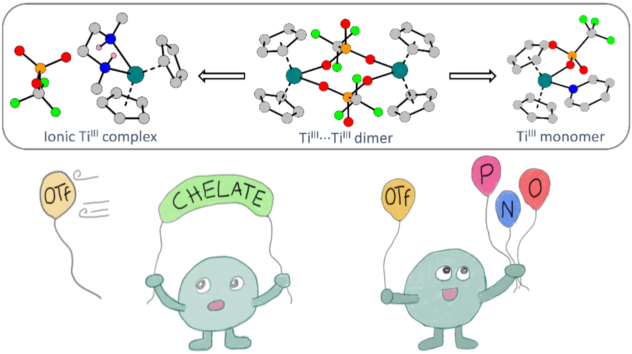

Figure 1: This work's concept of adduct formation and triflato ligand displacement in titanium complexes.

[1] Schwitalla, K.; Yusufzadeh, Z.; Schmidtmann, M.; Beckhaus, R., *Inorg. Chem.* **2024**, *63* (31), 14392-1440.

[2] *manusript in preparation*.

Development of cooperative late transition metal complexes for dehydrocoupling of amine boranes

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The historic analogy between B-N and carbon-based compounds and the expanding interest in polymeric materials based on main-group elements makes boron-nitrogen based polymers interesting targets. B-N polymers are promising materials for energy conversion and hydrogen-storage.[1] Catalytic dehydropolymerisation of amine boranes provides a promising atom efficient route to access these polymers. Compared to traditional methods such as reductive coupling or high temperature condensation this method allows to adjust polymer properties.[2] In 2010, the Manners group demonstrated that primary amine-borane adducts can be dehydrocoupled by various transition metal complexes to afford a linear polyaminoborane.[3] In recent years, our group focused on group 8/9 complexes bearing phosphorous based pincer ligands. Recently, we reported the use of Rh(I) PNN pincer complexes for dehydrocoupling of amine boranes. [4]

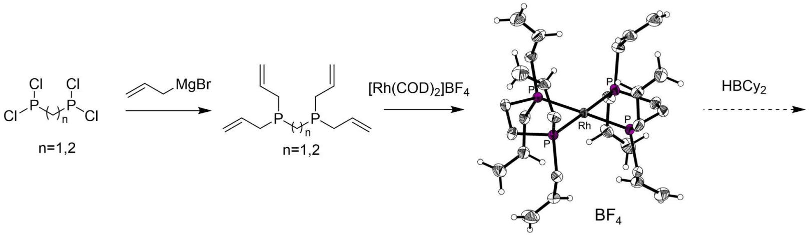

Figure 1: Synthesis of Rh(I) diphosphine complexes.

Here, we report the synthesis new phosphine ligands with introduction of Lewis acidic borane units in the secondary coordination sphere, as well as their complexation with rhodium, producing a set of new Rh(I) complexes that could be used as catalysts for the dehydrocoupling of amine boranes.

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Advances in the Kinetic Stabilization of p-Block Elements

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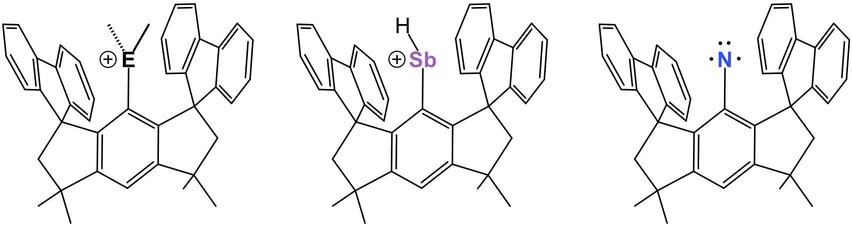
Sterically demanding substituents support the isolation of otherwise highly reactive low-valent main-group species by providing kinetic stabilization. These bulky substituents hinder unwanted reactions by physically blocking the reactive center, thus enhancing the stability of the targeted compounds such as cations and radicals. Recent advances in isolating low valent main group cations such as diarylpnictogenium cations [FluindMesE] with E = P, As, Sb, Bi have been achieved through the use of a 9-fluorenyl substituted tetramethyl-s-hydrindacen-4´-yl ("Fluind") group [1,2] originally designed by Tamao *et al.* [3] We now broadened the scope of reactive p-block element cations and radicals for applications known as "metallomimetics". In this context aryldimethyl tetrylium cations [$R_{ind}EMe_2$] **I** with E = Si, Sn, and Pb were successfully synthesized. [4] Additionally, for the group 15, we successfully isolated a stibenium ion **II** bonded only to a Fluind moiety and a hydride. These insights were instrumental for the recent preparation of the first thermally stable nitrene **III** featuring a triplet ground state. [5]



I **II** **III**

Figure 1: *Kinetically stabilized tetrylium ions **I** (E = Si, Sn, Pb), stibenium ion **II** and a thermally stable nitrene **III**.*

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Synthesis and Characterization of Lanthanide-Containing Asymmetric Wells-Dawson Ion

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Polyoxometalates (POMs) are a class of discrete, anionic metal-oxo clusters, comprising early transition metals in high oxidation states, such as W^{VI}, Mo^{VI}, and V^{V} with a large structural and compositional variety, associated with interesting physicochemical properties.[1] The aim of this work is based on the synthesis and structural characterization of *d*- and *f*-block metal-substituted POMs, with a special focus on the asymmetric Wells-Dawson ion.[2,3] To date, this system has not been investigated in much detail and hence a certain number of novel compounds can be envisioned.[4] Besides lanthanides, also *d*-block metal ions are of interest here, due to their catalytic potential. Herein, we have synthesized a family of novel polyanions, and structurally characterized them using FT-IR spectroscopy, ^{31}P and ^{183}W NMR spectroscopy and single-crystal X-ray diffraction. Some of these species are of interest in the fields of magnetism and catalysis.

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Unlocking the Lewis Acidity of Arylxenonium(II) Ions

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A plethora of organoxenon compounds have been obtained since the discovery of the first species containing a Xe−C bond, $[XeC_6F_5]^+$, in 1989.[1] Various routes for their synthesis have been established over the years, though they are often complex from the experimental point of view or proceed with low yields.[2] For the synthesis of arylxenonium(II) salts $[XeR^F][BF_4]$ (R^F = fluorinated aryl group), R^FBF_2 reagents are used, which are prepared through the defluorination of $K[R^FBF_3]$ with gaseous BF_3.[3] The ability of arylxenonium(II) ions to form Lewis acid-base adducts with N-donor bases has been demonstrated for the $[XeC_6F_5]^+$ cation.[4] On the contrary, the acidic behaviour of other arylxenonium(II) ions with partially fluorinated aryl groups has remained less investigated.

Here, a simplified synthetic route for the preparation of organoxenonium(II) salts containing aryl groups with different degrees of fluorination will be presented (Figure 1). Additionally, the Lewis acidity of those xenonium ions will be discussed, mainly in terms of the Gutmann-Beckett method, and complemented by theoretical methods such as the fluoride ion affinity (FIA) and the LUMO energy.

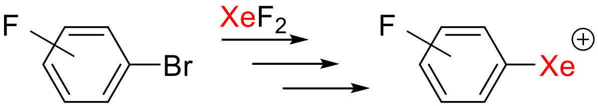

Figure 1: Synthesis of arylxenonium(II) salts.

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Interaction of DNA with Cu(II) complexes of monoalkylated oxacyclen derivatives

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Metal complexes of cyclen (1,4,7,10-tetraazacyclododecane) are suitable compounds for efficient oxidative cleavage of DNA. Thereby, a heteroatom substitution in a macrocyclic Cu(II) complex improves nuclease activity, which showed a higher catalytic property for reactive oxygen species (ROS) generation. The activity trend in substitution follows: O > S > N.[1-3]

Here, Cu(II) oxacyclen complexes with an additional monoalkylation have been investigated regarding their nuclease activity towards plasmid DNA. The length of the alkyl substituents differs: C_{12} to C_{18}. Our results have shown, that the alkylated Cu(II) complexes are able to cleave efficiently plasmid DNA at micromolar concentrations under near physiological conditions. It should be emphasised that ROS are involved in the cleavage. Furthermore, ROS are involved in the cleavage and increasing the complex concentration and length of the alkyl chain (C-12→C-18) lead to DNA aggregate formation, which was proved by atomic force microscope scanning (AFM). Additionally, formed amphiphiles of these Cu(II) complexes interact with calf thymus DNA electrostatically and by groove binding.

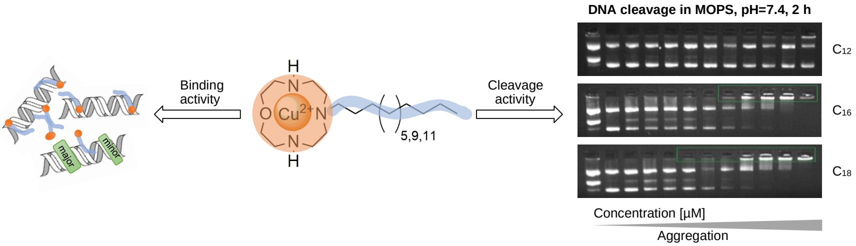

Figure 1: DNA cleavage and binding of monoalkylated Cu(II) oxacyclen complexes.

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Zinc Hydride Complexes Stabilized by Anionic N-Heterocyclic Carbenes: Application in the Hydrosilylation of Ketones, Aldehyde and CO_2

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Strategies to enhance the reactivity of zinc hydride complexes as reducing agents include generating open coordination sites and accessible terminal hydrides, resulting in the synthesis of cationic $[ZnH]^+$ species with increased Lewis acidity.[1-3] By employing anionic N-heterocyclic carbene (NHC) ligands which exhibit significant efficiency in forming neutral complexes with higher solubility,[4] we successfully generated low-coordinated and neutral zinc species. Additionally, active zinc hydride complexes ($[(WCA\text{-}IDipp)ZnH]_2$ **1** and $[(WCA\text{-}IDipp)ZnH(THF)_2]$ **2**, WCA = $B(C_6F_5)_3$, Dipp = 2,6-$iPr_2C_6H_3$), were characterized as dimers with two hydride bridges and monomers with one terminal hydride (Figure 1, a). Furthermore, complexes **1** and **2** demonstrate their capability to enhance catalytic processes with excellent catalytic activity and high selectivity in facilitating the hydrosilylation reactions of aldehyde, ketones, and carbon dioxide (Figure 1, b).

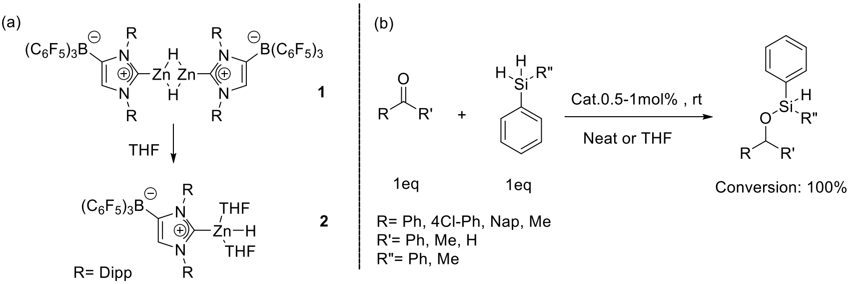

*Figure 1: (a) Structure of $[(WCA\text{-}IDipp)ZnH]_2$ **1** and $[(WCA\text{-}IDipp)ZnH(THF)_2]$ **2**. (b) Hydrosilylation reactions of aldehyde and ketones with catalysts **1** and **2**.*

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Diverse Reactivity of Cyanophosphide.

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1,3-Phosphaazallenes (RP=C=NR') are a subclass of heteroallenes which have been known for almost 40 years. Nevertheless, these heavier variants of carbodiimides are poorly investigated. Phosphaazallenes were first introduced by Kolodiazhnyi, who reacted *t*BuP(SiMe$_3$)C(OSiMe$_3$)=N*t*Bu with sodium hydroxide to yield *t*BuPCN*t*Bu.[1][2] Other synthetic routes were disclosed by Yoshifuji,[3] and Appel,[4] where they used isocyanates and in the reaction with Mes*P(Li)SiMe$_2$*t*Bu (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$) to give Mes*PCNR (R = Ph, *n*Pr, *t*Bu) in a Peterson-type reaction. In 2016, Bertrand and co-workers showed that an isolable phosphino-phosphinidene reacted with isonitriles to produce corresponding 1,3-phosphaazaallenes. Thus, RP=C=NR' can also be regarded as isocyanide adducts of phosphinidenes.[5] While investigating the reactivity of σ^4-phosphanylidenephosphoranes, our group has recently shown a facile route to access 1,3-phosphaazallenes.[6]

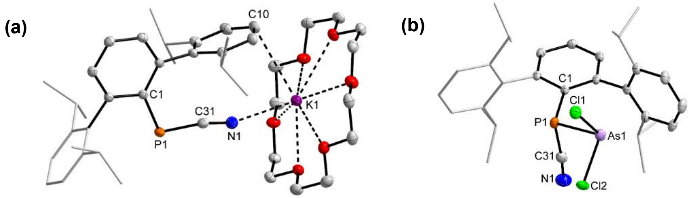

Figure 1: Molecular structure of [^{Dipp}TerPCN][K(18-c-6)], ***(a)*** *and ^{Dipp}TerP(CN)AsCl$_2$,* ***(b)****. Hydrogen atoms omitted and Dip-groups rendered as wireframe for clarity.*

In this previous work we reported the formation of cyanophosphines when heating the ^{t}Bu-NC derived phosphaazaallenes to 105 °C upon *iso*-butene elimination. In this work we optimised the synthesis of cyanophosphine ^{Dipp}TerP(H)CN (^{Dipp}Ter = 2,6-Dipp-C$_6$H$_3$) and report the molecular structures of the corresponding sodium and potassium cyanophosphides (Figure 1a). These cyanophosphides were then utilised as cyanophoshide transfer reagents and their reactivity towards various electrophiles was studied (Figure 1b).

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Syntheses of Pyridine-Stabilised Silyl Borates

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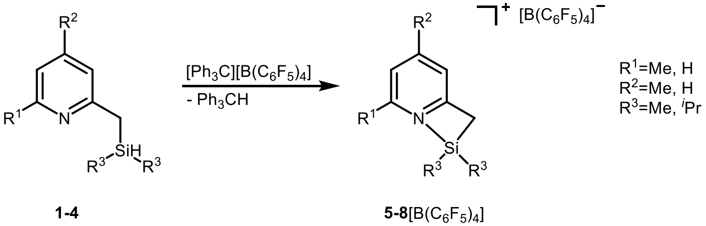
Silyl cations are strong Lewis acids which show exceptional reactivity due to their electron deficiency. The Lewis acidity can be influenced by electron donating groups and consequently the reactivity of the silyl cations can be tuned.[1] Herein we report the synthesis and characterisation of pyridine-stabilised silyl borates **5**-**8**[B(C_6F_5)$_4$] (scheme 1) and their corresponding precursor silanes **1**-**4**.[2, 3]



Scheme 1: Syntheses of silyl cations ***5-8****[B(C_6F_5)$_4$].*

By variation of the electron density of the pyridine ring as well as the substituents at the silicon atom, the Lewis acidity of these pyridine-stabilised silyl borates can be influenced. To estimate the Lewis acidity of these intramolecularly donor-stabilised silyl borates the FBN method was used.[4]

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P15

Lithium corroles – Synthesis and application for metathesis with early transition metal precursors

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In the porphyrinoid field corrole macrocycles are used to stabilze coordinated metals in high oxidation states due to a 18-π-system and trianionic nature. Structures containing early transition metals have hitheto remained scarce.[1] One possible route for coordination is metathesis via lithium corroles, as previously carried out with group 4 metals.[2]

Lithium corroles show potential for the preparation of previously unobtainable metal chelates, such as niobium or tantalum, and could even provide a way to coordinate further lanthanoids.[3,4]

The poster will present ongoing research and results on the synthesis of lithium corroles and their further use for coordination with rare earth metals.

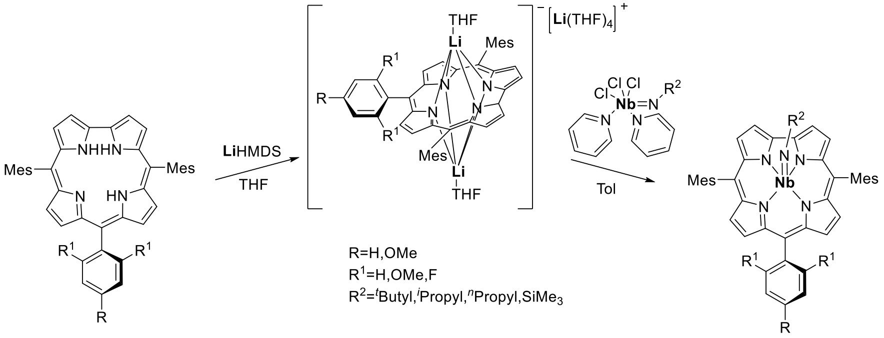

Figure 1: Synthesis route for niobium corroles via metathesis with lithium corroles and a niobium precursor.

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Fluorinated Arylarsonate-Containing Polyoxomolybdates: pH-dependent Formation of Mo_6 vs Mo_{12} Species and Their Solution Properties

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Polyoxometalates are discrete, anionic metal-oxo clusters of early transition metals in high oxidation states. The class of polyoxomolybdates comprises isopolyanions and heteropolyanions.[1-2] Polyanions with covalently bound organic groups are potentially of interest for biomedical applications.[3] Here, we report on the synthesis and characterization of several novel fluorinated arylarsonate-containing heteropolymolybdates. The reaction of different fluoro-arylarsonates with sodium molybdate in aqueous acidic medium resulted in the formation of three polyoxo-6-molybdates and three polyoxo-12-molydates, which can be interconverted reversibly as a function of pH. All six polyanions have been characterized in the solid state by single-crystal X-ray diffraction, infrared spectroscopy, elemental analysis, thermogravimetric analysis (TGA), and in solution by multinuclear NMR spectroscopy (^{1}H, ^{19}F).

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Electrochemical Hydrogenation of carbonyl compounds with a Manganese Catalyst

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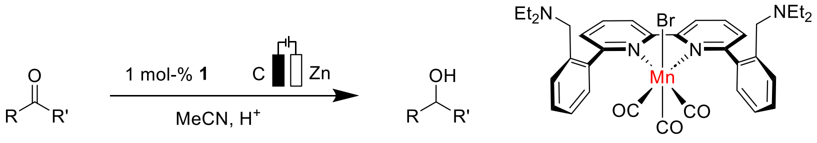
Hydrogenation reactions are key steps in the synthesis of bulk and fine chemicals and thus, have been investigated in detail over the last decades. Recently, also first row transition metal catalysts have been developed to accomplish such conversions.[1] However thermal reductions oftentimes require high pressures of H_2 and elevated temperatures.[2]

Electrochemistry has recently re-emerged as a tool in synthetic chemistry to harness energy from renewable sources for more sustainable synthesis.[3] Merging organometallic catalysis and electrochemistry is a promising strategy to direct the selectivity toward the specific target and represents an alternative approach to form catalytically active intermediates. Targeting hydrogenation reactions, we explored the electrochemical formation of the reactive metal hydride by reduction and protonation of the metal centre and established a dinuclear Mn-complex and phenol as a proton source for the chemoselective electrochemical hydrogenation of polar C=O-bonds over C=C-bonds.[4]



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Scheme 1: Electrochemical hydrogenation of carbonyl compounds using a literature known complex.[5,6]

Herein, we present a protocol for the electrochemical hydrogenation of carbonyl and carboxyl compounds using electrons and weak acids as a proton source.[5] Catalysis was achieved using a Mn-complex with an internal proton relay, previously shown to be active in the CO_2-reduction.[6]

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The Diverse Chemistry of Antimony Teflates: Superacids, Strong Oxidizers and Weakly Coordinating Anions

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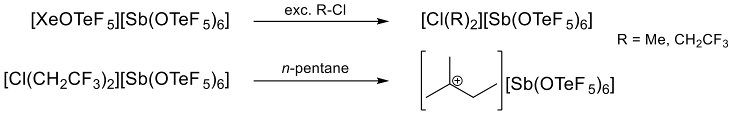
The teflate group has proven itself as a highly robust moiety which can withstand strong oxidizers and stabilizes unusual reactive cations like carbo-, halonium- and xenonium cations (Scheme 1).[1] Especially the antimony-based weakly coordinating anion (WCA) $[Sb(OTeF_5)_6]^-$ shows a high tolerance against these exotic compounds directing our interest toward further investigation of new antimony teflates.



Scheme 1: Reactivity of antimony teflates.

Furthermore, neutral antimony teflates like $SbF_3(OTeF_5)_2$ and $SbF_4(OTeF_5)$ exhibit high Lewis acidity.[2] The strength of these Sb(V) Lewis superacids can be further elevated by increasing the amount of teflate groups in the molecule. Utilizing the high reactivity of mixed antimony fluoro teflates enables the synthesis of new reactive species like $[XeOTeF_5][SbF_3(OTeF_5)_3]$ (Figure 1).

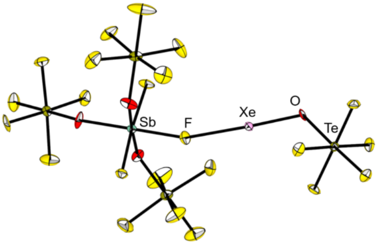


Figure 1: Molecular structure of $[XeOTeF_5][SbF_3(OTeF_5)_3]$ in the solid state.

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Synthesis of Hemilabile Cyclopentadienyl Phosphine Ligands and their Uranium Complexes for Small Molecule Activation

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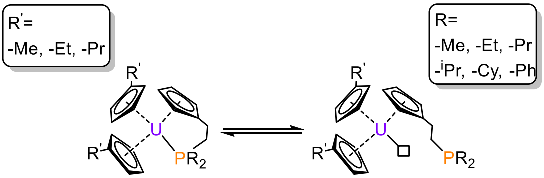
Low valent uranium complexes are strong reducing agents with reduction potentials for the U^{3+}/U^{4+} redox couple between -0.5 V and -2 V vs. Fc^{+}/Fc.[1] Therefore, they are promising candidates for reduction of e.g. CO or CO_2. However, releasing the reduction products still remains a challenge to this day. The release of reduction products from uranium is only possible by introducing groups which outcompete the binding energy of U-O bonds, such as silanes.[2]

A possible alternative approach could be the application of hemilabile phosphine ligands that allow the coordination, activation and transformation of a given substrate, as well as the dissociation of a reduction product by re-coordination of the phosphine to uranium.[3,4] In this work, we designed ligands containing a substitutionally inert cyclopentadienyl moiety and a substitutionally labile phosphine moiety, as depicted in scheme 1.



Scheme 1: Targeted behaviour of the synthesised hemilabile phosphine ligands.

Preliminary reactivity testing of the new U(III) complexes with CO and CO_2 showed promising shifts of the phosphine signals in $^{31}P\{^{1}H\}$ NMR.

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Pacman Phosphanes as Macrocyclic Ligands in Main-Group and Transition Metal Complexes

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Cofacial and so-called Pacman ligands have been used as model systems to mimic enzymes and investigate metal–metal interactions, due to their structural similarity (Figure 1, left).[1,2] We were able to introduce phosphorus instead of metals into such Pacman ligands,[3] which leads to a new class of macrocyclic bidentate phosphane ligands. We refer to such compounds as Pacman phosphanes. These Pacman phosphanes form a cavity in which metals can be coordinated in a well-defined environment (Figure 1, right).[4]

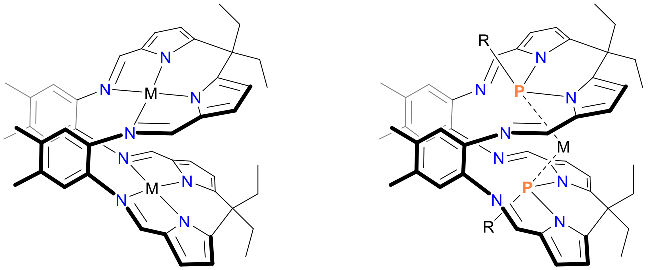

Figure 1: Pacman complex (left)[5] and a Pacman phosphane complex (right).

We used these Pacman phosphanes to synthesize complexes of main-group and transition metals ranging from boron and gallium to iron(II) and palladium(0). Due to the special structure of these complexes, interesting catalytic properties are expected. Especially the transition metal complexes might be interesting catalysts for cross-coupling reactions or CO_2 activation.

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Chemistry of η^2-dipnictene-titanocene complexes

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Strained group IV metallacycles have been shown to enable unusual ligand environments that can pave the way to new types of ligand architectures or new chemical transformations. Considering isolobal relation between alkenes and dipnictenes (R_2Pn_2), chemistry of $Cp_2M(Pn_2R_2)$ (M = Ti – Hf; Pn = P – Bi) complexes with η^2-dipnictene ligands might evolve into convenient approaches towards novel Pn-containing materials.[1]

Previous studies on this topic mainly focused on the synthesis and reactivity of $(Cp')_2Zr(\eta2\text{-}P_2Ar_2)$ systems.[2] Recently, we have demonstrated that Cp_2Ti(btmsa) (btmsa = bistrimethysilyl-acetylene) can selectively convert cyclo-Pn_3Ar_3 (Pn = P, As) into otherwise elusive $Cp_2Ti(\eta^2\text{-}Pn_2Ar_2)$ complexes, that are in focus of our current studies.[3]

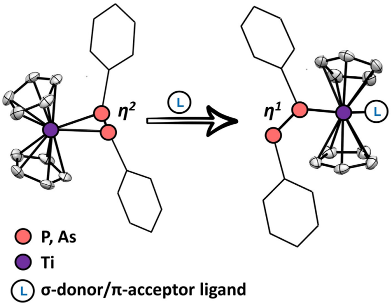

Figure 1: Reactivity of $Cp_2Ti(\eta^2\text{-}Pn_2Ar_2)$ species towards Lewis bases

Herein, we show their reactivity towards Lewis basic L-type donors, which results in an η^2 to η^1 haptotropic shift of the dipnictene ligands.

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Kinetic Stabilization of Chalcogen Radical Cations

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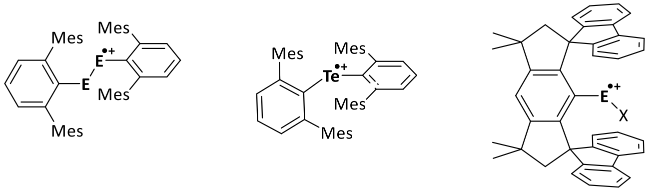
Redox processes of sulfur and selenium containing amino acids have been shown to play a major role in essential biological processes such as the protection against oxidative stress or DNA repair. When methionine residues undergo one-electron-oxidation, they can enter reaction pathways causing irreversible biological damage associated with cell aging and e.g. Alzheimer's disease.[1] Since sulfur radical cations have a very short lifetime, their isolation and characterization remains a fundamental challenge.

Previous efforts in our group using the *m*-terphenyl system led to the successful isolation and characterization of diaryl dichalcogenide $[R_2E_2]^{\bullet+}$ (**1**, E=S, Se, Te) and diaryl telluride $[R_2Te]^{\bullet+}$ (**2**) radical cations. Yet, $[R_2S]^{\bullet+}$ and $[R_2Se]^{\bullet+}$ species remain elusive.[2] Recently, major breakthroughs in the isolation of low-valent main-group species have been made using Tamao's bulky and rigid M^{S}Fluind-Ligand (see **3E**). The first example was the isolation of donor-free phosphenium and arsenium ions.[3]

Using said ligand, we prepared [M^{S}FluindEX] (E=S, Se, Te; X=aryl, halide) species as suitable precursors for one-electron-oxidations to afford the diaryl chalcogen radical cations **3E**, the isolation and characterization of which is currently ongoing.



1E **2** **3E**

*Figure 1: Previously isolated chalcogen radical cations **1E, 2** and current target compounds **3E** (E=S, Se, Te; X=aryl, halide), [B(C6F5)4]⁻ counter ions have been omitted.*

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Polynuclear complexes with a triazole dithiolate ligand

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Dithiolenes are dithiolate ligands, which are unsaturated in the carbon backbone. The associated delocalisation of electron density renders the sulfur atoms very soft Lewis bases. Combining a dithiolene unit with a triazole creates a versatile ligand, in which the nitrogen atoms serve as relatively hard donors compared to the sulfur centers. However, both sulfur and nitrogen donors can coordinate metal ions, resulting in a variety of different linking modes. Due to the versatility of redox states in dithiolene complexes, transition metal complexes of triazole dithiolate are of significant interest in regard to the synthesis of electrically conductive MOFs (Metal-organic framework).

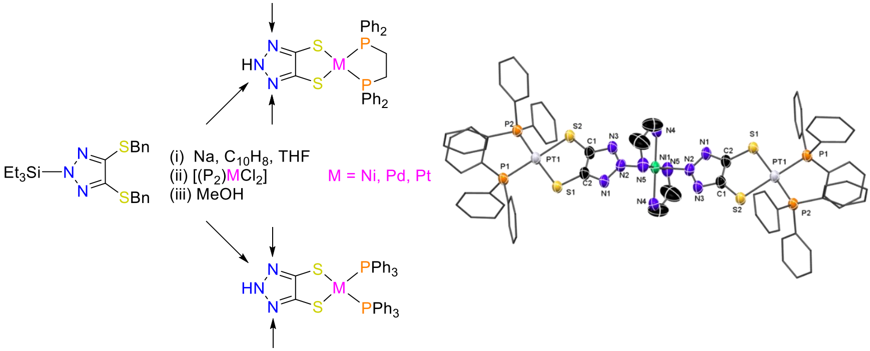

Figure 1: Synthesis of polynuclear triazole dithiolate complexes.

Mononuclear complexes can be obtained by reacting various metal precursors with the dithiolene unit. Subsequent reaction of neutral complexes with nickel(II) nitrate in the presence of ethylenediamine under basic conditions led to the formation of trinuclear complexes, in which the nickel(II) ion is coordinated by two trans-positioned triazole ligands.

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Synthesis and Coordination Chemistry of a Ferrocenyl substituted Phosphinine

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Phosphinines are six membered aromatic heterocycles containing a low coordinated phosphorus atom.[1] They are particularly interesting compounds due to their diverse coordination chemistry and their potential use in homogeneous catalysis or small molecule activation.[2,3] The first synthesis of a phosphinine by Märkl in 1966 proceeded via a pyrylium salt as starting material.[1a] Since then, other routes towards phosphinines with different substitution patterns have been developed.[1b,4] One synthetic pathway to *ortho*-substituted phosphinines is the pyrone route, in which a phosphaalkynes reacts in a [4+2]-cycloaddition.[4] However, the number of stable and readily available phosphaalkynes is limited. On the other hand, a few reactions using a phosphaalkene instead are known, but all of these reactions typically require harsh reaction conditions.[5] We now investigated the synthesis of a ferrocenyl-substituted phosphinine *via* the pyrone route using a trimethylsilyl substituted phosphaalkene, which allows mild reaction conditions. The reactivity of the novel phosphinine with various transition metal complexes afforded a series of phosphinine-based coordination compounds with the ligand in different coordination modes. Our results demonstrate the interesting structural varieties of these complexes. Further studies currently focus on the electrochemical properties of the phosphinine and the corresponding complexes.

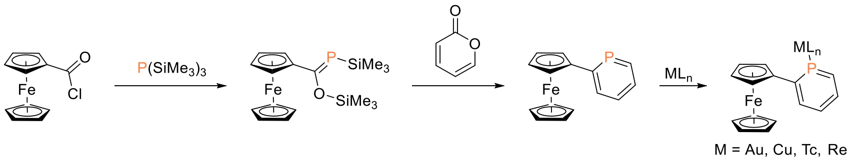

Figure 1: Synthesis of a ferrocenyl substituted phosphinine and the further reactivity with various transition metal complexes.

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Synthesis of Pacman pnictides

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In an effort to imitate the catalytic processes of chlorophyll-type enzymes, so-called Pacman ligands were first introduced in the 1970s.[1,2] Our work group got notice of a Schiff base calixpyrrole Pacman ligand **L1** and was able to introduce phosphorus into it, producing a range of Pacman phosphanes.[3–5] These Pacman phosphanes could then be used for the complexation of metals, as well as other follow-up reactions.[5,6] In this new study, the feasibility of introducing other pnictogens into **L1** was tested, in an effort to increase the reactivity and the possibility of biradical creation.

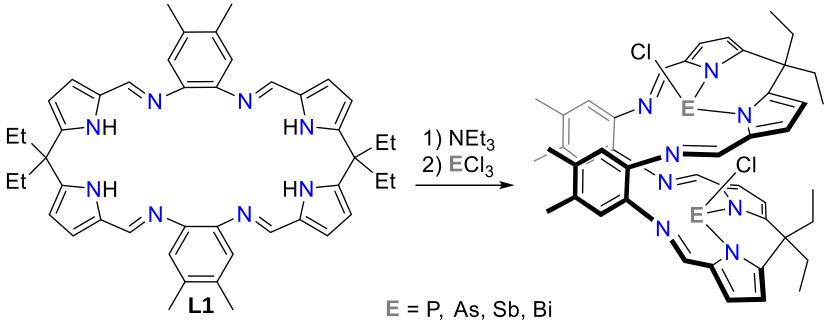

*Figure 1: Synthesis of Pacman pnictides (right) starting with Pacman ligand **L1** (left).*

We were able to synthesis new Pacman pnictides starting from **L1** and reacting it with arsenic trichloride and antimony trichloride, leading to the formation of an arsenic containing Pacman arsane as well as an antimony containing Pacman stibane.

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Synthesis and Characterization of Dimethylarsinate- and Organoarsonate-Functionalized Polyoxomolybdates

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In materials science, the rapidly evolving field of hybrid organic-inorganic materials is fostering groundbreaking innovations. Polyoxometalates (POMs), which are discrete, anionic, polynuclear metal-oxo clusters characterized by unparalleled compositional versatility and structural intricacy, exhibit distinctive physicochemical properties.[1] The synergistic integration of POMs with the flexibility and functionality of organic or organometallic components is opening new avenues in catalysis, molecular nanosciences, photo(electro-)chemistry, and biotechnology.[2,3]

Recently, we have demonstrated the incorporation of dimethylarsinate (also known as cacodylate) into polyoxo-platinates, palladates[4a], and molybdates[4b]. Here, we aimed to expand the cacodylate-containing polyoxomolybdate family by incorporating various sterically and electronically flexible organoarsonate groups in a controlled fashion. Several new compounds were synthesized efficiently via one-pot aqueous reaction and were structurally characterized in the solid state by FT-IR spectroscopy and single-crystal/powder X-ray diffraction and in solution by ^{1}H,^{19}F and ^{13}C NMR spectroscopy as well as ESI-mass spectrometry.

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Arsenic Corroles

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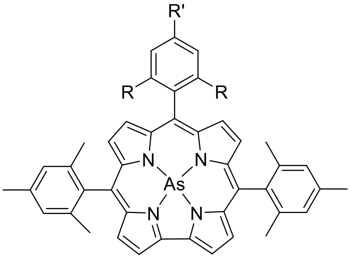
Corrole macrocycles have aroused research interest as part of porphyrinoid chemistry. Due to the trianionic nature, coordinated metals are stabilized in high oxidation states. Thus, a whole variety of metal corroles have been reported.[1] Despite this, publications of main group corroles are still few and far between, especially for the 5th main group.[2, 3]

Kadish *et al*. published As, Sb and Bi corroles with oxidation states of +3, +4 and +5.[4] Since then, no further report has been published about arsenic corroles, which might cohere with the toxic starting material $AsCl_3$ for this synthesis.

Hence, less toxic material was used as a new starting reagent for arsenic corroles with different functional groups. Furthermore, new synthetic routes were established to yield arsenic corroles in formal oxidation states of +4 and +5 with different axial ligands and will be presented on the poster.



R = OMe, F, H
R' = OMe, H

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P28

Bisimonophosphoranes as Synthetic Building Blocks

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Phosphorus-nitrogen compounds are ubiquitous in many subfields of chemistry. One class of inorganic polymers, so-called polyphosphazenes,[1] are one of the largest representatives of this substance class. Phosphinimines[2] with P^{III}=N double bonds represent another, very well researched group of substances. These can be found as synthetic building blocks in a wide variety of chemical reactions. However, the most important representatives in synthetic chemistry are the iminophosphoranes[3] of the type $R_3P=NR'$, also known as Aza-Wittig reagents, which are used in a variety of substitution reactions. These can be obtained by oxidation of a phosphine with an azide. Known, but forgotten, bisiminophosphoranes are produced in a similar way.[4] These are characterized by a particularly Lewis-acidic phosphorus atom in the center, which also has Lewis-basic neighboring nitrogen atoms. One could therefore say that the "planarization" of the molecule forces the phosphorus into a quite unique boron-like structure.

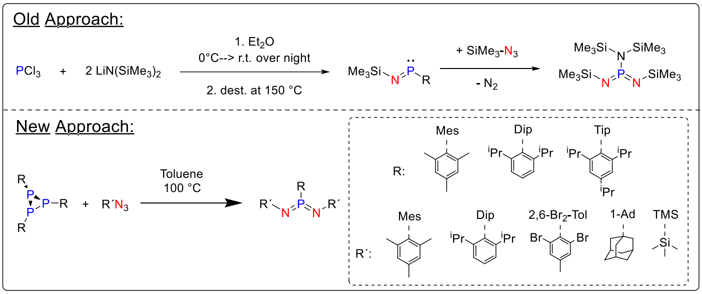

Figure 1: Synthesis of bisiminophosphoranes old and new approach

In here a new route towards bisiminophosphoranes, starting from so-called triphosphiranes, is outlined. Triphosphiranes can be considered as trimers of phosphinidenes and thus as "P-R" transfer reagents, which can be oxidized to bisiminophosphoranes by double Staudinger reactions with various azides. Aryl-triphosphiranes Ar_3P_3 (R = Tipp, Dipp, Mes) were treated with a sixfold excess of $R'N_3$ (R'= $SiMe_3$, 1-Ad, Mes, Dipp, 2,6-Br_2-Tol), and the desired bisiminophosphoranes were obtained and characterized using spectroscopic methods. A dependence of the reaction rate on the steric demand of the substrates was also established. In a subsequent reaction, the Lewis basic character of the free electron pairs of nitrogen was also demonstrated by the complexation with aluminum.

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Molybdenum mediated synthesis of bio-active indolizine-based pentathiepines: Synthesis and late-stage modification

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Pentathiepines (PTE) are organic polysulfides with a seven-membered ring of a C=C double bond and five linked sulfur atoms. The first characterized isolate of such a compound was varacin, a metabolite from the marine *Ascidiae Lissilinum vareau*, which exhibits various biological activities. PTE synthesis is often constrained by harsh, non-environmentally friendly, toxic reaction conditions and specific precursors requirements.[1] An exception is a synthetic route discovered in 2013 for synthesizing heterocyclic PTEs. This versatile method, involving the reaction of the molybdenum(IV) complex $(NEt_4)[MoO(S_4)_2]$ and elemental sulfur S_8 with N-heterocycles bearing an alkyne with a diethoxy acetal-protected aldehyde in the *ortho*-position to a nitrogen atom, has shown promising results.[2,3,4] Modifications in the heterocyclic backbone are suitable for influencing the chemical and biological properties of the PTE. Previously we observed that with increasing complexity of these substituents, the subsequent Sonogashira reaction and/or the PTE ring closure do not occur or only do so in very low yields.

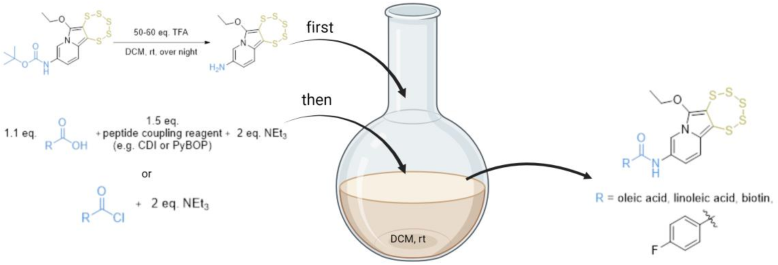

Figure 1: Graphical representation of the amino-based “late-stage” modification. The image was created with BioRender.com.

We now explore a new strategy with the amino-based “late-stage” modification, by which even larger substituents can be attached to an already synthesized PTE. This exploits our PTEs’ stability in even strong acids while they are very labile to bases.[3]

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Photoinduced hydrogenation of a N_2-derived Re-Imido complex

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The industrial production of ammonia but also of all other nitrogenous products beyond NH_3, directly depends on the energetically demanding Haber-Bosch process. As an entry to potential alternatives, the full cleavage of the N≡N triple bond by transition metal complexes at ambient conditions is well established.[1] In some cases, the resulting nitride complexes could be converted to organic nitrogenous products like amines, nitriles or amides.[2]

Our group previously reported light-driven N_2 splitting by rhenium pincer complexes. Subsequent N-atom transfer to organic electrophiles was accomplished upon chemical or electrochemical reduction at mild reduction potentials.[3] Here, we present the efficient use of H_2 as alternative reductant by using an iridium porphyrin hydride complex as new photocatalyst (Figure 1).

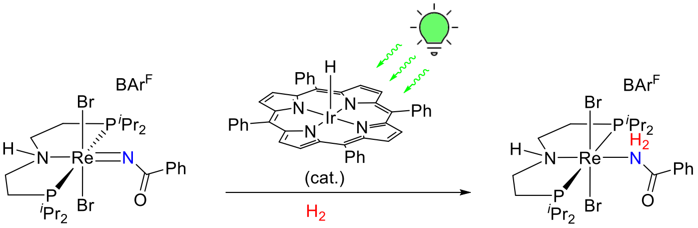

Figure 1: Photolytic hydrogenation of an N_2-derived rhenium-imido complex.

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Imidazoline-2-imine Iron(I) Complexes with Spin-Crossover Behaviour

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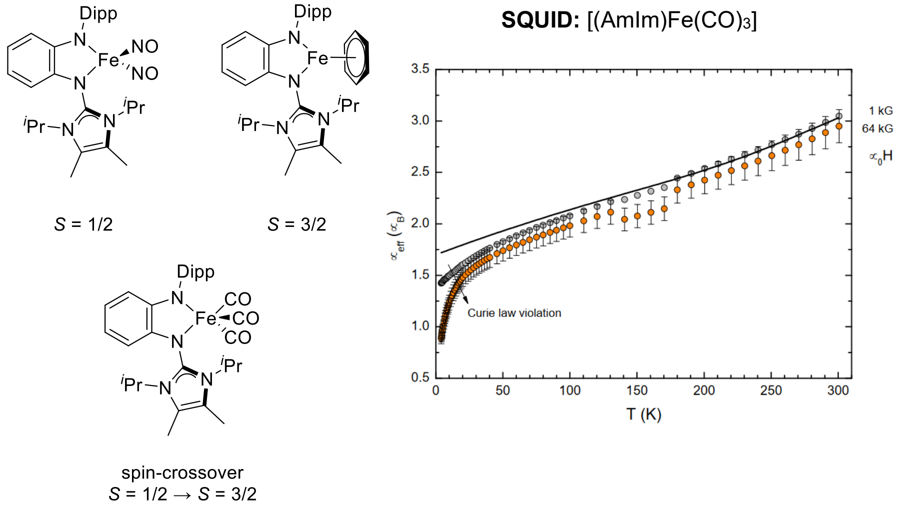
The unsymmetrical amino-imidazolin-2-imine ligand [HAmIm, 1,2-(DippNH)–C_6H_4–N=C(N*i*PrCMe)$_2$] is employed in the synthesis of the iron(I) arene complex [(AmIm)Fe(η^6-C_6H_6)], the iron(I) nitrosyl complex [(AmIm)Fe(NO)$_2$] and the iron(I) carbonyl complex [(AmIm)Fe(CO)$_3$]. The peculiar behaviour of this ligand system gives rise to both high-spin and low-spin iron(I) complexes and a spin-crossover behaviour was observed for the iron(I) carbonyl complex [(AmIm)Fe(CO)$_3$], which to the best of our knowledge is the first iron(I)-complex with this property.[1,2]



S = 1/2

S = 3/2

spin-crossover
S = 1/2 → *S* = 3/2

Figure 1: [(AmIm)Fe(I)]-complexes with different magnetic properties (left) and the SQUID for the iron(I) spin-crossover species [(AmIm)Fe(CO)$_3$] (right).[1,2]

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Oxidation of acetol with earth-abundant metal salts

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Oxidation reactions have transformed over the last few years from Cr(VI) reactants to TEMPO-mediated systems leading to highly selective synthesis routes.[1] However, these compounds have to be questioned in terms of green chemistry. Therefore, we aim for a more environmentally acceptable approach using earth-abundant metals as homogeneous catalysts in aqueous solutions and green oxidants, such as H_2O_2.

For this purpose, we chose the model substance acetol, as an α-hydroxy ketone to be selectively oxidized to its corresponding acid with, for instance, TBHP or H_2O_2. As the latter is a strong oxidant, the reaction design faces some obstacles. This problem is solved via variation of the reaction parameters. As shown in Fig. 1, the general process includes parallel synthesis and analysis of the product spectrum via HPLC.

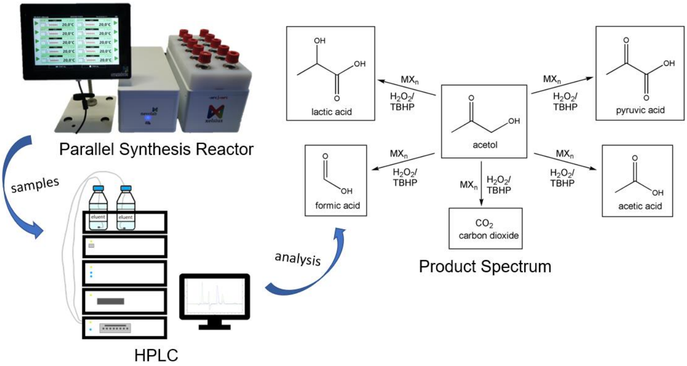

Figure 1: Experimental setting with the possible product spectrum of the oxidation of acetol

Through the variation of reaction conditions, for instance temperature, concentration and choice of catalyst, the most convenient system has to be found. Currently, the highest conversion can be obtained with a $FeCl_3/H_2O_2$ system, but the best selectivity was found with $MnCl_2/H_2O_2$ at 30 °C.

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Palladium(IV)-Containing Polyoxotungstate

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Polyoxometalates (POMs) are discrete, anionic, polynuclear transition metal-oxo complexes of early d-block elements in high oxidation states, such as W^{VI} or V^{V}.[1] POMs exhibit a large variety of shape, size and composition and potential applications ranging from material science to catalysis and biomedicine.[2] The incorporation of palladium(II) in lacunary heteropolytungstates has resulted in a number of polyanions, such as $[Pd_2(PW_{11}O_{39}H_{0.5})_2]^{9-}$, $[Pd_2(P_2W_{17}O_{61}H_{0.5})_2]^{15-}$, and $[Pd_3(H_2O)_9Bi_2W_{22}O_{76}]^{8-}$.[3] More recently the tetra-PdII-containing 30-tungsto-4-arsenate(V) $[Pd^{II}_4(As_2W_{15}O_{56})_2]^{16-}$ has been reported including some catalytic studies.[4]

Here, we report on the first example of a palladium(IV)-containing polyoxotungstate, which was characterized by single-crystal X-ray diffraction, FT-IR, XPS, and mass spectrometry.

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Synthesis and Reactivity of a square-planar Osmium(II) Complex

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The coordination chemistry of the heavier, divalent group 8 metals (Ru^{II}, Os^{II}) is dominated by octahedral complexes.[1] In contrast, four-coordinate Fe^{II} complexes are quite common and generally adopt tetrahedral ($S = 2$) or, in some cases, square-planar ($S = 1$) configurations. In comparison, four-coordinate Ru^{II} and Os^{II} tends to form seesaw structures ($S = 0$). While a few examples for square-planar Ru^{II} have been reported,[1-3] only a single square-planar osmium(II) complex is known to date.[4]
Here, the synthesis as well as the spectroscopic, structural and magnetic characterization of a rare osmium(II) complex with square-planer coordination geometry are reported (Figure 1). The electronic structure and the reactivity towards small molecules are discussed.

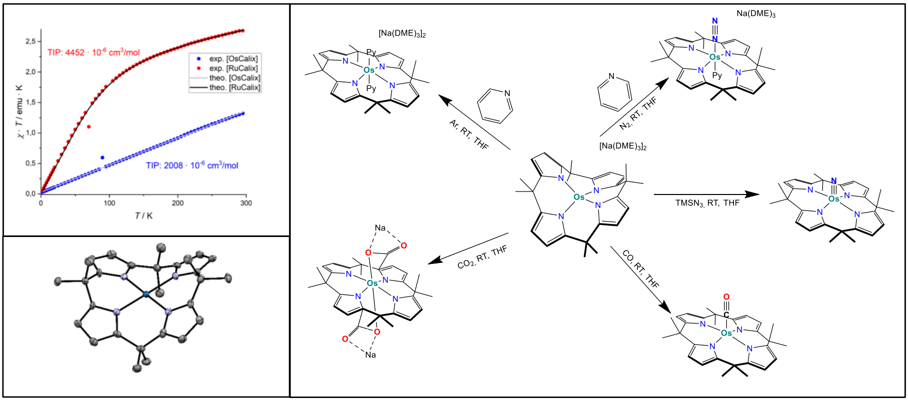

Figure 1: Magnetic squid data (top left), molecular structure of the anion in the crystal (bottom left), and reactivity (right) of osmium(II) meso-octamethylcalix[4]pyrrole.

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Influence of Supersaddling Modes on Copper Corroles: Studying Reactivity in Regioselective ß-ß'-Coupling

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Regioselective ß,ß'-coupling of A_2B-Corroles in the 2,2'-positions was achieved in 35% yield using a copper 1,10-phenanthroline catalyst in a Suzuki-Miyaura like reaction.[1,2] Copper was also used as a blocking agent for the corrole cavity. Ortho substituents of aryl substituents in the 10-position of the borylcorrole impact the conversion rate, showing high conversions for ortho substituents und low conversion for ortho free aryl groups. Attempts are presented to correlate these findings to the degree of a specific non-planar distortion mode of copper corroles, the so-called supersaddling.[3-5]

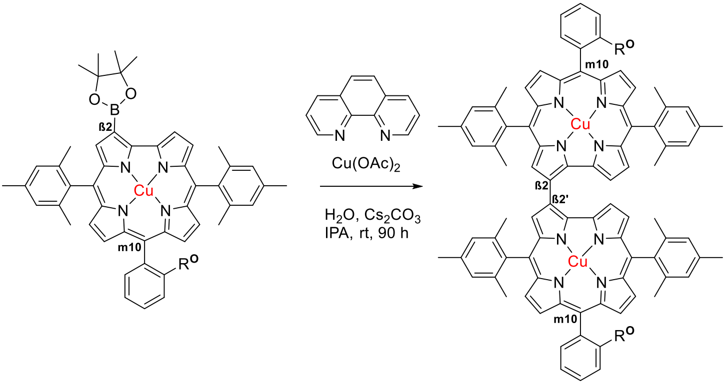

Figure 1: Regioselective coupling of copper borylcorroles.

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P36

Palladium(II)-Containing Tungstophosphate

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Polyoxometalates (POMs), a significant branch of inorganic chemistry, are formed through the condensation of high-valence transition metal ions from Group V or VI elements (e.g., V^{V}, Nb^{V}, Ta^{V}, Mo^{VI}, W^{VI}).[1] These discrete, anionic metal-oxo clusters are known for their ability to incorporate a variety of guest metal ions into lacunary derivatives.[2] However, examples of noble metal-containing POMs remain relatively scarce due to the low reactivity of these elements.[3] In 1994 the Angus-Dunne group reported the first palladium(II)-containing polyoxotungstate, $[Pd_2W_{10}O_{36}]^{8-}$.[4] Since then several more examples of palladium-containing POMs have been reported, mainly by the Kortz group.[5]

Herein, a novel palladium(II)-containing tungstophosphate has been synthesized via a one-pot aqueous route and comprehensively characterized using single-crystal X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, and NMR spectroscopy.

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Imidazolium-substituted diphosphaindenylides – synthesis, biradical character and reactivity

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Recently, a series of five-membered, resonance-stabilized bi- and tetraradicals in the form of azadiphosphaindane-1,3-diyls and 2,6-diaza-1,3,5,7-tetraphospha-s-hydrindacene-1,3,5,6-tetrayls were synthesized in our research group.[1,2] By substituting nitrogen with other elements, the reactivity and biradical character are now being varied, potentially enabling photo-switchability.

The introduction of carbon into the five-membered ring is achieved through the reaction of *N*-heterocyclic olefins (NHO) with bis-(dichlorophosphanyl)benzene in the presence of a base. The resulting dichloro-diphosphaheteroindanes can then be reduced to yield **2a-d**. Notably, in the case of derivative **d**, a partial overreduction occurs, leading to the formation of a radical anion.

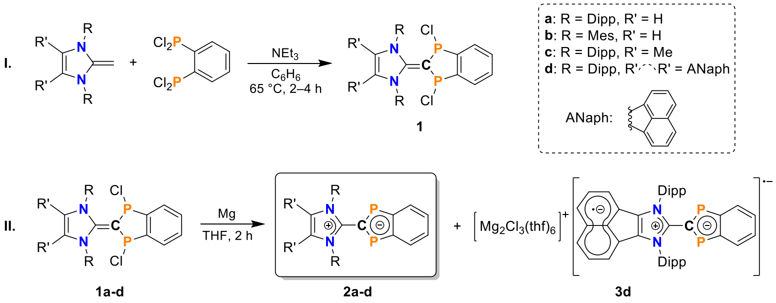

Figure 1: *Synthesis of imidazolium-substituted diphosphaindenylides* ***2a-d*** *and overreduction to the radical anion* ***3d****.*

CASSCF calculations of the four derivatives **2a-d** suggest a low biradical character of 14%. Nevertheless, **2a-d** exhibit open-shell singlet biradical-type reactivity towards triple and double bonds upon heating, leading to the formation of 1,4-diphosphanorbornene and 1,4-diphosphanorbornadiene derivatives.

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Antiferromagnetic Coupling of Dimeric Iridium PDI Complexes

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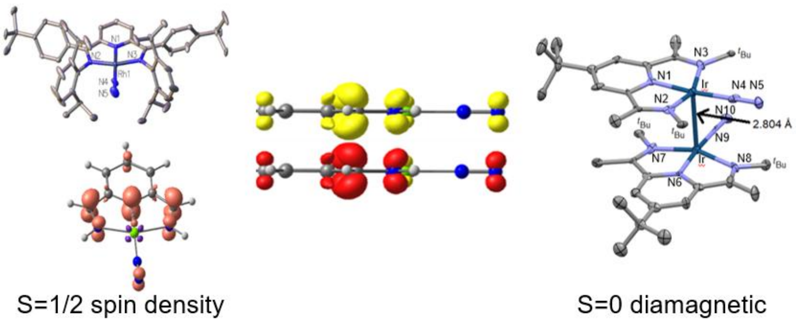

Figure 1: Example of a monomeric rhodium dinitrogen complex (left), pancake bonding / antiferromagnetic coupling (middle) and crystal structure of dimeric iridium dinitrogen complex.[1-3]

Paramagnetic transition pyridine, diimine (PDI) metal complexes frequently contain non-innocent (reduced) PDI ligands. This best illustrated by the monomeric PDI(Rh)N_2 (S=1/2) dinitrogen complex shown in Fig. 1, which is best described with an anionic ligand and a d^8-configured sq.-pl. Rh(I) center.[1-2] The main spin density is localized on the PDI unit, which is consistent with the results of X-/Q-EPR and ENDOR measurements.

We were questioning, if the spin density could be antiferromagnetically coupled through π-stacking of the PDI units. This so-called “pancake” bonding is well-known for organic radicals[3] and was envisaged for paramagnetic monomers with steric less-hindered substituents (Fig.1 middle).

We present diamagnetic iridium dimers, which display diamagnetic ground states and will discuss their reactivities and electronic properties (Fig. 1.). In addition, a range of local CCSD(T) methods and programs (LNO, PNO, DLPNO) are evaluated for their performance in calculating the monomer/dimer thermodynamics by comparison with canonical CCSD(T) calculations.

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Anionic 1*H*-/2*H*-tetrolide rearrangement: a computational investigation

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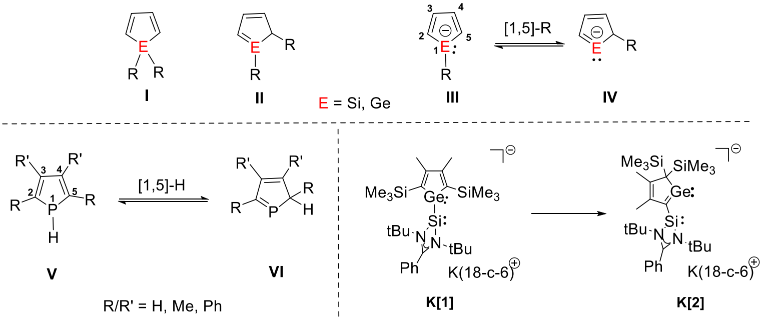
1*H*-siloles and -germoles (**I**) are well established classes of heterocycles.[1] In contrast, their 2*H*-isomers (**II**) are only discussed as short-living intermediates. [2] Anionic 1*H*-tetrolides (**III**) are isoelectronic to 1*H*-phospholes (**V**). Tautomerisation between 1*H*-/2*H*-phospholes (**V**/**VI**) are well established.[3] In contrast, the anionic 1*H*-/2*H*-tetrolides (**III**/**IV**) rearrangement were still unknown, until we recently reported that the 1*H*-germolide [**1**]$^-$ undergoes a series of three sigmatropic [1,5]-silicon shifts to give 2*H*-germolide [**2**]$^-$.[4] In this work, computational investigations are used to determine the effect of different substituents and elements on the mechanism of the anionic 1*H*-/2*H*-tetrolides rearrangement **III**⇌**IV**.



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