23. Norddeutsches Doktorandenkolloquium in Berlin

05. und 06. Oktober 2023

Inhaltsverzeichnis

Grußwort zum 23. NDDK

Liebe Kolleginnen und Kollegen, liebe Doktorandinnen und Doktoranden,

im Namen des Instituts für Chemie und Biochemie der Freien Universität Berlin möchten wir Sie ganz herzlich zum 23. Norddeutschen Doktorandenkolloquium (NDDK) in Berlin-Dahlem begrüßen. Es ist uns eine große Freude, nach der Corona-bedingten Aussetzung seit 2020, diese Tagung nun endlich ausrichten zu dürfen.

Das NDDK blickt bereits auf eine sehr lange und äußerst erfolgreiche Tradition zurück. Auf Initiative von Prof. Dr. Jürgen Heck (Universität Hamburg) und inspiriert durch den Verbund Norddeutscher Universitäten, wurde das NDDK 1998 ins Leben gerufen und bietet seitdem dem wissenschaftlichen Nachwuchs die Gelegenheit, nicht nur aktuelle Forschungsergebnisse in Form von Vorträgen und Postern zu präsentieren, sondern auch in angenehmer Atmosphäre diese in persönlichen Gesprächen zu diskutieren, neue Kontakte zu knüpfen und bestehende zu vertiefen.

Traditionell umfasst das NDDK die Chemie-Universitätsstandorte der Bundesländer Bremen, Hamburg, Mecklenburg-Vorpommern, Niedersachen und Schleswig-Holstein. Seit 2018 ist auch Berlin mit seinen drei Universitäten vertreten. Auch in diesem Jahr ist die thematische Bandbreit der wissenschaftlichen Beiträge wieder äußerst beeindruckend und bildet die unterschiedlichsten Forschungsgebiete der anorganischen Chemie eindrucksvoll ab, zu denen beispielsweite die homogene und heterogene Katalyse, die anorganische Molekül- und Festkörperchemie, die Material- und Koordinationschemie sowie die metallorganische Chemie in ganzer Breit zählen. Zusammen mit den ca. 134 angemeldeten Teilnehmerinnen und Teilnehmern können wir uns auf 26 spannende Vorträge und 62 Posterpräsentationen freuen. In diesem Jahr finden zum ersten Mal auch Vorträge von Nachwuchswissenschaftlerinnen und Nachwuchswissenschaftlern sowie ein Industrievortrag statt.

Wir möchten uns an dieser Stelle für die großzügige Unterstützung durch den Fachbereich Biologie-Chemie-Pharmazie der Freien Universität Berlin aber insbesondere auch für die Zuwendungen durch Sponsoren bedanken. Ohne diese wäre es uns nicht möglich gewesen, die Veranstaltung in dieser Form zu realisieren. Ein besonderer Dank gilt dabei auch allen Helferinnen und Helfern aus den Arbeitskreisen der anorganischen Chemie, die zum Gelingen des 23. NDDKs beitragen.

Zu guter Letzt wünschen wir uns allen zwei wissenschaftlich interessante und anregende Tage voller schöner Chemie und einen inspirierenden Gedankenaustausch.

Die Dozentinnen und Dozenten der anorganischen Chemie

Christian Müller   Günther Thiele

Sebastian Hasenstab-Riedel   Moritz Malischewski

Nina Huittinen   Alex Plajer

Norddeutsches Doktorandenkolloquium
Tagungsorte– 1998 bis 2023

NDDK	Jahr	Ausrichter
1	1998	
2	1999	Universität Hamburg
3	2000	
4	2001	
5	2002	Carl von Ossietzky Universität Oldenburg
6	2003	Christian-Albrechts-Universität Kiel
7	2004	Universität Hamburg
8	2005	Universität Rostock
9	2006	
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

Ein herzliches Dankeschön an den Fachbereich BCP der Freien Universität Berlin sowie den Firmen, die das 23. NDDK 2023 tatkräftig unterstützen.

BRUKER

Vacuum Spectrometers
VERTEX Series

The Peak in FT-IR Research.

- Vacuum optics for outstanding stability and sensitivity
- Prepared for Rapid and Step Scan R&D application
- FIR/THz, NIR and VIS/UV spectral range extension
- Wear-free high resolution interferometer scanner
- For numerous research fields such as solid state physics, semiconductor material and device development, time-resolved reaction monitoring under exclusion of air, catalysis, battery research etc.

For more information please visit www.bruker.com/vertex

Innovation with Integrity

Spinsolve 90

90 MHz Spinsolve
SETTING A NEW STANDARD IN BENCHTOP NMR SPECTROSCOPY

The Spinsolve 90 Benchtop NMR brings chemists more sensitivity and more resolving power than ever before, in a compact design for the lab bench.

Magritek's intuitive and powerful software includes the most advanced multinuclear spectroscopic methods that they can all run with the push of a button.

These NMR sequences include 1D and 2D methods; such as HSQC-ME, HMBC, COSY, TOCSY, ROESY, DEPT, as well as NOAH and NUS. The software also includes optional modules for routine QC/QA and GxP operation.

The Spinsolve 90 can be fitted with an autosampler for higher throughput, or a flow-cell setup for monitoring chemical reactions, delivering quality NMR data where you need it.

magritek

www.magritek.com

thermo scientific | Chemicals

Thermo Scientific™ Chemicals bietet über 80.000 Laborchemikalien zur Unterstützung Ihrer Forschung und Entwicklung in den Bereichen Analytik, Synthese, Materialwissenschaften und Biowissenschaften - vom Labor bis zur Produktion, für kleine und große Projekte. Stöbern Sie in unserem Angebot an Laborchemikalien, darunter Säuren, Basen, Biochemikalien, Lösungsmittel, Puffer und Standards, Verbindungen für die anorganische und organische Chemie, Organometallverbindungen und vieles mehr.

Verlassen Sie sich auf die globale Expertise in Produktion und Beschaffung von Thermo Fisher Scientific und die strengen Qualitätsstandards, die wir ansetzen.

Sie möchten Ihr Angebot erweitern? Vertrauen Sie den Teams von Custom and Bulk Chemical Services, die Ihre Bedürfnisse verstehen und gemeinsam mit Ihnen Tests, maßgeschneiderte Formulierungen und Verpackungslösungen nach Ihrem Zeitplan entwickeln.

Die wissenschaftliche Reise beginnt mit Chemikalien und Thermo Scientific Chemicals freut sich darauf, Ihr Partner im Dienste der Wissenschaft zu sein.

Besuchen Sie noch heute www.thermofisher.com/chemicals und decken Sie Ihren Bedarf an Chemikalien aller Art.

Lageplan

Konferenzgebäude

Sowohl die Vorträge und die anschließende Postersession des 23. NDDK finden in dem Institut der Anorganischen Chemie der FU Berlin Fabeckstraße 34/36 statt.

Über die Haltestelle der Linie U3, Dahlem Dorf ist das Konferenzgebäude fußläufig in 10 min erreichbar. Die Vorträge werden im HS-Anorganik und die Postersession am 04.10. im Foyer stattfinden. Das Abendessen am 05.10 auf dem Platz vor dem Gebäude.
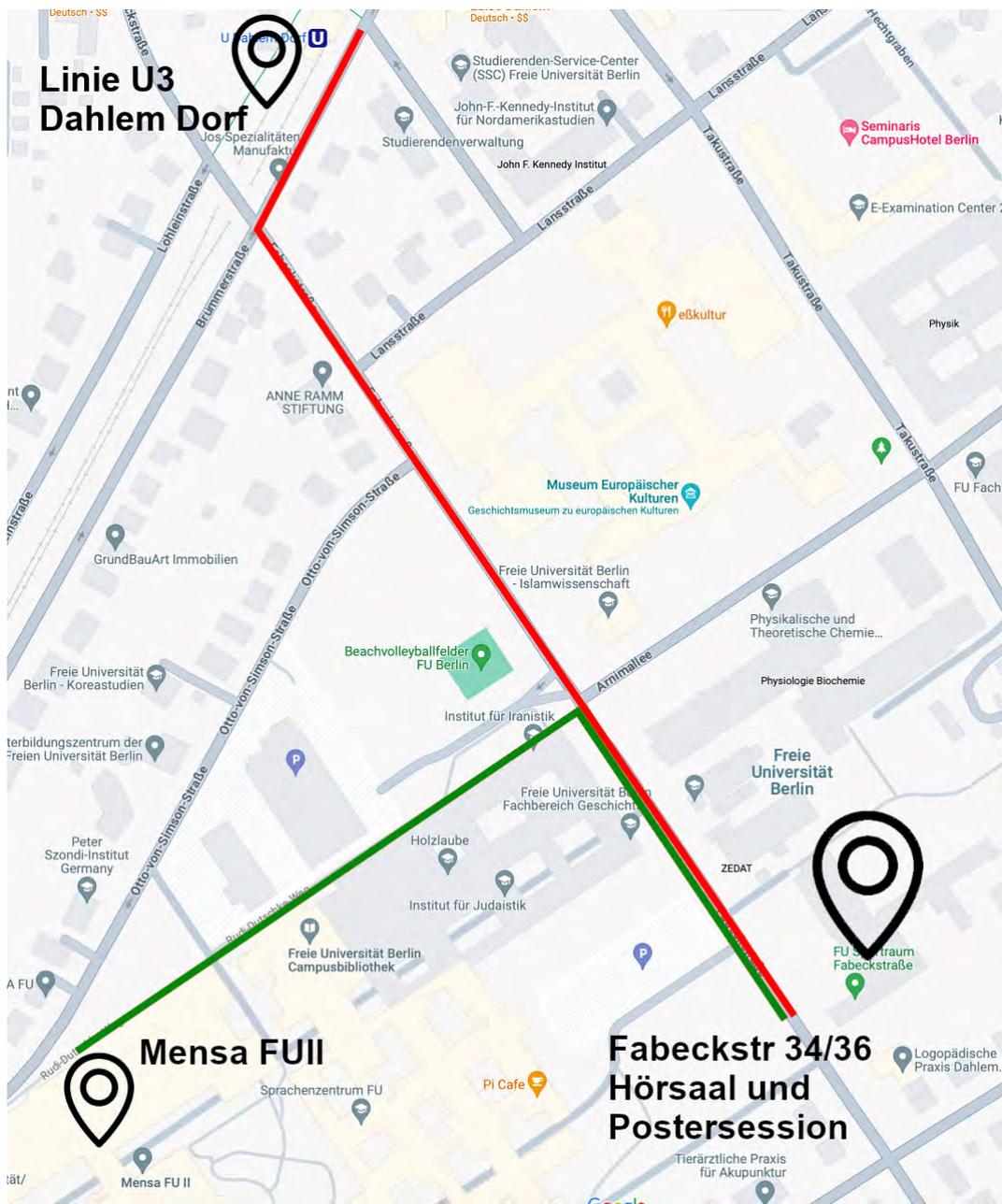
Tagungsprogramm des 23. Norddeutschen Doktorandenkolloquiums

Zeit	Aktivität	Vortragende
12:00-13:00	**Anmeldung**	
12:50	**Begrüßung**	
13:00-14.20	**Vortragsblock 1**	
13:00	O1	Josh Abbenseth
13:20	O2	N. Beims
13:40	O3	S. Eulberg
14:00	O4	R. Kopp
14:20-14:40	**Pause**	
14:40-16:00	**Vortragsblock 2**	
14:40	O5	Alex Plajer
15:00	O6	R. Tallarita
15:20	O7	S. Pätsch
15:40	O8	S. Suljić (Magritek)
16:00-16:20	**Pause**	
16:20-17:40	**Vortragsblock 3**	
16:20	O9	Malte Fischer
16:40	O10	N. Geibel
17:00	O11	J.-E. Siewert
17:20	O12	P. Fritz
17:40 - 19:00	**Poster Session**	
19:00	**BBQ**	
8:30-9:00	**Anmeldung**	
9:00-10:00	**Vortragsblock 4**	
09:00	O13	M.E. Mahmoud
09:20	O14	M. Ghanzanfari
09:40	O15	S. Wittmann
10:00-10:20	**Pause**	

10:20-11:40	**Vortragsblock 5**	
10:20	O16	A. Pérez-Bitrián
10:40	O17	T. Streit
9:00-10:00	O18	L. Fischer
11:20	O19	R. Meißner
11:40- 13:00	**Mittagspause**	
13:00-14:20	**Vortragsblock 6**	
13:00	O20	L. Vondung
13:20	O21	A.-M. Vogt
13:40	O22	M. Reihwald
14:00	O23	L. Körner
14:20-14:40	**Pause**	
14:40-15:40	**Vortragsblock 7**	
14:40	O24	C. Schwitalla
15:00	O25	M. Neben
15:20	O26	A. Linke
15:40-16:00	Abschluss	

Vortragsprogramm
Donnerstag, 05.10.2023

1. Vortragsblock

Chairman: Christian Müller

O1	J. Abbenseth	HU Berlin		Small molecule activation reactions and transition metal complexes of T-shaped pnictogens
O2	N. Beims	U Oldenburg	AK van der Vlugt	Reactivity and coordination chemistry of a Geometrically Deformed, nonsymmetric phosphorus trisamide
O3	S. Eulberg	TU Braunschweig	AK Bröning	Antimony Corroles
O4	R. Kopp	FU Berlin	AK Müller	Pyridyl-functionalised phosphinines: synthesis, coordination chemistry and reversable activation of water

2. Vortragsblock

Chairman: Günther Thiele

O5	A. Plajer	FU Berlin		Inorganic catalysis for main group rich polymers
O6	R. Tallarita	U Greifswald	AK Schulzke	Pentathiepins: insights into the molybdenum mediated synthesis of bio-active indolizine-based polysulfides
O7	S. Pätsch	U Greifswald	AK Fischer	Mechanistic studies of biomimetic OAT reactivity under aqueous conditions with bis(dithiolene) complexes of molybdenum and tungsten
O8	S. Suljić		Magritek	

3. Vortragsblock

Chairman: Sebastian Hasenstab-Riedel

O9	M. Fischer	U Göttingen		Tailored Ligand Design to Trigger Unusual and Reversible Bond Activations at Group 14 Centres
O10	N. Geibel	U Oldenburg	AK Müller	Germaaluminocenes – Masked Heterofulvenes

O11	J.-E. Siewert	LIKAT Rostock	AK Hering-Junghans	Synthesis and ligand properties of chelating bis(NHC)- stabilized bis(phosphinidenes)
O12	P. Fritz	U Rostock	AK Schulz	A reversible, selective molecular photo-switch based on a hybrid early transition metal/main group bis-biradicaloid

Freitag, 06.10.2023

4. Vortragsblock

Chairman: Alex Plajer

O13	M.E. Mahmoud	U Bremen	AK Kortz	Synthesis and Characterization of Lanthanide-Containing Asymmetric Wells-Dawson Ion
O14	M. Ghanzanfari	FU Berlin	AK Thiele	Electrical and magnetic characteristics of novel chalcogenido metalates
O15	S. Wittmann	U Bremen	AK Gesing	Synthesis and temperature-dependent structure property relations of mullite-type $SnMBO_4$ compounds

5. Vortragsblock

Chairman: Moritz Malischewski

O16	A. Pérez-Bitrián	HU Berlin		Organoxenon Compounds in Synthetic Organotransition Metal Chemistry
O17	T. Streit	FU Berlin	AK Malischewski	Reactivity of Cyanometalates towards Electrophiles
O18	L. Fischer	FU Berlin	AK Hasenstab-Riedel	A Trip to the Extreme: From Superacids and High Potential Oxidizers to Electrophilic Xenonium and Halonium Cations
O19	R. Meißner	U Hamburg	AK Schaarschmidt	Al complexes with redox-active iminophenanthrenones

6. Vortragsblock

Chairman: Nina Huittinen

O20	L. Vondung	U Hamburg	AK Urbank	Attempting to Make Uranium Behave in Small Molecule Activation
O21	A.-M. Vogt	U Kiel	AK Tuczek	A tungsten complex catalyzing the conversion of dinitrogen to ammonia
O22	M. Reihwald	U Rostock	AK Seidel	Synthesis and Characterization of Polynuclear Metalla-Ketiminate Complexes
O23	L. Körner	TU Braunschweig	AK Tamm	Diaminoacetylenes: Electron-Rich Precursors for the Preparation of Efficient Iron Cyclopentadienone Hydrogenation Catalysts

7. Vortragsblock

Chairman: Christian Müller

O24	C. Schwitalla	U Oldenburg	AK Beckhaus	Syntheses, Characterization and Multifaceted Coordination Chemistry of Hydrazonido Titanium Complexes
O25	M. Neben	U Göttingen	AK Schneider	Platinum(II) Metallopnictinidenes
O26	A. Linke	LIKAT Rostock	AK Beweries	Sulfur makes the difference: unusual C-H activation in novel iridium bis(thiophosphinite)pincer complexes

Abstracts der Vorträge

O1 - Small molecule activation reactions and transition metal complexes of T-shaped pnictogens

Josh Abbenseth*[a]

[a] Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin

josh.abbenseth@hu-berlin.de

Exploring non-VSEPR structural arrangements in main group compounds has emerged as a captivating avenue to unearth new reactivity patterns for elements within groups 13 to 15.[1] For pnictogens, the concept of planarization leading to a T-shaped configuration has been proposed as a means to generate highly Lewis-acidic compounds. However, the exploration of such species has remained limited, primarily due to challenges associated with low-yielding syntheses or the use of supporting frameworks that either disintegrate during subsequent small molecule activation reactions or fail to enforce the desired strict planarity.[1b, 2]

In this presentation, a straightforward and efficient synthesis for T-shaped pnictogen compounds will be demonstrated. These scaffolds not only enable the systematic study of the reactivity of planarized pnictogens toward small molecules but also facilitate the investigation of their potential as ligands for transition metal complexes (Figure 1).[3] The exceptional rigidity of the utilized ligand frameworks, coupled with their intriguing redox properties,[4] not only paves the way for a deeper understanding of the reactivity of planarized pnictogens but also opens up unprecedented opportunities for main group-transition metal cooperativity and   metal-free hydroelementation catalysis.
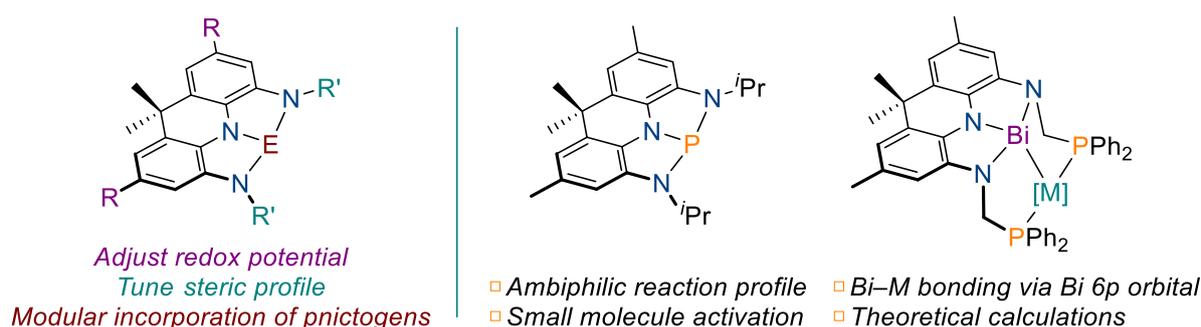
Figure 1: Key features of planarized pnictogens synthesized in our group.

[1] a) L. Greb, F. Ebner, Y. Ginzburg, L. M. Sigmund, *Eur. J. Inorg. Chem.* **2020**, 3030–3047; b) J. Abbenseth, J. M. Goicoechea, *Chem. Sci.* **2020**, *11*, 9728–9740.
[2] A. J. Arduengo, C. A. Stewart, *Chem. Rev.* **1994**, *94*, 1215–1237.
[3] A. J. King, J. Abbenseth, J. M. Goicoechea, *Chem. Eur. J.* **2023**, *29*, e202300818.
[4] J. Underhill, E. S. Yang, T. Schmidt-Räntsch, W. K. Myers, J. M. Goicoechea, J. Abbenseth, *Chem. Eur. J.* **2023**, *29*, e202203266.

O2- Reactivity and coordination chemistry of a Geometrically Deformed, nonsymmetric phosphorus trisamide

Niklas Beims,[a] Jarl Ivar van der Vlugt[a]

[a] Bioinspired Coordination Chemistry & Catalysis Group, Institute of Chemistry, Carl von Ossietzky University of Oldenburg, Germany.

niklas.beims@uni-oldenburg.de

Constraining the geometry of σ^3-P^{III} molecules effects their electronic structure and as a result also their reactivity. After pioneering work from Arduengo[1], various groups[2] developed trisamido-type P^{III} systems using tridentate NNN platforms, wherein the phosphorus is significantly distorted and thus show reactivity different from $P(NMe_2)_3$ as the 'open' congener, such as the heterolytic bond activation of protic substrates. Most of the recent research in this area has utilized a relatively narrow set of central donor functionalities, backbone structure and side group variation.
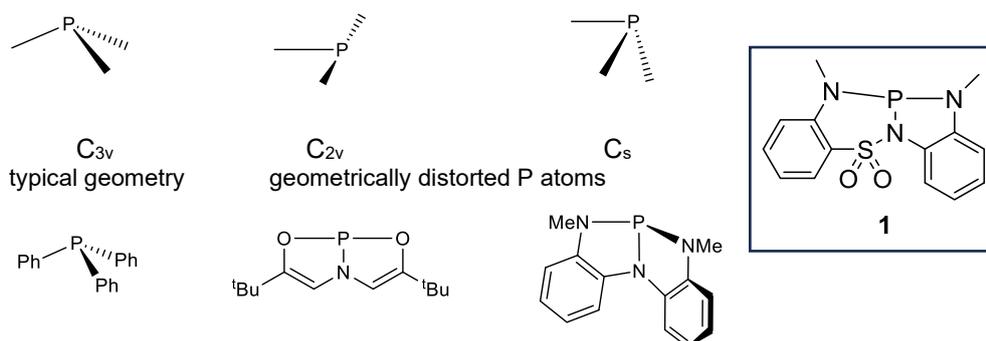
Figure 1: Illustration of different geometries in σ^3-P^{III} compounds and our new platform **1**.

We have thus recently synthesized a nonsymmetric P^{III} compound based on a 5,6-NNN ligand, featuring an electron-withdrawing sulfonamide group in its backbone. The combined features of this system provide site-selective reactivity and very high rigidity of the PN_3, eliminating umbrella-type inversions of the molecule, alongside a typically low hybridisation, and a high s-character of the P-based lone pair.

One of our main goals is to explore the effect of these factors on the σ-donor/π-acceptor abilities toward coordination of transition metals. We will discuss some of the synthesis and reactivity of this geometrically distorted P^{III} species, both as a stand-alone entity, e.g. toward oxidation and bond activation, as well as our preliminary results in the context of understanding and controlling the coordination chemistry of this platform.

[1] S.A. Culley, A.J. Arduengo III, *J. Am. Chem. Soc.* **1984**, *106*, 1164-1165; A.J. Arduengo III, C.A. Stewart, *Chem. Rev.* **1994**, *94*, 1215-1237.
[2] a) A. Brand, W. Uhl, *Chem. Eur. J.* **2019**, *25*, 1391-1404; b) J. Abbenseth, J. Goicoechea, *Chem. Sci.* **2020**, *11*, 9728-9740, c) S. Kundu, *Chem. Asian J.* **2020**, *15*, 3209-3224.

O3 - Antimony Corroles

Simon Eulberg,[a] Nina Schulze[a], Jens Krumsieck[a], Martin Bröring*[a]

[a] Institut für Anorganische und Analytische Chemie, TU Braunschweig, Germany.

simon.eulberg@tu-braunschweig.de

Porphyrinoid macrocycles are enjoying constant popularity, not least because of their versatile occurrence in nature, for example as leaf and blood pigments [1, 2]. Corroles, in contrast to porphyrins, are reduced by one methine unit, leading to a smaller N_4 cavity and a formal trianionic nature. This enables the ability to stabilize not only transition but also main group metals in unusually high oxidation states. Thus, in the past, a small number of antimony corroles in the oxidation states +III and +V have already successfully been synthesized, including the attachment of oxygen and halogens as axial ligands [3, 4, 5]. Furthermore, evidence has been found for the existence of an antimony (IV) species [6].
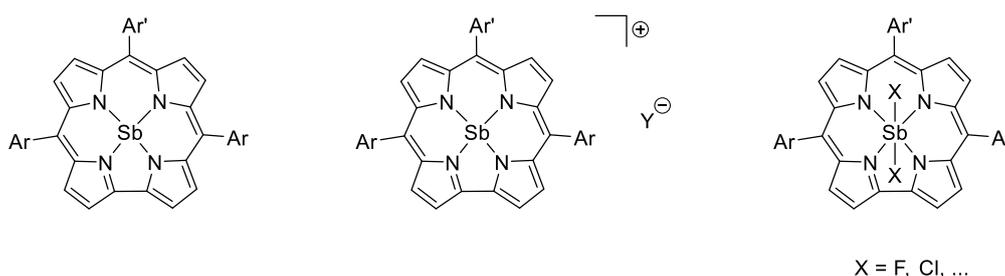
Figure 1: Overview over some of the investigated antimony corroles in the oxidation states +III (left), +IV (middle) and +V (right).

We have investigated antimony corroles from a coordination chemists perspective and will present our recent result on the synthesis and characterization of novel antimony corroles in the oxidation states +III, +IV and +V, including the attachment of various functionalized groups.

[1] I. Fleming, *Nature* **1967**, *216*, 151-152.
[2] M. F. Perutz, M. G. Rossmann, A. F. N. N. Cuillis, H. Muirhead, G. Will, A. C. T. North, *Nature* **1960**, *185*, 416-422.
[3] I. Luobeznova, M. Raizman, I. Goldberg, Z. Gross, *Inorg Chem* **2006**, *45*, 386-394.
[4] A. Mahammed, Z. Gross, *Angew Chem Int Ed* **2015**, *54*, 12370-12373.
[5] C. M. Lemon, S. J. Hwang, A. G. Maher, D. C. Powers, D. G. Nocera, *Inorg Chem* **2018**, *57*, 5333-5342.
[6] K. M. Kadish, C. Erben, Z. Ou, V. A. Adamian, S. Will, E. Vogel, *Inorg Chem* **2000**, *39,* 3312-3319.

O4 - Pyridyl-functionalised phosphinines: synthesis, coordination chemistry and reversible activation of water

Richard O. Kopp,[a] Sabrina Kleynemeyer,[a] Lucie J. Groth,[a] Moritz J. Ernst,[a] Manuela Weber,[a] Susanne Rupf,[a] Nathan T. Coles,*[a,b] Samuel E. Neale,*[c] and Christian Müller*[a]

[a] Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany, [b] School of Chemistry, University of Nottingham, United Kingdom, [c] Department of Chemistry, University of Bath, United Kingdom

richard.kopp@fu-berlin.de

Phosphinines are intruiging ligands for coordination chemistry due to their highly diverse substitution pattern. In particular, pyridyl-functionalized phosphinines can show interesting binding motifs in transition metal complexes due to their hard N- and soft P-donor properties.[1] However, the list of such compounds described in the past is short, besides NIPHOS, 2-pyridyl-4,6-diphenyl-phosphinines[2] or the phosphorus analog of terpyridine.[3] Therefore, we started to prepare NPN-pincer ligands (1) via the synthetic route reported by MATHEY and co-workers.[3] During the course of our investigations on the synthesis, coordination chemistry and reactivity of such λ^3-phosphinines, we now found that compounds of type 1 do not only show an interesting coordination chemistry, but readily react fully reversible with H_2O to the corresponding 1,2-dihydrophosphinine oxides (2) and its tautomer, the λ^5-phosphinin-1-ols 3.
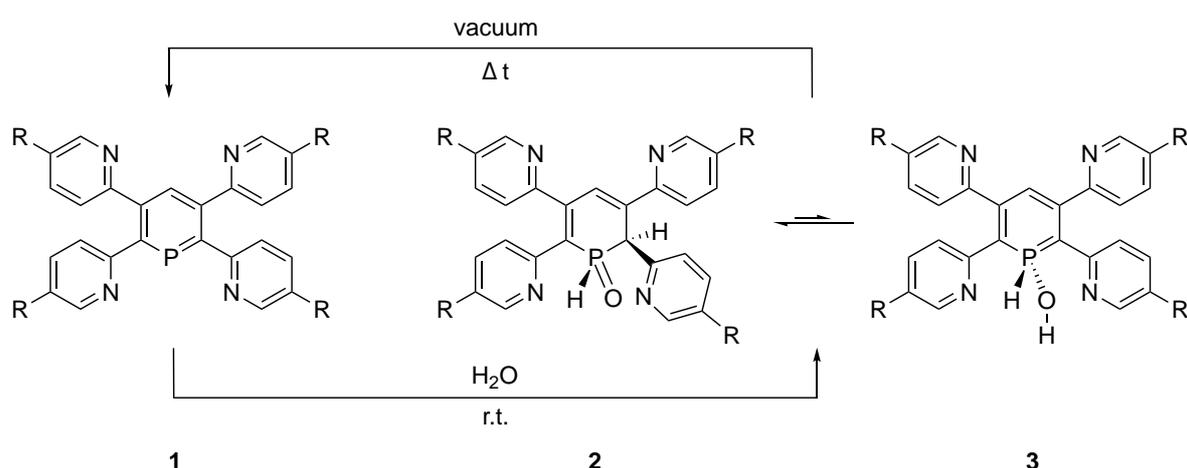
Figure 1: Reversable H_2O addition to 1 to afford the 1,2-phosphinine oxide (2) and phosphinine-1-ol (3) tautomer.

[1]   N. Coles, A. Sofie Abels, J. Leitl, R. Wolf, H. Grützmacher, C. Müller, *Coord. Chem. Rev.* **2021**, *432*

[2]   C. Müller, D. Wasserberg, J. J. M. Weemers, E. A. Pidko, S. Hoffmann, M. Lutz, A. L. Spek, S. C. J. Meskers, R. A. J. Janssen, R. A. Van Santen, et al., *Chem. - A Eur. J.* **2007**, *13*, 4548–4559.

[3]   C. Müller, E. A. Pidko, M. Lutz, A. L. Spek, D. Vogt, *Chem. - A Eur. J.* **2008**, *14*, 8803–8807.

[4]   N. Avarvari, P. Le Floch, F. Mathey, *J. Am. Chem. Soc* **1996**, *118*, 11978–11979

O5 - Inorganic catalysis for main group rich polymers

Alex J. Plajer*[a]

[a] Institut für Chemie und Biochemie, Freie Universität Berlin. *plajer@zedat.fu-berlin.de

CS_2 promises easy access to degradable sulfur-rich polymers and insights into how main-group derivatisation affects polymer formation and properties, though its ring-opening copolymerisation is plagued by low linkage selectivity and small-molecule by-products.[1-5] We demonstrate that a cooperative Cr(III)/K catalyst selectively delivers poly(dithiocarbonates) from CS_2 and oxetanes while state-of-the-art strategies produce linkage scrambled polymers and heterocyclic by-products.[6] The formal introduction of sulfur centres into the parent polycarbonates results in a net shift of the polymerisation equilibrium towards, and therefore facilitating, depolymerisation. During copolymerisation however, the catalyst enables near quantitative generation of the metastable polymers in high sequence selectivity by limiting the lifetime of alkoxide intermediates. Furthermore, linkage selectivity is key to obtain semi-crystalline materials that can be moulded into self-standing objects as well as to enable chemoselective depolymerisation into cyclic dithiocarbonates which can themselves serve as monomers in ring-opening polymerisation. Furthermore, the methodology can be expanded to the copolymerisation of cyclic thioanhydrides to produces alternating polyester-thioester which show degradability benefits over all oxygen polymers.[7] Our work demonstrates the potential of cooperative catalysis to produce previously inaccessible main-group rich materials with beneficial chemical and physical properties.
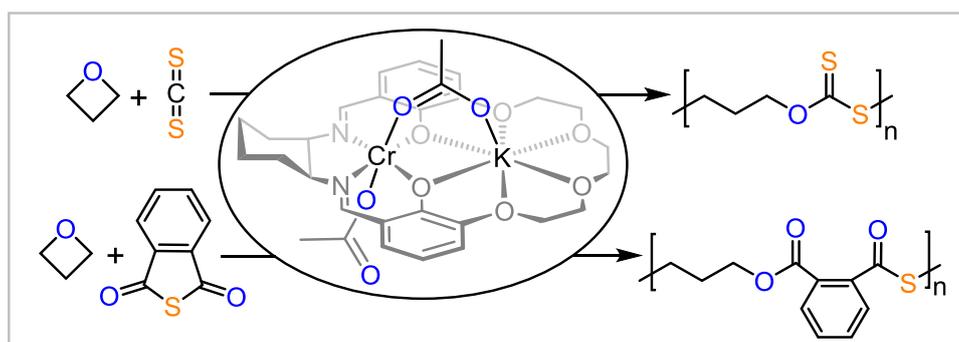
Figure 1: Copolymerisation of CS_2 or phthalic thioanhydride with oxetane .

[1]   S. M. Rupf et int., A. J. Plajer* Chem. Sci. 2022, 13, 6355-6365
[2]   D. Silbernagl et int., A. J. Plajer* Polym. Chem. 2022, 13, 3981-3985
[3]   A. J. Plajer* ChemCatChem 2022, 14, e2022008
[4]   P. Deglmann et int., A. J. Plajer* Cat. Sci. Tech. 2023, 13, 2937-2945
[5]   J. Stephan et int., A. J. Plajer* Cell Rep. Phy. Sci. 2023, 4, 101510
[6]   C. Fornacon-Wood et int., Alex J. Plajer* Nat. Commun. 2023, 14, 4525
[7]   C. Fornacon-Wood et int, Alex J. Plajer* Chem. Commun. 2023, DOI: 10.1039/D3CC03315E

O6 - Pentathiepins: insights into the molybdenum mediated synthesis of bio-active indolizine-based polysulfides.

Roberto Tallarita[a], Carola Schulzke *[b]

a,b *Institut für Biochemie, Universität Greifswald, Germany.*

roberto.tallarita@uni-greifswald.de, carola.schulzke@uni-greifswald.de

Pentathiepins (PTTs) are heterocycles bearing a seven-membered ring, five of which are interconnected sulfur atoms and two are sp^2 carbons C=C. They comprised a chemical curiosity until their identification in marine animals belonging to *Ascidiae,* displaying formidable cytotoxic properties against pathogens such as bacteria.[1] Their synthesis typically required conditions and chemicals hard to handle,[2] except for the serendipitous breakthrough case involving the bistetrasulfido(oxo)molybdate(IV) complex $(NEt_4)_2[Mo^{IV}O(S_4)_2]$. [3] This most convenient approach involves the use of azines possessing an alkyne decorated with a diethoxy acetal-protected aldehyde in *ortho* position to the nitrogen atom, easily achievable with the widely explored Sonogashira cross coupling reaction.[4] Further treatment with half equivalent of the complex and one eq. of elemental sulfur (S_8) leads to the formation of a PTT ring fused on a pyrrole cycle (Figure 1). The product is a [1,2,3,4,5]pentathiepino[6,7-a]indolizine.
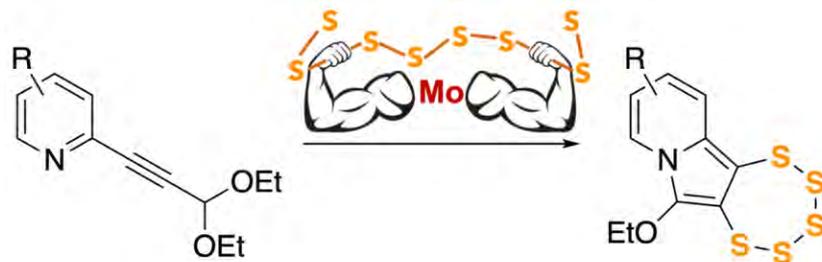
Figure 1: Graphical representation of molybdenum complex generating bio-active poly-sulfur species.

Previous studies limited the execution of the reaction to inert and anhydrous conditions.[5] Our recent findings broaden the procedure to an easier operation with non-dried solvents in air in some cases. The chosen combination of conditions in relation to the azine functional groups, can boost or drop the yields with remarkable differences. Furthermore, the possibility of decorating the pyrrole side of the indolizine scaffold is amplified by the revelation that one ethoxy (EtO^-) on propargylic position is sufficient as leaving group to facilitate the reaction.

[1]   T.N. Makarieva, V.A. Stonik, A.S. Dmitrenok, B.B. Grebnev, V.V. Isakov, N.M. Rebachyk, *Journal of Natural Products* **1995**, *58*, 2, 254-258.
[2]   L.S. Konstantinova, O.A. Rakitin, C.W. Rees, *Chemical Reviews* **2004**, *104*, 5, 2617-2630.
[3]   M. Zubair, A.C. Gosh, C. Schulzke, *Chemical Communications* **2013**, *49*, 4343-4345.
[4]   R. Chinchilla, C. Nájera, *Chemical Reviews* **2007**, *107*, 3, 874-922.
[5]   S. Behnisch-Cornwell, S. Bandaru, M. Napierkowski, L. Wolff, M. Zubair, C. Urbainsky, C. Lillig, C. Schulzke, P.J. Bednarski, *ChemMedChem* **2020**, *15*, 1515-1528.

O7 - Mechanistic studies of biomimetic OAT reactivity under aqueous conditions with bis(dithiolene) complexes of molybdenum and tungsten

Sebastian Pätsch,[a] Anna-Lena Land,[a] Carola Schulzke,[a] Christian Fischer*[a]

[a] *Department of Bioinorganic Chemistry, Institute of Biochemistry, University of Greifswald, Germany.*

sebastian.paetsch@uni-greifswald.de

Molybdenum and tungsten containing oxidoreductases comprise a ubiquitous enzyme class that catalyzes the transfer of a single oxygen atom (oxygen atom transfer, OAT) to a suitable substrate (SO_3^{2-}, SeO_3^{2-}, AsO_3^{3-}) or *vice versa*.[1] Water, coupled via a proton-coupled electron transfer (PCET), equally takes on the role as sink or source of the oxygen. In bioinspired model chemistry, the use of organic solvents and artificial oxidizing or reducing agents may only reflect the reality in the enzyme to a limited extent, also with regard to the pH dependence.[2]
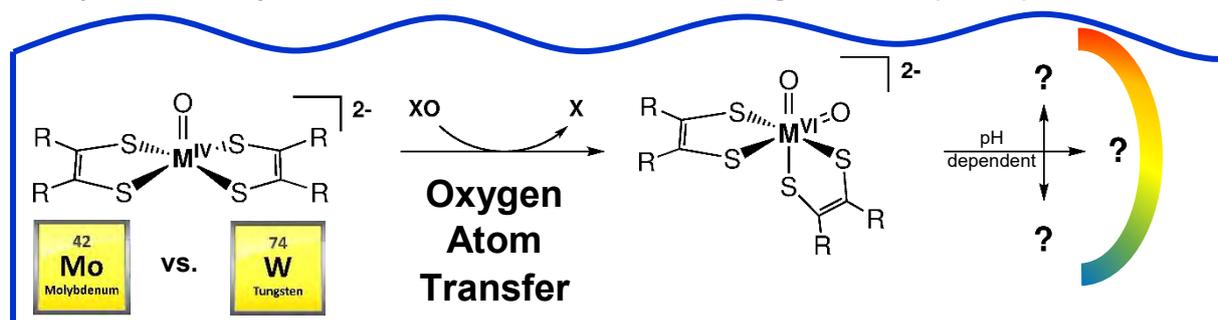
The most frequently used scaffold for these functional analogues is represented by two dithiolene ligands plus one or two additional oxo moieties, $[M^{IV}O(dt)_2]^{2-}$ and $[M^{VI}O_2(dt)_2]^{2-}$ (M=Mo,W; dt=dithiolene).[3] The introduction of alkali metal ions increased the solubility in water to enable investigations under aqueous conditions. As secondary information, all of these substances generate an unusual solid state structure for mononuclear coordination compounds, a coordination polymer.

Spectroscopic (UV/vis) examination of OAT reactivity in dependence of the pH revealed a substantial difference to literature-known mechanistic studies. The isolation of the first water-soluble bis(dithiolene) tungsten(VI) complex in combination with pH-dependent kinetic investigations supported the unravelling of the processes after oxygen transfer. The electronic effects of the dithiolene backbone as well as the pH value are affecting the observed follow-up reaction which opens up a possibility to adjust the reactivity in the desired direction.

[1] S. Pätsch; J.V. Correia; B.J. Elvers; M. Steuer; C. Schulzke *Molecules* **2022**, *27*, 3695
[2] Z. Xiao, M. A. Bruck, J. H. Enemark, C. G. Young, A. G. Wedd, *Inorg. Chem*. **1996,** 35, 7508–7515. H. Sugimoto, H. Tano, H. Miyake, S. Itoh, *Dalton Trans.* **2011,** 40, 2358-2365.
[3] R. H. Holm, E. I. Solomon, A. Majumdar, A. Tenderholt *Coord. Chem. Rev.* **2011**, 255, 993-1015

O9 - Tailored Ligand Design to Trigger Unusual and Reversible Bond Activations at Group 14 Centres

Malte Fischer

a Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstr. 4, D-37077 Göttingen

malte.fischer@uni-goettingen.de

A major focus line in molecular chemistry is based on the development of systems extending and mimicking the well-established chemistry of increasingly scarce transition metals, both in challenging bond activation reactions and catalysis.[1] Whereas examples of formal oxidative addition (OA) steps at low-valent main group centres are increasing tremendously, these bond activation steps often demonstrate a high thermodynamic driving force, often hampering their use in catalysis.[1]

Our recently launched research group aims at tackling these issues by modern strategies in ligand design to develop a profound basis in understanding the crucial factors for enabling catalytic turnover.

In this talk, a glimpse on the overall research targets of the group in conjunction with first results will be introduced.[2]
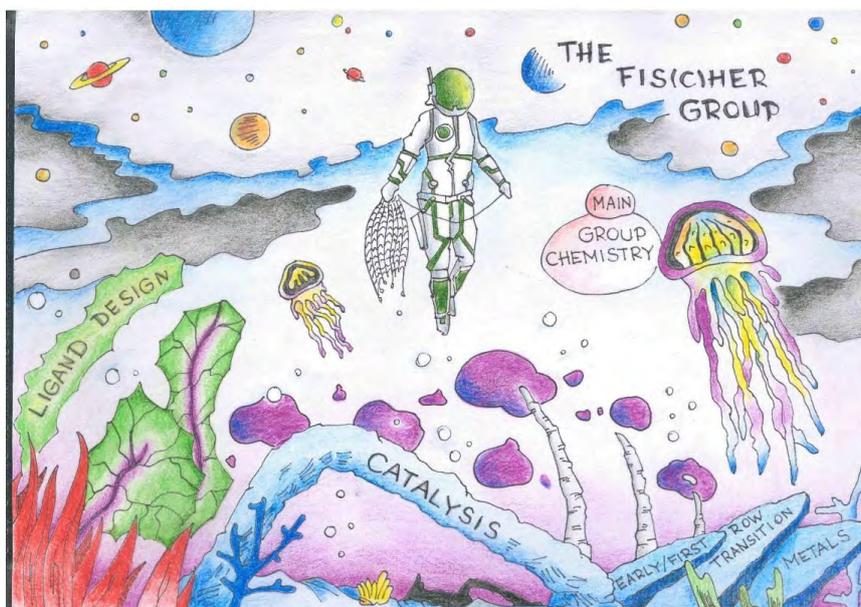
Figure 1. Grourp logo (Illustration: Vladyslav Kukulevskyy).

[1]   P. P. Power, *Nature* **2010**, *463*, 171.
[2]   a) M. Fischer, M. M. D. Roy, L. L. Wales, M. A. Ellwanger, A. Heilmann, S. Aldridge, *J. Am. Chem. Soc.* **2022**, *144*, 8908-8913; b) M. Fischer, M. M. D. Roy, L. L. Wales, M. A. Ellwanger, C. McManus, A. F. Roper, A. Heilmann, S. Aldridge, *Angew. Chem. Int. Ed.* **2022**, *61*, e202211616.

O10 - Germaaluminocenes – Masked Heterofulvenes

Nadeschda Geibel,[a] Lukas Bührmann,[a] Lena Albers,[a] Thomas Müller*[a]

[a] Institute of Chemistry, Carl von Ossietzky University Oldenburg, Germany.

nadeschda.geibel@uni-oldenburg.de

In recent years, we have studied intensively the synthetic potential of dipotassium germacyclopentadienediides, K$_2$[**1**], towards various main group electrophiles.[1] Of particular interest is the reactivity of germoledianions [**1**]$^{2-}$ versus aluminum(III)-dichlorides RAlCl$_2$. Here, the transiently formed heterofulvenes **2** undergo intramolecular rearrangement reactions via bicyclic intermediates **3** and **4**. Depending on the substituent R at the aluminum atom, products such as alumoles, **5**, germanium complexes of alumoledianions, **6**, or aluminum complexes of germoledianions, **7**, are observed.[2–3] Thus, reaction of K$_2$[**1**] with Cp*AlCl$_2$ provides germaaluminocenes **8** in high yields. Studies on the reactivity of these sandwich compounds **8** towards electrophiles, nucleophiles and amphiphiles will be presented.[4–5]
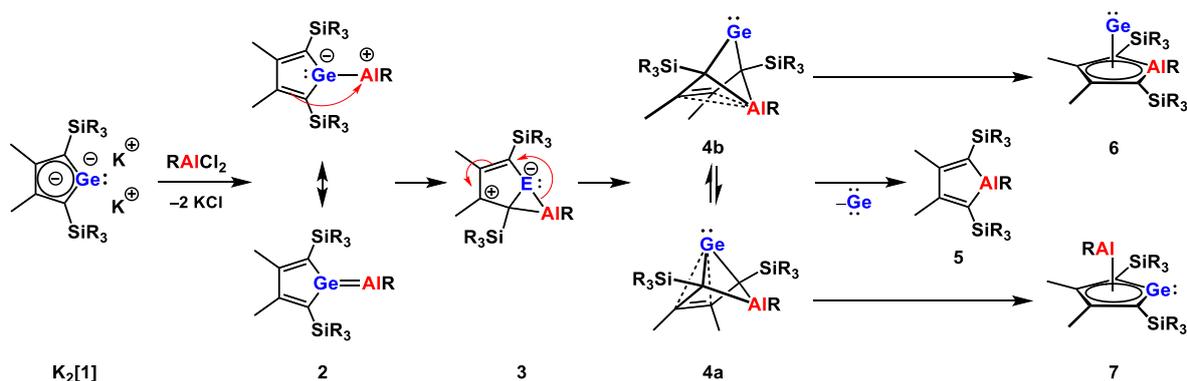
Figure 1: Reactivity of dipotassium germacyclopentadienediides K$_2$[*1*] versus aluminum(III)dichlorides.
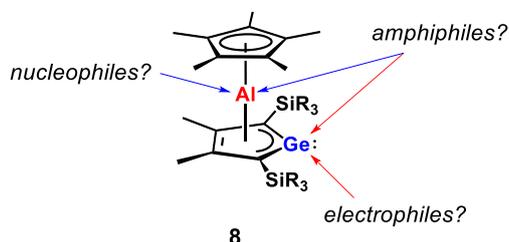
Figure 2: Reactivity studies of germaaluminocenes **8** towards electrophiles, nucleophiles and amphiphiles.

[1] Z. Dong, L. Albers, T. Müller, *Acc. Chem. Res.* **2020**, *53*, 532.
[2] L. Albers, T. Müller **2023**, submitted.
[3] L. Bührmann, T. Müller **2023**, submitted.
[4] L. Albers, P. Tholen, M. Schmidtmann, T. Müller, *Chem. Sci.* **2020**, *11*, 2982.
[5] N. Geibel, T. Müller **2023**, submitted.

O11 - Synthesis and ligand properties of chelating bis(NHC)-stabilized bis(phosphinidenes)

Jan-Erik Siewert,[a] Braulio M. Puerta Lombardi,[b] Nora Jannsen,[a] Roland Roesler,[b,*] Christian Hering-Junghans[a,*]

[a]Leibniz Institut für Katalyse e.V. (LIKAT), A.-Einstein-Str. 3a, 18059 Rostock, Germany. [b] Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, Canada.

jan-erik.siewert@catalysis.de

Chelating phosphine ligands, like diphenylphosphinoethane (dppe), have found widespread application in catalysis, due to the additional entropic stabilization imposed by these ligands.[1] In contrast to phosphines, phosphinidenes can act as potential 4 electron η^1-η^2 ligands. NHC-stabilized phosphinidenes can be described as inversely polarized phosphaalkenes. The electron-withdrawing N-atoms adjacent to P=C bond leads to an accumulation of π-density at P.

Recently, the groups of Inoue and simultaneously Hadlington and Driess introduced two chelating bis(NHC)-stabilized phosphinidene ligands (bis(NHP)s).[2–3] A Xantphos derived bis(NHP), which could act as a bidentate ligand for element dihalides (e.g. $FeCl_2$, $SnBr_2$) and as multidentate ligand generating a cationic Cu_3P_3 cluster.[3]

In this contribution the synthesis of a novel methylene bridged bis(NHP) ligand and its application in the coordination chemistry of Rh is discussed. The second lone pair can be selectively addressed by coordination of AuCl. The catalytic utilization of the novel Rh(cod) complex was tested in the catalytic hydrogenation of model alkenes at ambient conditions (rt, 1 bar).[4]
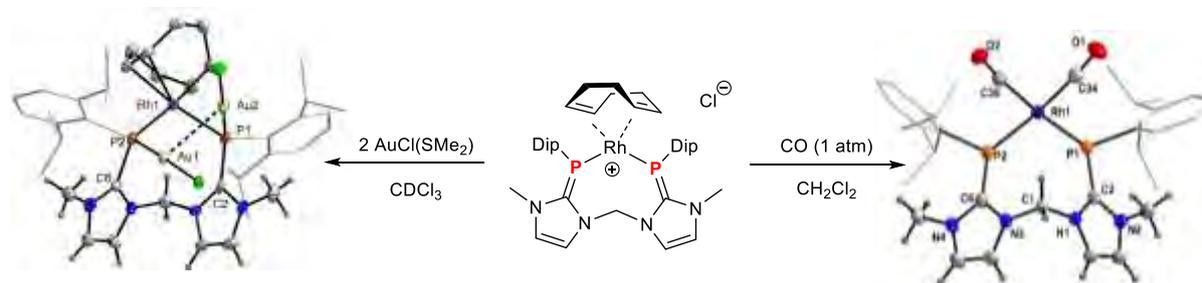
Figure 1: Novel bis(NHP) Rh(I) complex and selected reactivity at the metal or P center. (Dip = 2,6-Diisopropylphenyl)

[1]   E. I. Musina, A. S. Balueva, A. A. Karasik, in Organophosphorus Chemistry: Volume 48, *The Royal Society of Chemistry*, **2019**, 1-63.
[2]   R. Baierl, A. Kostenko, F. Hanusch, S. Inoue, *Dalton Trans*., **2021**, *50*, 14842-14848.
[3]   T. J. Hadlington, A. Kostenko, M. Driess, *Chem. Eur. J.* **2021**, *27*, 2476-2482.
[4]   J.-E. Siewert, B. M. P. Lombardi, N. Janssen, R. Roesler, C. Hering-Junghans, *ChemRXiv*, **2023**, 10.26434/chemrxiv-2023-1f1ct.

O12 - A reversible, selective molecular photo-switch based on a hybrid early transition metal/main group bisbiradicaloid

Peter Fritz,[a,b] Fabian Reiß,[b] Jonas Bresien,[a] Torsten Beweries,*[b] Axel Schulz*[a,b]

[a] Universität Rostock, Institut für Chemie Albert-Einstein-Straße 3a, 18059 Rostock, Germany.
[b] Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany.

peter.fritz@catalysis.de

The activation of small molecules such as H_2 is a desired goal in chemistry. However, the selective transformation of this often inert molecule remains a challenging task. It has been shown that the phosphorus-centred biradical (**A**) has great potential in activating small molecules and also interacts with isonitriles[1] under ring expansion to form a new biradical species (**3**). These five-membered ring systems undergo photoisomerisation to form housane type structures (**4**).[1] This behaviour is used to switch small molecule activation on or off.[2] Since complexes of group 4 metals can also show photochemical activation of small molecules,[3] it is of great interest to combine these reactivities.

The use of a functional group in the substituent of the isonitrile allowed this reactive system to be anchored to a organometallic fragment such as zirconocene (**3**). This system undergoes photoisomerisation in both directions (Figure 1, equlibrium between **3** and **4**) which allows photoinduced small molecule activation (e.g. H_2, see species **5**) that can be influenced by irradiating with light of different wavelength.
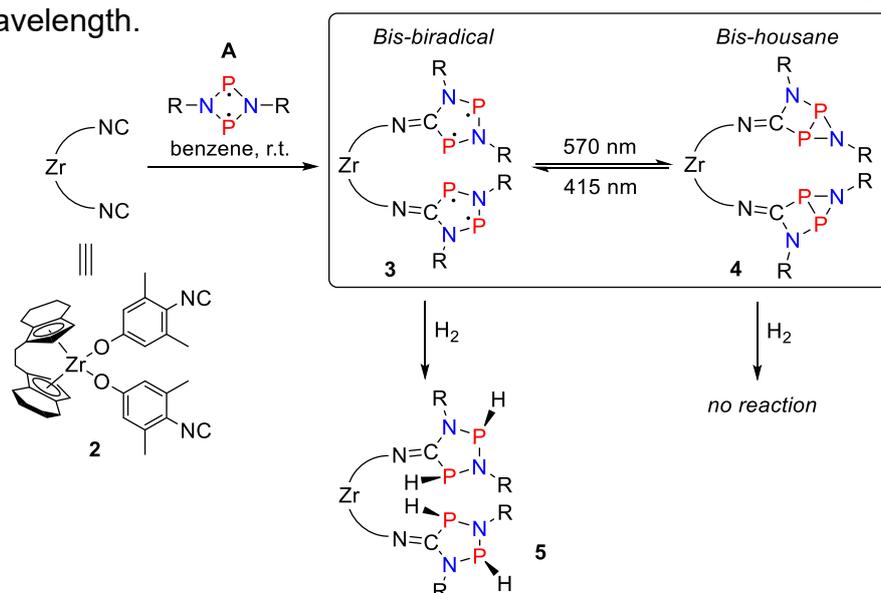
*Figure 1: Synthesis of transition metal bound phosphorus biradicaloids and their reversible photo-switchable isomerisation between bis-biradicaloid **3** and bis-housane **4**.*

[1]   A. Hinz, A. Schulz, A. Villinger, *J. Am. Chem. Soc*. **2015**, *137*, 9953–9962.
[2]   J. Bresien, T. Kröger-Badge, S. Lochbrunner, D. Michalik, H. Müller, A. Schulz, E. Zander, *Chem. Sci*. **2019**, *10*, 3486–3493.
[3]   E. P. Beaumier, A. J. Pearce, X. Y. See, I. A. Tonks, *Nat. Rev. Chem.* **2019**, *3*, 15–34.

O13 - Synthesis and Characterization of Lanthanide-Containing Asymmetric Wells-Dawson Ion

Mahmoud Elcheikh Mahmoud, Bassem S. Bassil, and Ulrich Kortz[*]

a School of Science, Constructor University, Campus Ring 1, 28759 Bremen, Germany.

ukortz@constructor.university

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.

[1] Dawson, B., *Acta Cryst.* **1953**, *6*, 113-126.
[2] Contant, R.; Piro-Sellem, S.; Canny, J.; Thouvenot, R., *Compt. Rend. Acad. Sc. – Ser. IIC-Chem.* **2000**, *3*, 157-161.
[3] Mbomekalle, I. M.; Keita, B.; Lu, Y. W.; Nadjo, L.; Contant, R.; Belai, N.; Pope, M. T., *Eur. J. Inorg. Chem.* **2004**, 276-285.
[4] Belai, N.; Dickman, M. H.; Pope, M. T.; Contant, R.; Keita, B.; Mbomekalle, I.-M.; Nadjo, L., *Inorg. Chem.* **2005,** *44*, 169-171.

O14 - Electrical and magnetic characteristics of novel chalcogenido metalates

Mohammadreza Ghazanfari, Günther Thiele

Inorganic Chemistry division, Department of Biology, Chemistry, and Pharmacy, Freie Universität Berlin, Fabeckstr. 34-36, 14195 Berlin

Ghazanfari.mr@fu-berlin.de

We present a novel class of sulfido and selenido metalates of the general formula $A_2[M_3Ch_4]$ with A = Na, K; M = Cr…Cu; and Ch = S, Se. The materials contain a two-dimensionally extended anionic sublattice with sodium or potassium ions in between these layers. The majority of compounds, such as $K_2[Fe_3S_4]$ and $K_2[Co_3S_4]$,[1] within this series crystallizes isotypic as a defect variant of the $ThCr_2Si_2$ structure type with the transition-metals obtaining a statistic occupation of 75%. This variety of elemental composition is used to tune their physical properties and the performance. The materials provide high dielectric constants (up to 4132 at 1 kHz for $K_2[Fe_3Se_4]$) as high-k materials as well as extraordinary ionic conductivities (up to 31.04 mS·cm^{-1} at 295 K for $K_2[Fe_3Se_4]$), in the range of highest ever reported values, as potential electrode and solid-state electrolyte materials in next-generation sodium- or potassium-ion batteries. Moreover, the obtained compounds indicate large spontaneous magnetic exchange bias fields (up to 0.52 T at ≤ 20 K for $K_2[Co_3S_4]$), for potential spintronic applications. This phenomenon might be a consequence of the coexistence of spin glass and antiferromagnetic ordering, due to the transition-metal vacancies in the lattice. The findings introduce novel materials with potential for technological applications by an electronic and magnetic tuning through the choice of elemental constituents.
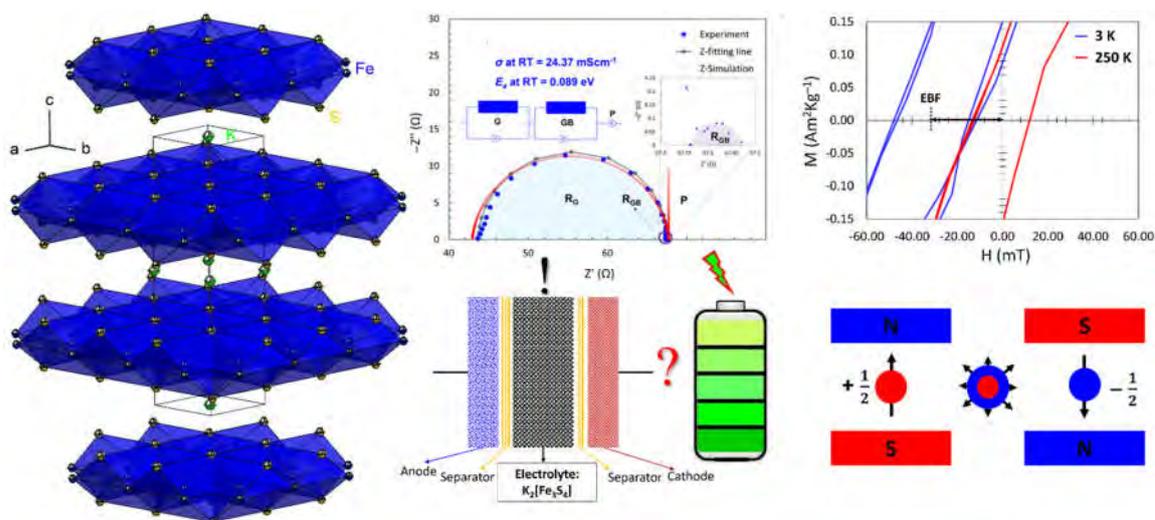
[1] M. R. Ghazanfari, A. Santhosh, K. Siemensmeyer, F. Fuß, L. Staab, J. C. Vrijmoed, B. Peters, M. Liesegang, S. Dehnen, O. Oeckler, P. Jerabek, G. Thiele, Adv. Elctron. Mater. 2022, 8, 2200483.

O15 - Synthesis and temperature-dependent structure property relations of mullite-type SnMBO₄ compounds

<u>Sarah Wittmann</u>,[a] M. Mangir Murshed,[a,b] Thorsten M. Gesing[a,b]

ᵃ Chemische Kristallographie fester Stoffe, Institut für Anorganische Chemie und Kristallographie, Universität Bremen, Germany. ᵇ MAPEX Center for Materials and Processes, Universität Bremen, Germany

swittman@uni-bremen.de
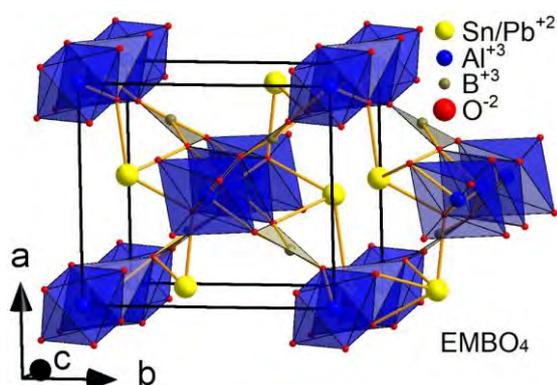
Figure 1: Crystal structure of $SnAlBO_4$ with AlO_6 octahedra, planar BO_3 groups and SnO_4 square pyramids.

Mullite- type $EMBO_4$ compounds ($E_2M_2B_2O_8$ ≡ O8-phase) have drawn a considerable interest due to the influence of stereochemical activity of the $6s^2$ lone electron pairs (LEPs) of Pb^{2+} cation on crystal-chemico-physical properties. The crystal structure the mullite-type setting is described in the orthorhombic space group *Pnam* with edge-sharing MO_6 octahedra, trigonal planar BO_3 groups, and distorted PbO_4 square pyramids [1]. The influence of the LEP and the rigidity of the planar BO_3 groups play important roles to stabilize the O8-structures. In response to the toxicity of lead and the associated environmental issues, replacement of Pb^{2+} by suitable LEP-containing divalent cation is a demanding alternative. As such, mullite-type $SnMBO_4$ (M = Al, Ga, Cr, V) are synthesized. Whereas the almost similar cationic size of Sn^{2+} and Pb^{2+} predict a complete replacement of Pb^{2+} by Sn^{2+} in the O8-structure, the significantly different Wang-Liebau eccentricity parameter [2] and the susceptibility of Sn^{2+} into Sn^{4+} oxidation requires ingenious exploitation of the solid-state reactions. The crystal structure features are obtained from the X-ray powder data Rietveld refinements where the bond valence sum indicates that tin and the M-elements are slightly under bonded whereas boron is slightly over bonded. This can be described in terms of the contraction of the BO_3 group and the distortion of the MO_6 octahedra via strong influence of the $5s^2$ LEPs of Sn^{2+} cation. Temperature-dependent XRPD investigations did not show any phase transition from 13 K to decomposition. ^{119}Sn Mössbauer spectroscopy shows only one Sn^{2+} environment at room temperature which was also proven by solid state NMR spectroscopy. In comparison, the Mössbauer measurement at 78 K shows two different Sn^{2+} environments which suggests an unknown phase transition which could also be measured with differential scanning calorimetry. For the magnetic compounds a change in the magnetic properties can be obtained by magnetic susceptibility measurements.

[1]   T.M. Gesing, C.B. Mendive, M. Curti, D. Hansmann, G. Nenert, P.E. Kalita, K.E. Lipinska, A. Huq, A.L. Cornelius, M.M. Murshed, *Z. Krist. Cryst. Mater.* **2013**, *228(10)*, 532-543.
[2]   M. Curti, C.B. Mendive, T. Bredow, M. Mangir Murshed, T.M. Gesing, *J Phys Condens Matter* **2019**, *31(34),* 345701.

O16 - Organoxenon Compounds in Synthetic Organotransition Metal Chemistry

Alberto Pérez-Bitrián*[a]

[a] Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany.

alberto.perez-bitrian@hu-berlin.de

The first Xe(II) compound was reported by Bartlett in 1962, changing the paradigm of the inertness of noble gases.[1] In 1989, the synthesis of the first compounds containing Xe–C bonds, namely salts of the $[XeC_6F_5]^+$ cation, entailed a key breakthrough in the rapid development of noble-gas chemistry. Since then, the field of organoxenon chemistry has expanded significantly making many different species available,[3] yet their application in synthesis has been barely investigated.

The aim of our recently founded lab is to explore the applicability of organoxenon compounds in the synthesis of organometallic complexes in high oxidation states (Figure 1). We plan to investigate a broad variety of organoxenon species containing several types of organic groups with different degrees of fluorination. Regarding the metal complexes, those containing 3d metals will be of special interest because the stabilization of their higher oxidation states is more challenging than in their heavier homologues and therefore they have been far less studied.[4] Here we will introduce our new lab and our preliminary results on this topic.
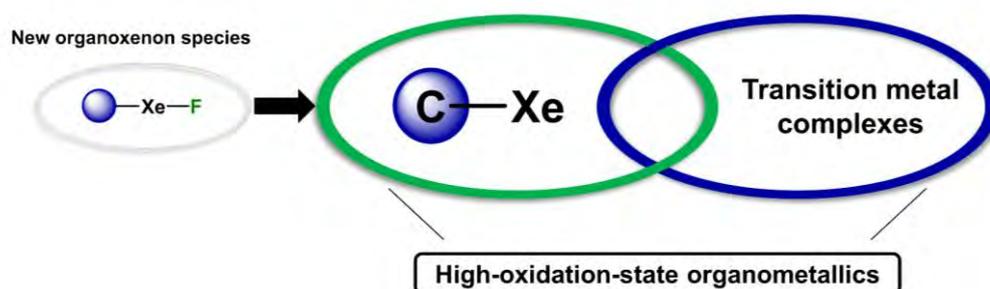
Figure 1: Overview of the envisioned use of organoxenon compounds for the synthesis of organotransition metal complexes.

[1]   N. Bartlett, *Proc. Chem. Soc.* **1962**, 218.
[2]   a) H. J. Frohn, S. Jakobs, *J. Chem. Soc., Chem. Commun.* **1989**, 625–627; b) D. Naumann, W. Tyrra, *J. Chem. Soc., Chem. Commun.* **1989**, 47–50.
[3]   H.-J. Frohn, V. V. Bardin, *Organometallics* **2001**, *20*, 4750–4762.
[4]   M. Malischewski, in *Comprehensive Organometallic Chemistry IV, Vol. 1* (Ed.: P. L. Holland), Elsevier, Amsterdam, **2022**, pp. 109–134.

O17 - Reactivity of Cyanometalates towards Electrophiles

Tim-Niclas Streit[a], Moritz Malischewski[a]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin*

tim.streit@fu-berlin.de, moritz.malischewski@fu-berlin.de

The combination of polycyanometalates and superacids has led to the isolation of unprecedented metal isocyanide complexes $[M(CNH)_8]^{4+}$ (M=Mo,W).[1] Similarly, strong alkylating reagents have been utilized to prepare complexes featuring up to eight methyl isocyanide ligands.[2] Following the success of perprotonation and peralkylation, the triple protonation of a single MCN ligand in a heteroleptic metal cyanide complex is under investigation to access the CNH_3 ligand. Our recent attempts in this regard to use super-acidic-robust ligands in order to stabilize the potentially labile and highly electrophilic complexes are presented.
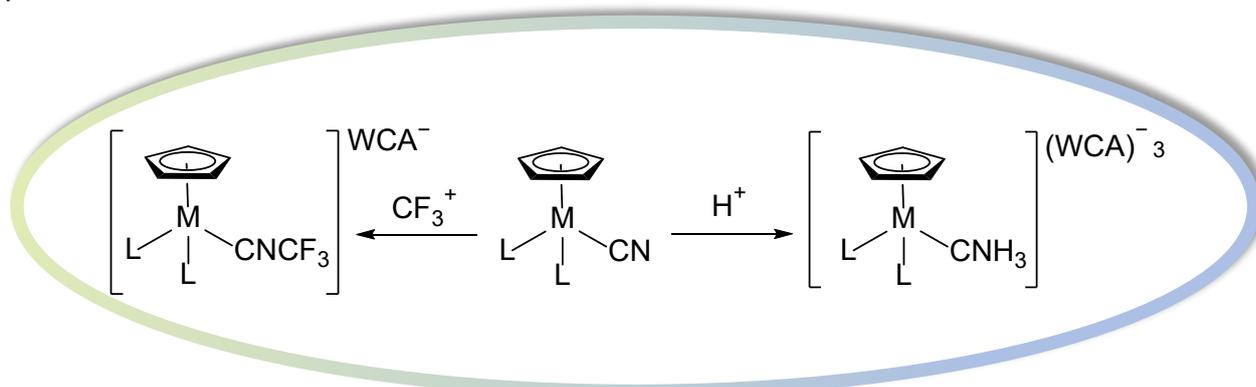
Figure 1: Trifluoromethylation (left) and triple protonation (right) of a metal-bound cyanide group

Several trifluoromethylisocyanide metal complexes have been isolated in the past century,[3] their further research hampered by the synthetic problems associated with accessing the $CNCF_3$ ligand.[4] With the discovery of several organic electrophilic trifluoromethylation reagents[5] a facile access to this ligand from cyanide complexes seems feasible and could enable a more comprehensive understanding of this rare and synthetically challenging ligand. The reactivity of half-sandwich complexes containing one cyanide group towards Togni and Umemoto reagents is discussed.

[1] M. Sellin, V. Marvaud, M. Malischewski *Angew. Chem. Int. Ed.* **2020**, *59*, 10519−10522.
[2] M. Sellin, S. M. Rupf, U. Abram, M. Malischewski, *Inorg. Chem.* **2021**, *60,* 5917−5924.
[3] D. Lentz, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1315−1331.
[4] D. Lentz, *J. Fluor. Chem.* **1984**, *24*, 523−530.
[5] M. Li, X.-S. Xue, J.-P. Cheng *Acc. Chem. Res.* **2020**, *53*, 182−197.

O18 - A Trip to the Extreme: From Superacids and High Potential Oxidizers to Electrophilic Xenonium and Halonium Cations

Lukas Fischer,[a] Ahmet N. Toraman,[a], Sebastian Riedel*[a]

[a] Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.

Lukas.fischer@fu-berlin.de

The strongly electron withdrawing and chemically robust teflate group (-$OTeF_5$) has proven to be an effective building block in the design of Lewis superacids and weakly coordinating anions (WCAs).[1] However, the synthesis of teflate-containing compounds can be challenging and requires the use of special equipment and technics, as the precursors for these compounds like FSO_3H and HF are highly toxic, corrosive and reactive. Clear examples of the interesting properties and applicability of teflate compounds are for example the Lewis superacid $Al(OTeF_5)_3$ and the corresponding WCA $[Al(OTeF_5)_4]^-$ recently reported by our group. The outstandingly high Lewis acidity of the group 13 teflate compounds $M(OTeF_5)_3$ (M = B, Al) prompted us to study the heavier gallium analogue. Both the aluminum and the gallium compounds are able to form Lewis and Brønsted superacidic solutions which have been effectively used in the preparation of reactive cations, as for example unusual silyl-oxonium cations (Figure 1 A) and strong electrophilic chloronium cations (Figure 1 B).[2]

Furthermore, the combination of the noble gas compound $Xe(OTeF_5)_2$ and the Lewis acids $M(OTeF_5)_3$ (M = Al, Ga) leads to a highly oxidizing system, from which upon addition of an oxidation-resistant base like pentafluoropyridine, the xenonium cation $[Xe(OTeF_5)(NC_5F_5)]^+$ can be isolated (Figure 1 C).

$[HO(Si(CH_3)_3)_2]^+$ $[Cl(CH_3)_2]^+$ $[Xe(NC_5F_5)(OTeF_5)]^+$

A   **B**   **C**
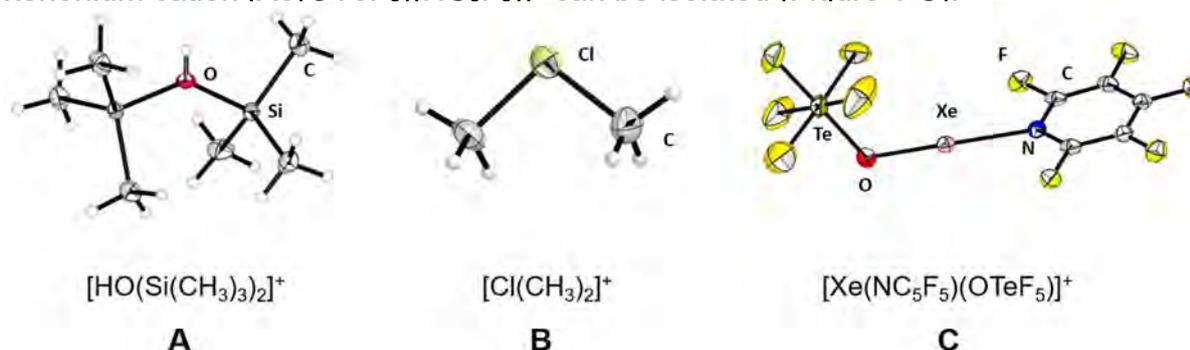
Figure 1: Selected cations obtained from superacidic / strong oxidizing systems. Anions $[M(OTeF_5)_n]^-$ (M = Al, Ga; n = 4, M = Sb; n = 6) are omitted for clarity.

[1] a) A. Wiesner, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel, *Angew. Chem. Int. Ed.* **2017**, *56*, 8263; b) K. F. Hoffmann, A. Wiesner, S. Steinhauer, S. Riedel, *Chem. Eur. J.* **2022**, *28*, e202201958.
[2] S. Hämmerling, G. Thiele, S. Steinhauer, H. Beckers, C. Müller, S. Riedel, *Angew. Chem. Int. Ed.* **2019**, *58*, 9807.

O19 - Al complexes with redox-active iminophenanthrenones

Roderich Meißner,[a] Dieter Schaarschmidt*[a]

[a] *Institute of Inorganic and Applied Chemistry, University of Hamburg, Germany.*

roderich.meissner@uni-hamburg.de

Imines are well-established ligands in coordination chemistry. For example acenaphthoquinone based diimines (BIAN) have been widely applied for the synthesis of transition metal complexes since the 1990s[1] documented in almost 1000 structurally characterized examples in the CSD. In contrast, the chemistry of imines derived from related phenanthrenequinone is underexplored, information on their electrochemical behaviour are hardly available. However, mono(imino)phenanthrenones (MIP) are easily accessible[2] and offer due to their N-O motif a more versatile coordination behaviour compared to BIAN (e. g. formation of μ-O bridged dinuclear metal complexes).
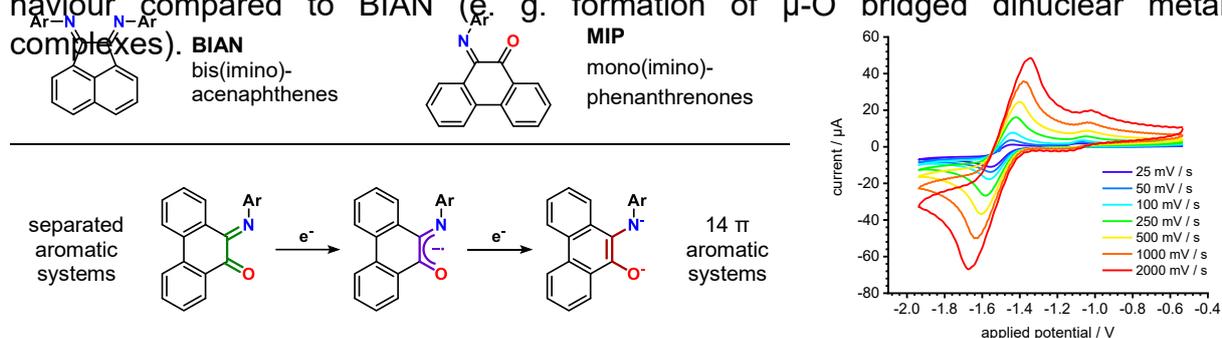
Figure 1: BIAN and MIP ligand (left, top), stepwise reduction of the MIP ligand (left, bottom) and cyclic voltammogram of its quasi-reversible first reduction (right).

Within this contribution, the synthesis of mono(imino)phenanthrenones bearing different aryl substituents will be presented. Their reduction to the corresponding aminophenanthrenols and the accessibility of Al complexes will be discussed in detail. First applications of selected compounds in the polymerisation of ε-caprolactone will be shown.
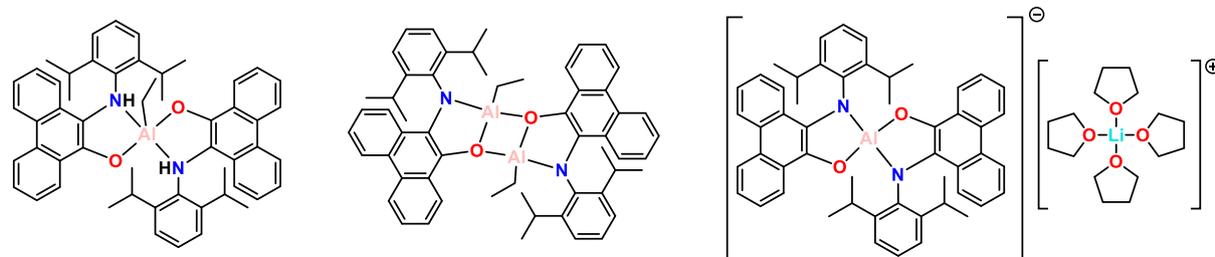
Figure 2: Structural variety of (arylamino)phenanthrenol-based Al complexes.

[1]   N. J. Hill, I. Vargas-Baca, A. H. Cowley, *Dalton Trans.* **2009**, 240–253.
[2]   G. A. Abakumov, V. K. Cherkasov, N. O. Druzhkov, Y. A. Kurskii, G. K. Fukin, L. G. Abakumova, T. N. Kocherova, *Synth. Commun.* **2006**, *36*, 3241–3247.

O20 - Attempting to Make Uranium Behave in Small Molecule Activation

Lisa Vondung,[a*] Leonard Naß,[b] León Hillers,[a] Christian Urbank[a,b]

[a] *Institute of Inorganic and Applied Chemistry, University of Hamburg, Germany.*
[b] *Institute of Inorganic Chemistry, Georg-August-University Göttingen, Germany.*

lisa.vondung@uni-hamburg.de

During the uranium enrichment process for nuclear power, approximately 5.5 kg weakly radioactive depleted uranium (DU) are produced as a by-product for each kg of enriched uranium with the world-wide stocks of DU estimated at > 1 Mio. tonnes. Currently there are no major applications for DU except for highly debated military armour and only temporary civilian uses as counter weights.[1] However, molecular uranium compounds have shown promising properties for applications as catalysts or in materials, as the bonding and reactivity of uranium complexes is often significantly different compared with transition metals and lanthanides.[2]

Uranium(III) complexes are highly promising for reductive bond activation due to their large reduction potential, large ionic radius and both 6d- and 5f-orbitals available for bonding.[3,4] Despite these properties, catalytic small molecule activation with uranium is still largely underdeveloped. This is due to several challenges, such as the formation of highly stable reaction products.[5] Our approach to tackle these issues is to develop new uranium complexes with multidentate hybrid ligands with a hemilabile donor group, which allow a better control over the reactivity of uranium complexes in small molecule activation and potentially enable catalytic transformations.

A = Cp, pyridine, NR_2^-
B = PR_3, SR_2
Sub = Substrate
L = ancillary ligands
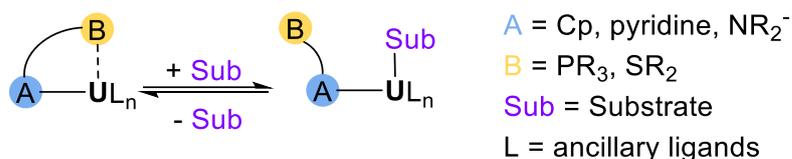
Figure 1: General scheme of the concept of uranium complexes with hemilabile hybrid ligands and the targeted reactivity.

[1] European Commission, "Depleted Uranium," ec.europa.eu/health/scientific_committees/ opinions_layman/depleted-uranium/en, **2010**.
[2] A. Formanuik, A. M. Ariciu, F. Ortu, R. Beekmeyer, A. Kerridge, F. Tuna, E. J. L. McInnes, D. P. Mills, *Nat. Chem.* **2017**, *9*, 578–583.
[3] W. J. Evans, S. A. Kozimor, *Coord. Chem. Rev.* **2006**, *250*, 911–935.
[4] A. R. Fox, S. C. Bart, K. Meyer, C. C. Cummins, *Nature* **2008**, *455*, 341–349.
[5] D. R. Hartline, K. Meyer, *JACS Au* **2021**, *1*, 698–709.

O21 - A tungsten complex catalyzing the conversion of dinitrogen to ammonia

Anna-Marlene Vogt, Tobias A. Engesser, Jan Krahmer, Christian Näther, [a] Nicolas Le Poul [b] and Felix Tuczek *[a]

[a] *Institute of Inorganic Chemistry, University of Kiel, Germany,* [b] *UMR CNRS UMR 6521, Université de Bretagne Occidentale, France.*

mvogt@ ac.uni-kiel.de

Synthetic nitrogen fixation provides a basic understanding of the activation of the highly inert N_2 molecule and its catalytic conversion to NH_3 by transition metal complexes. [1,2] Differences in reactivity between molybdenum and tungsten complexes supported by pentadentate tetrapodal (pentaPod^P) ligands are of special interest.[3-6] Despite similar redox potentials, cyclic voltammetry reveals that the properties of molybdenum and tungsten pentaPod^P-complexes are different.[6]

Compared to the original pentaPod^P ligand $P_2^{Me}PP_2^{Ph}$ (**1**) the newly synthesized $P_2^{Pln}PP_2^{Ph}$ (**2**) bears phospholane (Pln) instead of dimethylphosphine groups (Me), allowing to investigate steric and electronic effects of Pln-donors.[4,5] So far, X-ray diffraction as well as IR and NMR spectroscopic studies of $[M(N_2)(P_2^{Me}PP_2^{Ph})]$ (**3,4**) and $[M(N_2)(P_2^{Pln}PP_2^{Ph})]$ (**5,6**) suggest strong analogies.[3,6] Nevertheless, in contrast to $[W(N_2)(P_2^{Me}PP_2^{Ph})]$ (**3**),[6] a catalytic activity in N_2 to NH_3 conversion by $[W(N_2)(P_2^{Pln}PP_2^{Ph})]$ (**5**) is observed in the presence of SmI_2/H_2O. This renders **5** the first example of a tungsten complex catalyzing the synthesis of ammonia from N_2.
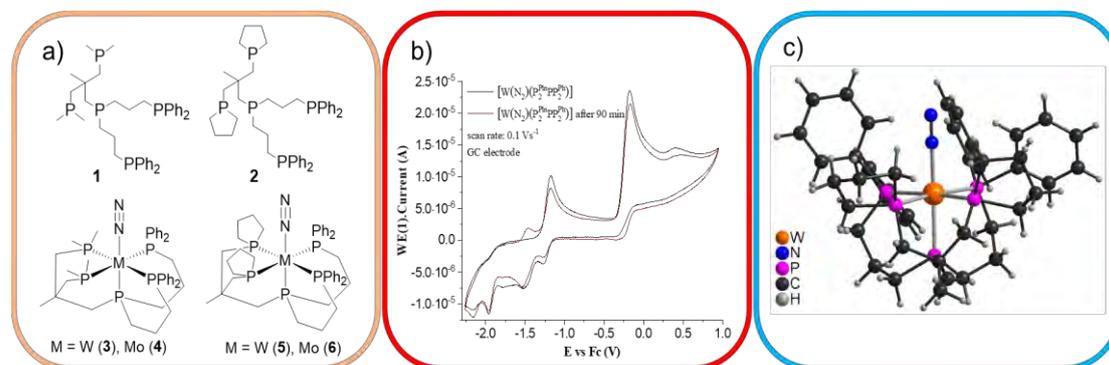
Figure 1: a) pentaPod^P ligands and Mo and W dinitrogen complexes, b) CV of $[W(N_2)(P_2^{Pln}PP_2^{Ph})]$ and c) single-crystal structure of $[W(N_2)(P_2^{Pln}PP_2^{Ph})]$.

[1] Y. Ashida, T. Mizushima, K. Arashiba, A. Egi, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *Nature Synthesis,* **2023**, *2*, 635-644.

[2] M. J. Chalkley, M. W. Drover, J. C. Peters, *Chem. Rev.* **2020**, *120*, 5582 – 5636.

[3] T. A. Engesser, A. Kindjajev, J. Junge, J. Krahmer, F. Tuczek, *Chem. Eur. J.* **2020**, *26*, 14807–14812.

[4] S. Hinrichsen, A. Kindjajev, S. Adomeit, J. Krahmer, C. Näther, F. Tuczek, *Inorg. Chem.* **2016**, *55*, 8712–8722.

[5] M. Pfeil, T. A. Engesser, A. Koch, J. Junge, J. Krahmer, C. Näther, F. Tuczek, *Eur. J. Inorg. Chem. 2020,* 1437-1448*.*

[6] J. Junge, S. Froitzheim, T. A. Engesser, J. Krahmer, Christian Näther, N. Le Poul and F. Tuczek *Dalton Trans.* **2022**, *51*, 6166–6176.

O22 - Synthesis and Characterization of Polynuclear Metalla-Ketiminate Complexes

Malte Reihwald,[a] Christopher Timmermann,[a] Alexander Villinger,[a] Wolfram W. Seidel*[a]

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

malte.reihwald@uni-rostock.de

Alkynes with proximate donor substitution are electronically flexible linkers with high conjugation potential. Side-on coordination at the triple bond converts such alkynes into chelate ligands.[1–2] In dinuclear complexes the resulting μ-η^2-C,C'-κ^2-X,X' coordination mode provides a basis for strong intermetallic cooperativity.[1] In this contribution novel approaches with X = NR (R = Me$_2$C$_6$H$_3$, t-Bu) are shown.

The introduction of terminal nitrogen substituents is accomplished by isocyanide coupling at a W^{II}-metal template via reductive coupling.[3] After deprotonation of the resulting monocation (**1**) via base the present system is similar to the well-known NacNac-motif. Addition of a Cu^I-reagent results in two different Cu^I- building blocks (**2**, **3**).[4] Synthetic strategies of such systems depicted in Figure 1 will be discussed as well as their coordination behavior and various electrochemical and spectroscopic studies. In addition, details and side reactions of the isocyanide coupling will be presented.
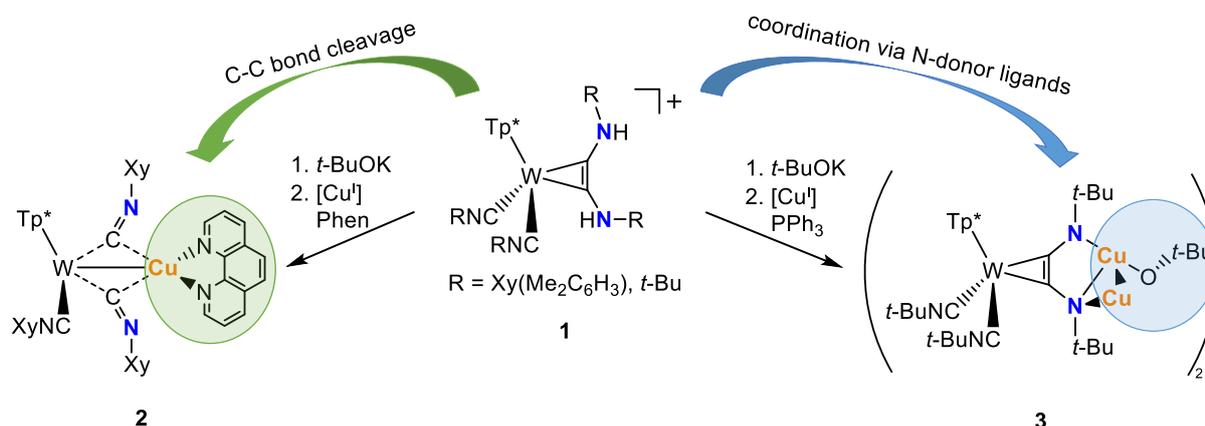
Figure 1: Metalla-ketiminate approach to polynuclear copper complexes.

[1] J. Rüger, C. Timmermann, A. Villinger, A. Hinz, D. Hollmann, W. W. Seidel, *Chem. Eur. J.* **2016**, *22*, 11191–11195.

[2] K. Helmdach, S. Dörk, A. Villinger, W. W. Seidel, *Dalton Trans.* **2017**, *46*, 11140–11144.

[3] a) C. T. Lam, M. Novotny, D. L. Lewis, S. J. Lippard, *Inorg. Chem.* **1978**, *17*, 2127–2133; b) J. C. Dewan, C. M. Giandomenico, S. J. Lippard, Inorg. Chem. **1981**, *20*, 4069–4074; c) F. A. Cotton, S. A. Duraj, W. J. Roth, *J. Am. Chem. Soc.* **1984**, *106*, 6987–6993; d) A. C. Filippou, W. Grünleitner, C. Völkl, P. Kiprof, *Angew. Chem. Int. Ed.* **1991**, *30*, 1167–1169.

[4] T. K. Salvador, C. H. Arnett, S. Kundu, N. G. Sapiezynski, J. A. Bertke, M. Raghibi Boroujeni, T. H. Warren, *J. Am. Chem. Soc.* **2016**, *138*, 16580–16583.

O23 - Diaminoacetylenes: Electron-Rich Precursors for the Preparation of Efficient Iron Cyclopentadienone Hydrogenation Catalysts

Lukas Körner,[a] Ludwig Hackl,[a] Matthias Tamm*[a]

[a] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Germany.

lukas.koerner@tu-braunschweig.de

The reactivity of electron-rich diaminoacetylenes (DAAs) is driven by their "hidden diaminodicarbene character", which enables versatile transformations.[1] In the past, we showed for instance the thermal dimerization and subsequent cyclization to strong σ-donor cyclic bent allene (CBA) ligands.[2] In contrast, a proton-induced dimerization followed by oxidation led to the first fully characterized cyclobutadiene dication, whose aromaticity was evaluated by detailed computational methods.[3] Our current research interest is focused on the synthesis and application of amino-substituted cyclopentadienone (CPD) iron complexes. Symmetric as well as asymmetric tetraamino-CPD iron tricarbonyl complexes can be obtained from DAAs and $Fe(CO)_5$ via a unique ferracyclobutenone intermediate (Scheme 1).[4] Diaminodiaryl substituted CPD iron tricarbonyl complexes are accessible from the free CPD ligands, which are synthesized from a DAA and a cyclopropenone. The transformations into dicarbonyl-acetonitrile complexes provide highly active precatalysts which hydrogenate a variety of ketones in the presence of a hydrogen donor such as H_2 at low overpressures (3 bar) and room temperature or with isopropanol at 80 °C in 2h, both with low catalyst loadings. The new diamino CPD complexes are currently being tested in reductive amination reactions providing first promising results.
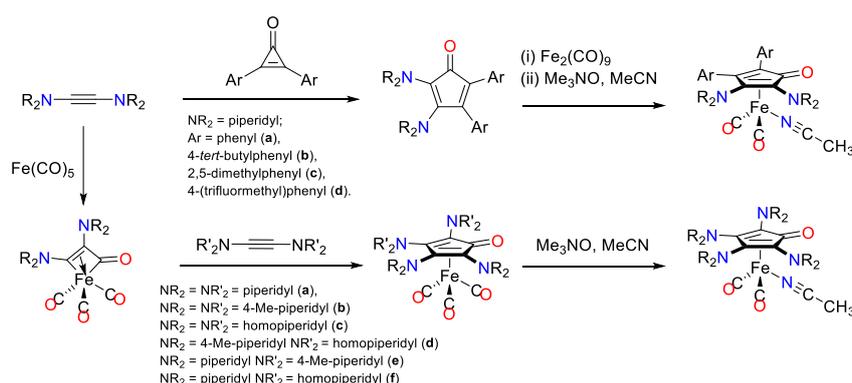
Scheme 1: Synthesis of various CPD iron complexes which are applied in hydrogenation catalysis.

[1] L. Hackl, L. Körner, M. Tamm, Diaminoacetylenes: Synthesis and Coordination Chemistry, *Chem. Lett.*, **2021**, *50*, 1428.

[2] L. Hackl, A. R. Petrov, T. Bannenberg, M. Bannenberg, P. G. Jones, M. Tamm, *Chem. Eur. J.*, **2019**, *25*, 16148.

[3] L. Körner, L. P. Ho, R. Puchta, A. Stanger, M. Tamm, *Chem. Eur. J.*, **2022**, *28*, e202202737.

[4] L. Hackl, L. P. Ho, D. Bockhardt, T. Bannenberg, M. Tamm, *Organometallics*, **2022**, *41*, 836.

O24 - Syntheses, Characterization and Multifaceted Coordination Chemistry of Hydrazonido Titanium Complexes

Kevin Schwitalla,[a] Fares Sad,[a] Marc Schmidtmann[a] and Rüdiger Beckhaus[a]*

[a] Institut für Chemie, Carl von Ossietzky Universität Oldenburg, D-26111 Oldenburg, Federal Republic of Germany

kevin.schwitalla@uni.oldenburg.de

The chemistry of bis(π-η^5:σ-η^1-pentafulvene)titanium complexes (**1**) is characterized by a broad range of E–H activation and Ti–C functionalisation reactions.[1] The reaction of **1** with of hydrazones (**2**) lead to both hydrazonido and hydrazido complexes depending on the interaction of the hydrazone (**2**) with the fulvene ligand of **1**. The molecular structures mostly reveal $\kappa^2 N,N$ side-on coordination of the hydrazonido ligand (**3**) due to the deprotonation of the N–H bond by one of the fulvene moieties. Instead of deprotonation, the reaction of **1** (CR$_2$: adamantylidene) with cinnamon aldehyde phenylhydrazone leads to a $\kappa^1 N$ coordination (**4**). By using donating groups in the backbone of **2**, there are exceptions to this coordination mode due to unexpected insertion of the C=N double bond into the Ti–C$_{exo}$ bond of the pentafulvene moiety. Using 2-pyridincarboxaldehyde phenylhydrazone, a formal $\kappa^3 N,N,N$ ligand system (**5**) is formed by coordination of the pyridine nitrogen atom to the metal center via consecutive N–H deprotonation and insertion. Finally, the use of salicylaldehyde phenylhydrazone ultimately produces a complex with the $\kappa^3 N,N,O$ coordination mode (**6**) by double deprotonation of the hydrazone N–H and O–H funct
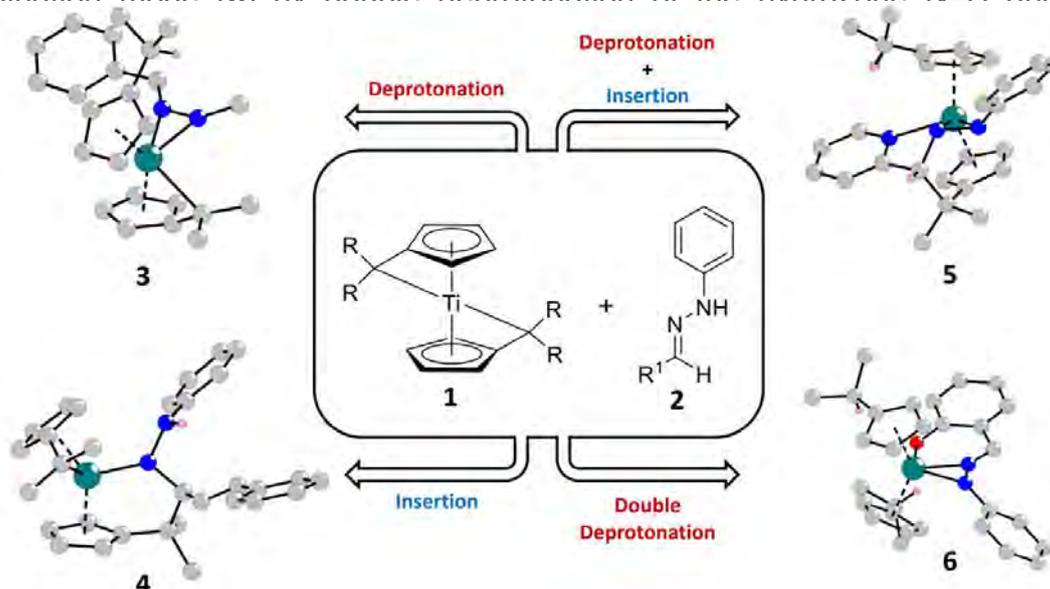
Figure 1: Reactions of bis(π-η^5:σ-η^1-pentafulvene)titanium complexes (1) with hydrazones 2.

[1]   R. Beckhaus, *Coord. Chem. Rev.* **2018**, *376*, 467–477.
[2]   K. Schwitalla et al. **2023**, Syntheses, Characterization and Multifaceted Coordination Chemistry of Hydrazonido Titanium Complexes, *submitted for publication*.

O25 - Platinum(II) Metallopnictinidenes

Marc C. Neben,[a] Hendrik Verplancke,[b] Richard Thompson,[c] Igor Tkach,[d] Serhiy Demeshko,[a] Matthias Otte,[a] David C. Powers,[c] Max C. Holthausen[b] and Sven Schneider*[a]

[a] Institute of Inorganic Chemistry, Georg-August-University Göttingen, Germany.
[b] Institute of Inorganic and Analytical Chemistry, Goethe-University, Germany.
[c] Department of Chemistry, Texas A&M University, USA.
[d] Max-Planck Institute for Multidisciplinary Science, Göttingen, Germany.

marc.neben@uni-goettingen.de

Nitrenes (N–R) are subvalent key intermediates in organic synthesis. Their reactivity strongly depends on the spin energetics of their closed-shell *vs* open-shell singlet and triplet configurations.[1] The electronic structures of the heavier pnicitinidene analogues also attracted attention,[2] but their use as pnictogen building blocks is scarcely examined. Our group synthesized the first authentic metallonitrenes (M–N; M = Pd, Pt) and examined their role in catalytic N-atom transfer.[3] Photolytic decarbonylation of phosphaethynolate also gave rise to phosphinidene coupling products.[4] Here, we report the crystallographic, magnetic, and computational characterization of the platinaphosphinidene key intermediate (Figure 1) and heavier pnictinidene analogues (As, Sb), as well as their reactivity towards pnictinidene coupling and bond activation.
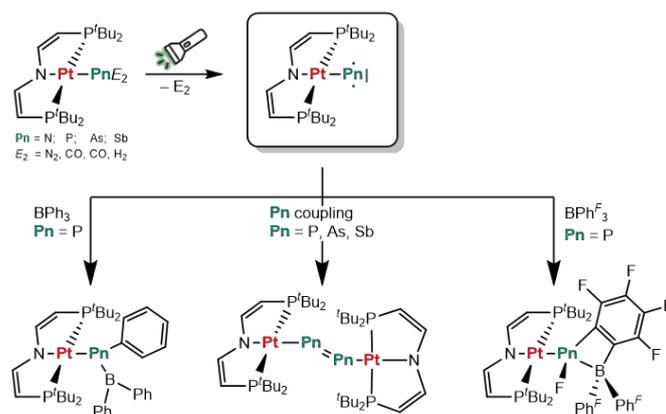
Figure 1: Characterization and exploration into the reactivity of platinum(ii)metallopnictinidenes.

[1]   D. E. Falvey, A. D. Gudmundsdottir, *Nitrenes and Nitrenium Ions*, John Wiley & Sons, Inc., Hobolken, NJ, **2013**.
[2]   Y. Pang, N. Nöthling, M. Leutzsch, L. Kang, E. Bill, M. van Gastel, E. Reijerse, R. Goddard, L. Wagner, D. Santa Lucia, S. De Beer, F. Neese, J. Cornella, *Science* **2023**, *380*, 104.
[3]   (a) J. Sun, J. Abbenseth, H. Verplancke, M. Diefenbach, B. de Bruin, D. Hunger, C. Würtele, J. van Slageren, M. C. Holthausen, S. Schneider, *Nat. Chem.* **2020**, *12*, 1054. (b) T. Schmidt-Räntsch, H. Verplancke, J. N. Lienert, S. Demeshko, M. Otte, G. P. Van Trieste,III, K. A. Reid, J. H. Reibenspies, D. C. Powers, M. C. Holthausen, S. Schneider, *Angew. Chem.* **2022**, *61*, e2021156.
[4]   J. Sun, H. Verplancke, J. I. Schweizer, M. Diefenbach, C. Würtele, M. Otte, I. Tkach, C. Herwig, C. Limberg, S. Demeshko, M. C. Holthausen, S. Schneider, *Chem.* **2021**, *7*, 1952.

O26 - Sulfur makes the difference: unusual C-H activation in novel iridium bis(thiophosphinite)pincer complexes

Alexander Linke,[a] Hans-Joachim Drexler,[a] Torsten Beweries*[a]

[a] Leibniz Institute for Catalysis, Albert-Einstein-Str. 29a, 18059 Rostock, Germany.

alexander.linke@catalysis.de

In the last two decades, bis(phosphinite) Ir pincer complexes of the type [(^{R}POCOP^R)Ir(H)(X)] {^{R}POCOP^R = κ^3-1,3-(OPR$_2$)$_2$-C$_6$H$_3$; R = organic substituent; X = H, Cl} have been applied as versatile catalysts in many organic transformations.[1] We were recently able to synthesise the corresponding Ir(III) bis(thiophosphinite) complexes **2-R** (R = iPr, tBu, Ph) from suitable Ir precursors in refluxing toluene and an atmosphere of H$_2$.[2]
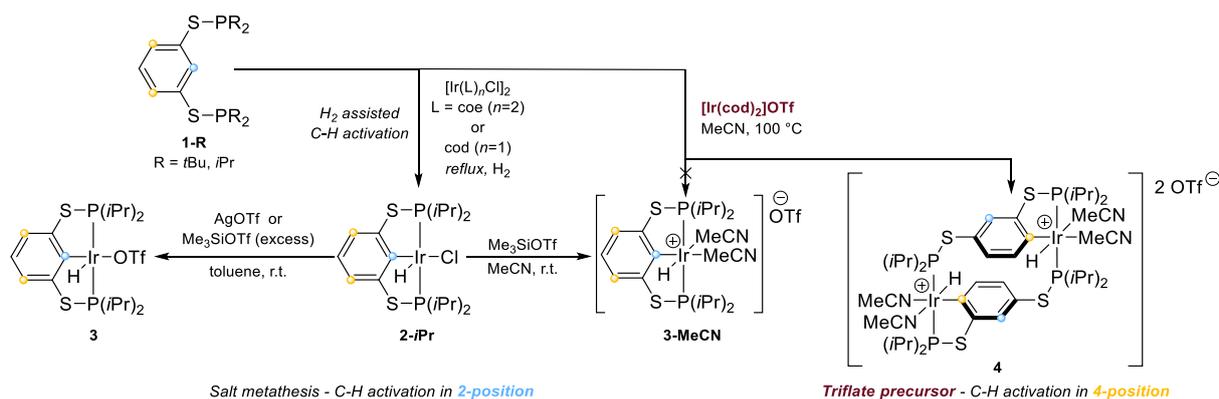
Figure 1: Synthesis of new Ir(III) bis(thiophosphinite) complexes **2-R** *and unusual C-H activation in 4-position.*

Ligand exchange reactions at **2-iPr** yielded in dependence on the solvent **3** and **3-MeCN**. Aiming for synthesising **3-MeCN** directly from ligand **1-iPr** and cationic Ir-precursor [Ir(cod)$_2$]OTf we observed unusual C-H activation in 4-position of the arene fragment. To the best of our knowledge, this type of reactivity is so far only known for Ir-PCP[3] and Pd-NCN-pincer[4] complexes.

[1]   J. Choi, A. H. R. MacArthur, M. Brookhart, A. S. Goldman, *Chem. Rev.* **2011**, *111*, 1761-1779.
[2]   A. Linke, D. Decker, H.-J. Drexler, T. Beweries, *Dalton Trans.* **2022**, *51*, 10266-10271.
[3]   X. Zhang, T. J. Emge, A. S. Goldman, *Inorg. Chim. Acta* **2004**, *357*, 3014-3018.
[4]   P. Steenwinkel, R. A. Gossage, T. Maunula, D. M. Grove, G. van Koten, *Chem. Eur. J.* **1998**, *4*, 763-768.

Abstracts der Poster

Novel hard carbon anodes to unravel the sodium storage mechanism

Shu-Han Wu,[a] Jonas Krug von Nidda,[a] Tim-Patrick Fellinger *[a]

a Division 3.6 Electrochemical Energy Materials, Federal Institute for Materials Research and Testing, Germany.

shu-han.wu@bam.de

Lithium-ion batteries (LIBs) have been one of the greatest achievements in the field of energy storage of the last century. However, with the increasing demand for energy storage, battery technologies must be diversified according to their specific requirements in different applications. In terms of stationary energy storage and electric vehicles, sodium-ion batteries (SIBs) are considered to be the most attractive alternative to LIBs due to the uniformly high abundance and cost-effectiveness of raw materials, enabling large-scale and low-cost energy storage.

Unlike LIBs where crystalline graphite is commonly used as the anode material, disordered carbons are regarded as more promising for SIBs. However, further advances towards better reversibility and higher specific capacity are still needed to match or exceed that of graphite in LIBs. The main challenge is the complex and unpredictable Na^+ storage mechanism in disordered carbons, as they may have different properties depending on the precursors and carbonization conditions.[1] Recently, Matsukawa et al. have reported that the reversibility of (de)sodiation processes of disordered carbons is better for ultramicroporous carbons.[2] These pores are accessible only to Na^+ ions and not to solvent molecules. Therefore, the (de)sodiation processes are protected from the side reactions caused by the solvent, which reduces the related irreversible capacity loss.

With this idea, the origin of the specific capacity and irreversible losses will be further investigated by tailoring chemical composition (e.g., heteroatom doping) as well as pore structure of hard carbons used as anode materials in SIBs.

For the synthesis scalable and industrially relevant processes will be used. The structure and morphology of the materials will be characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. In addition, different gas sorption techniques will be carried out to analyze the porosity, pore sizes and specific surface areas. The electrochemical performance of the prepared materials will be evaluated based on coin cells, three-electrode Swagelok cells, and pouch cells. Moreover, solid-state nuclear magnetic resonance spectroscopy will be performed to help understand the mechanism of Na^+ storage.

[1] Nuria Tapia-Ruiz et al., *J. Phys. Energy.* **2021**, *3, 031503*.
[2] Y. Matsukawa, Beilstein J., *Nanotechnol.* **2020**, *11,* 1217–1229.

X-Ray Absorption Spectroscopy to Reveal the „Molecular" Structure of Metal and Nitrogen doped Carbons (M-N-Cs) Electrocatalysts

Simon Dietzmann,[a] A. Mehmood,[a] S.-H. Wu,[a] A. Guilherme Buzanich,[b] F. Emmerling,[b] T. Fellinger,[a]*

[a] Bundesanstalt für Materialforschung und -prüfung (BAM) Fachbereich 3.6 _Elektrochemische Energiematerialien, [b] BAM Fachbereich 6.3 – Strukturanalytik

Simon.Dietzmann@bam.de

High-performance electrocatalysts are required for energy storage of highly intermittent renewable energy. Metal and nitrogen doped carbons (M-N-Cs) are promising candidates as they are conductive and can be tuned to the desired properties by appropriate doping. In our division we focus on the oxygen reduction reaction (ORR) for fuel cell applications and CO_2 conversion. Structural characterization is essential to understand and optimize the catalytically active sites at their pseudo-molecular level. M-N-Cs are amorphous materials and X-ray absorption spectroscopy (XAS) is the best method to determine the coordination sphere around the catalytically active metal center and to compare it with molecular models.

First results from XAS-measurements and the synthesis of M-N-Cs will be presented.

Degradation and Impact of Fluorinated Electrolytes from Lithium-Ion Batteries

Juliane Scholl,[a,b] Hajo Haase,[a] Matthias Koch [b]

[a]Technische Universität Berlin – Institut für „Lebensmitteltechnologie und Lebensmittelchemie" [b]Bundesanstalt für Materialforschung und -prüfung (BAM); Department of Analytical Chemistry and Reference Materials

Juliane.Scholl@bam.de

Lithium-based batteries (LiBs) have become increasingly important in modern society, as cutting-edge portable energy storage systems and as a crucial component in the energy revolution. However, they still face challenges such as safety concerns, capacity degradation, and the ever-growing demand for higher energy density. To address these issues, researchers have turned their attention to fluorinated organic compounds (FOCs) as part of LiBs electrolytes. These substances, closely related to per- and polyfluorinated alkyl substances (PFAS), have shown great potential in optimizing LiBs[1-3]. Specifically, their strong fluorine-carbon bond offers enhanced oxidative and chemical resistance. Nevertheless, their environmental impact is a cause for concern. Fluorinated organics can persist in the environment or can lead to the formation of persistent end-products, which accumulate and contribute to global health problems.

To study the fate of fluorinated organic electrolytes in different environmental and application scenarios, a range of simulation methods are employed, including the TOP (Total Oxidizable Precursor) Assay, electrochemistry, photo-induced degradation, and cycling of self-assembled coin cells prepared with FOCs. Transformation products (TP) are identified using gas chromatography and liquid chromatography coupled with high resolution mass spectrometry (GC/LC-HRMS).

[1]   P. Li, Y. Cheng, R. Li, B. Yo. *Appl. Surf. Sci.* **2022**, *593*, 153434.
[2]   H. Q. Pham, H-Y. Lee, E-H. Hwang, Y-G. Kwon. *J. Power Sources* **2018**, *404*, 13-19.
[3]   L. Xia, B. Tang, K. Wang, A. Cheris. *ChemistrySelect* **2017**, *2*, 7353-7361.

Trimethylsilyl-substituted triazaphospholes: formation of a unprecedented phosphorus-containing mesoionic carbene

L. Dettling,[a] N. Limberg,[a] R. Küppers,[a] M. Weber,[a] C. Müller*[a]

[a] Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany leadettling@zedat.fu-berlin.de

Due to the isolobal relationship between a trivalent P-atom and a C-H fragment, 3H-1,2,3,4-triazaphospholes can be considered as the phosphorus analogues of 1,4-disubstituted 1,2,3-triazoles.[1] These $\lambda^3\sigma^2$-phosphorus heterocycles can be synthesized in a [3+2] cycloaddition reaction starting from organic azides and phosphaalkynes. Recently, we achieved successfully the synthesis of 3H-1,2,3,4-triazaphospholenium salts (**1a/b**) by alkylating triazaphospholes with Meerwein salts ([Me$_3$O][BF$_4$]/ ([Et$_3$O][PF$_6$]).[2] **1a/b** are the formal phosphorus analogues of mesoionic 1,2,3-triazolylidenes (**2**), following the principle of valence isoelectronicity.[3]
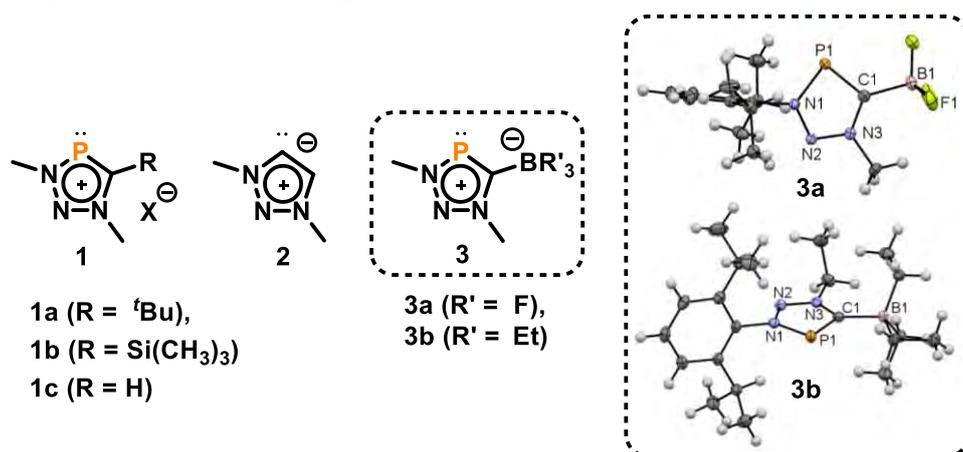
Figure 1: Left: Mesoionic carbene (**2**), its phosphorus analogue (**1**) and the BR$_3$-adduct of a phosphorus-containing mesoionic carbene (**3**). Right: Molecular structure of **3a/b** in the crystal.

The Si(CH$_3$)$_3$-substituted 3H-1,2,3,4-triazaphospholenium salts (**1b**) are of particular interest, as they provide access to protodesilylation products (**1c**). During the study of such reactions, a product was observed that can be described as a BF$_3$-adduct of a phosphorus-containing mesoionic carbene (**3a**). While originally obtained as a minor product, we were able to synthesize the BF$_3$-adduct in a directed synthesis and were even able to extend the scope to the BEt$_3$-adducts (**3b**).[4]

[1]   W. Rösch, M. Regitz, *Angew. Chem*. **1984,** 11, 898.
[2]   M. Papke, L. Dettling, J. A. W. Sklorz, D. Szieberth, L. Nyulászi, C. Müller, *Angew. Chem. Int. Ed*. **2017**, 56, 16484.
[3]   G. Guisado-Barrios, J. Bouffard, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed*. **2010**, 49, 4759.
[4]   L. Dettling, N. Limberg, R. Küppers, D. Frost, M. Weber, N. T. Coles, D. M. Andrada, C. Müller, *Chem. Commun*. **2023**, 59, 10243-10246 (Hot paper).

Incorporation of β-Alanine in Cu(II) ATCUN Peptide Complexes Increases ROS Levels, DNA Cleavage and Antiproliferative Activity

Julian Heinrich,[a, b] Christian G. Hartinger,[c] Wojciech Bal,[d] Nora Kulak,*[a, b, e]

[a] Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany. [b] Institute of Chemistry, Otto-von-Guericke-Universität Magdeburg, Germany. [c] School of Chemical Sciences, University of Auckland, New Zealand. [d] Institute of Biochemistry and Biophysics, Polish Academy of Science, Poland. [e] Institute of Chemistry, University Potsdam, Germany.

julian.heinrich@ovgu.de

DNA can be oxidatively cleaved by Cu(II) complexes of the ATCUN peptide (amino terminal Cu(II)- and Ni(II)-binding motif) through reactive oxygen species (ROS) production. The simplest peptide mimicking the ATCUN motif is the tripeptide glycine-glycine-histidine, the Cu(II) complex of which exhibits antitumor activity.[1] Here, ATCUN-based peptides were synthesized by exchanging glycine for β-alanine at position 2 of the sequence. These metallopeptides were characterized at pH 7.4 via potentiometric titrations (competitivity indices, CI). High cytotoxic activity of the investigated metallopeptides correlates with their oxidative DNA cleavage activity and high cellular uptake into cancer cells.[2]
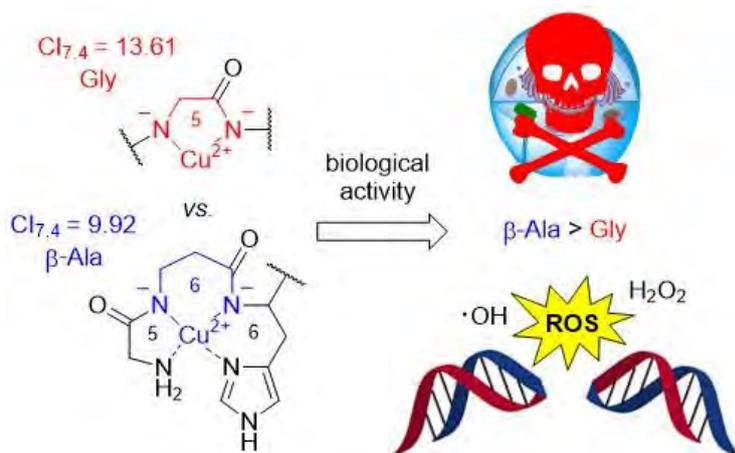
Biological activity of ATCUN-based metallopeptides (glycine vs. β-alanine on position 2 of the peptide sequence).

[1] E. Kimoto, H. Tanaka, J. Gyotoku, F. Morishige, L. Pauling, *Cancer Res.*, **1983**, *43*, 824–828.
[2] J. Heinrich, K. Bossak-Ahmad, M. Riisom, H. H. Haeri, T. R. Steel, V. Hergl, A. Langhans, C. Schattschneider, J. Barrera, S. M. F. Jamieson, M. Stein, D. Hinderberger, C. G. Hartinger, W. Bal, N. Kulak, *Chem. Eur. J.*, **2021**, *27*, 18093–18102.

Amphiphilic Cu(II) oxacyclen complexes cause condensation of DNA

Olga Verbitsky,[a] Sebastián Hinojosa,[b] Amr Mostafa,[a] Ilko Bald,[a] Nora Kulak[*a]

a Institute of Chemistry, University of Potsdam, Germany. b b Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.

olga.verbitsky@uni-potsdam.de

Metal complexes of cyclen (1,4,7,10-tetraazacyclododecane) have proven to be suitable compounds for the efficient oxidative cleavage of DNA. Current studies have focused on further derivatisation of this scaffold to increase DNA binding affinity and thus DNA cleavage activity. Heteroatom substitution in a macrocyclic Cu(II) complex can improve nuclease activity, which showed the better catalytic properties for reactive oxygen species (ROS) generation. The reactivity strongly depends on the heteroatom inserted into the macrocycle, with the following order: O > S > N.[1-4]

The Cu(II) complexes with monoalkylated oxacyclen ligands (1-oxa-4,7,10-triazacyclododecane) have been investigated regarding their nuclease activity towards plasmid DNA, whereby the complexes differed in the length of the alkyl substituents. Our results have shown, that the alkylated Cu(II) complexes are able to cleave plasmid DNA at micromolar concentrations under near physiological conditions. It should be emphasised that ROS are involved in the cleavage. Furthermore, increasing the concentration of complex and increasing the length of the alkyl chain (C-12→C-18) lead to aggregates with increased sizes. Atomic force microscope scanning (AFM) also supports the above observation. Also, we have been able to show that amphiphilic Cu(II) derivates interact with calf thymus DNA electrostatically and by groove binding.
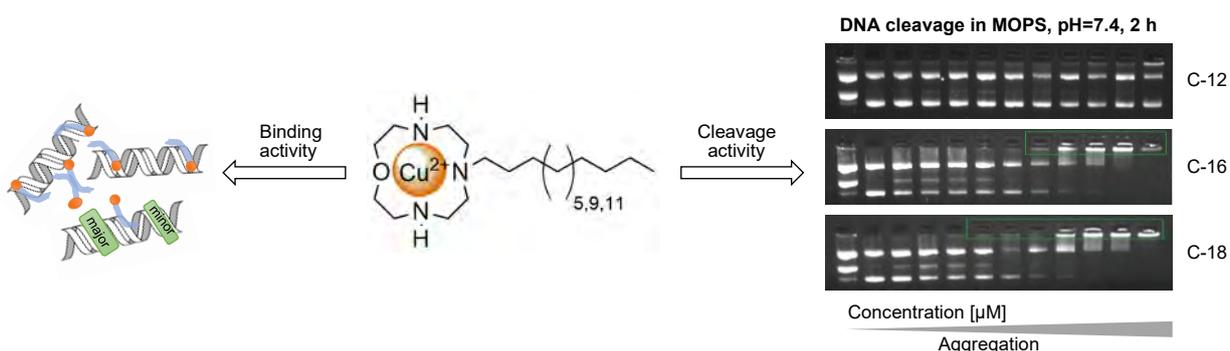
[1]   J. Hormann, C. Perera, N. Deibel, D. Lentz, B. Sarkar, N. Kulak, *Dalton Trans.* **2013**, *42*, 4357–4360.
[2]   J. Hormann, O. Verbitsky, X. Zhou, B. Battistella, M. van der Meer, B. Sarkar, C. Zhao, N. Kulak, *Dalton Trans.* **2023**, *52*, 3176–3187.
[3]   J. Hormann, M. van der Meer, B. Sarkar, N. Kulak, *Eur. J. Inorg. Chem.* **2015**, *2015*, 4722–4730.
[4]   S. Hinojosa, C. Weise, U. Albold, N. Kulak, *ChemistrySelect* **2018**, *3*, 12552–12559.

Synthesis of pholide anions from white phosphorus

Moritz Ernst,[a] Andrey Petrov,[a] Christian Müller*[a]

[a] *Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.*

moritz.ernst@fu-berlin.de

Activation of white phosphorus with alkali metals leads to different polyphosphide anions depending on the stoichiometry. The aromatic pentaphospholide anion (**1**) and the heptaphosphide anion (**2**) are notable examples of this substance class.[1,2] In contrast to white phosphorus P_4, which shows only weak nucleophilicity, these anions react with common electrophiles to form valuable organophosphorus compounds, such as aromatic heterocycles.[2] Compounds **1** and **2** are reactive towards C≡E (E = C, N) triple bonds, yielding 1,2,3-triphospholide and azatriphospholide anions.[3,4] The coordination chemistry of these phosphorus heterocycles is of particular interest because of their isolobal relationship to the classical cyclopentadienyl anion.
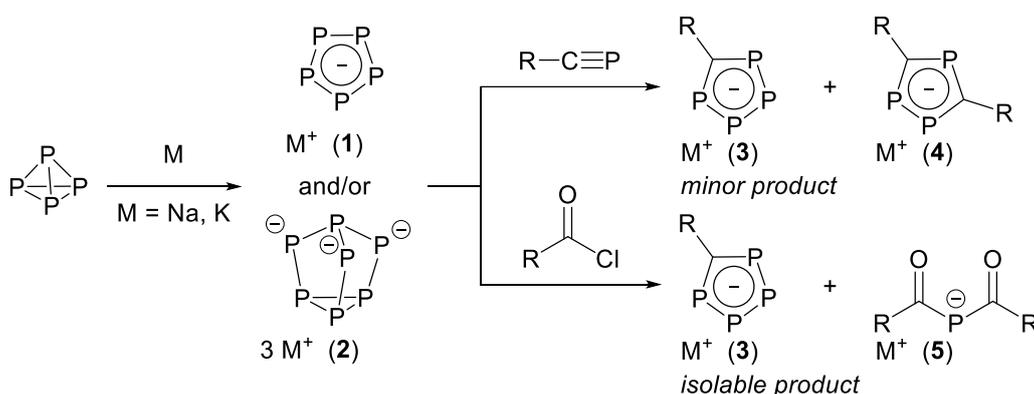
Figure 1: Synthetic pathways towards tetraphospholide anions.

We present here that **1** and **2** are reactive towards differently substituted phosphaalkynes, resulting in a mixture of the respective tetra- (**3**), and the 1,3,4-triphospholide (**4**) anions. In addition, we introduce the synthesis of **4** by a reaction between acid chlorides and a mixture of different polyphosphides generated *in situ* from white phosphorus. This synthetic pathway opens up the possibility of new substitution patterns due to the more accessible acid chlorides compared to the limited amount of stable phosphaalkynes.

[1]   V.A. Milyukov, Yu. H. Budnikova, *Russ. Chem. Rev.* **2005**, *74*, 781-805.
[2]   M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher, D. Gudat, *Eur. J. Inorg. Chem.* **2016**, *2016*, 649–658.
[3]   R.S.P. Turbervill, J.M. Goicoechea, *Chem. Rev.* **2014**, *114*, 10807−10828.
[4]   A. Petrov, L. Conrad, N.T. Coles, M. Weber, D. Andrae, A.A. Zagidullin, V.A. Miluykov, C. Müller, *Chem. Eur. J.* **2022**, e202203056.

A phosphinine-B(C$_6$F$_5$)$_3$ Lewis pair initiates C-N bond cleavage

Samantha Frank,[a] Moritz Ernst,[a] Christian Müller*[a]

[a]*Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.*

samantha.frank@fu-berlin.de

Classical frustrated Lewis pairs (FLP), such as (^{t}Bu)$_3$P/B(C$_6$F$_5$)$_3$, are known to activate small molecules.[1] MÜLLER *et al.* reported recently on the stable 3,5-bis(trimethylsilyl)-phosphinine-B(C$_6$F$_5$)$_3$ Lewis pair (**1**). Unlike classical FLPs, **1** features a dative P–B bond and an activated aromatic phosphorus heterocycle. The reaction of **1** with phenylacetylene leads to the 1-*R*-phosphabarrelenium salt **2**, formed by a [4+2] cycloaddition at the phosphinine and FLP-type insertion into the dative P–B bond. In contrast, styrene instead of phenylacetylene reacts with **1** only in a [4+2] cycloaddition reaction to the borane adduct of dihydro-1-phosphabarrelene **3**.[2]
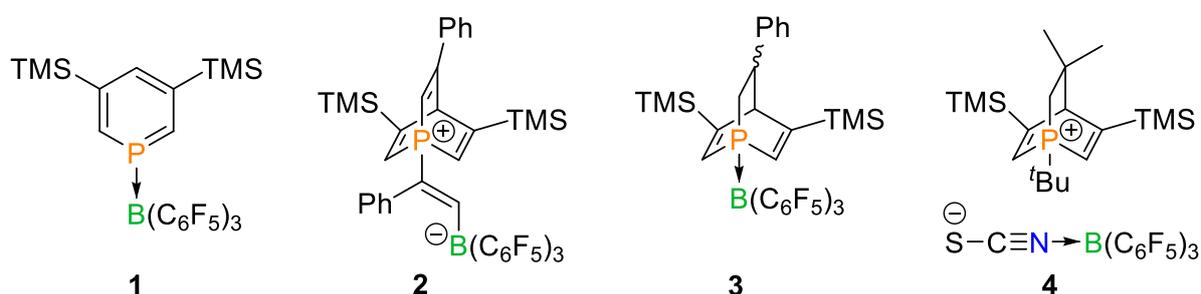
Figure 1: Phosphinine borane adduct **1** and cycloaddition products **2-4**.

The interesting properties of **1** have now been further investigated. *tert*-Butyl substituted isothiocyanide reacts with **1** to the dihydrophosphabarrelenium salt **4**. NMR ivestigations showed, that adduct **1** initiates first a C–N single bond cleavage, resulting in a transient alkylated phosphininium cation, which reacts subsequently with *in situ* formed isobutene to **4**. This reacvitity contrasts classical FLPs. The reaction of (^{t}Bu)$_3$P/B(C$_6$F$_5$)$_3$ with ^{t}Bu-NCS does not lead to an alkylation at the phosphorus atom, only protonation and liberation of isobutene were observed.

[1] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124.

[2] J. Lin, F. Wossidlo, N. T. Coles, M. Weber, S. Steinhauer, T. Böttcher, C. Müller, *Chem. Eur. J.* **2022**, *28*, e202104135.

Different Reactivity of Dinuclear Rhodium and Iridium Pyridine, Diimine Complexes

Thomas Marx, Peter Burger*

Institute of Inorganic and Applied Chemistry, University of Hamburg, Germany.

Thomas.Marx@chemie.uni-hamburg.de
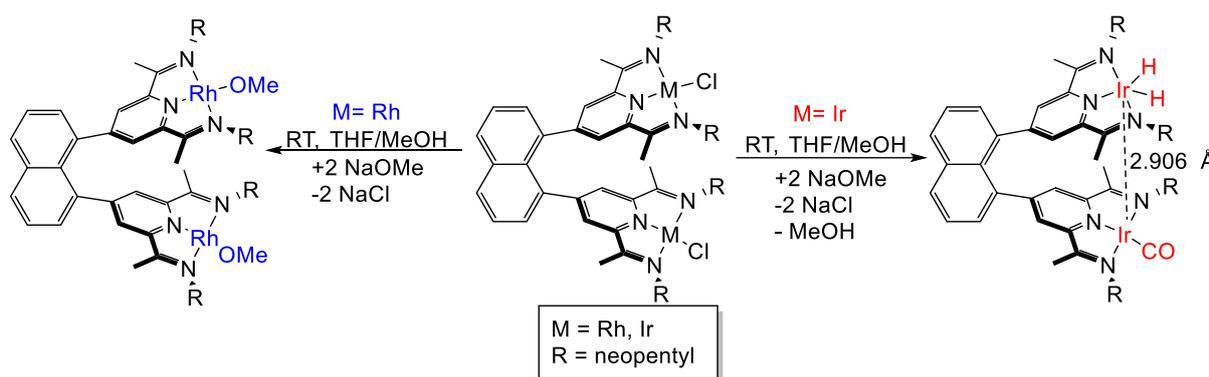
Figure 1: Example of different reactivity of bimetallic rhodium (left) and iridium complex (right).

We are currently investigating dinuclear aryl bridged pyridine diimine rhodium and iridium complexes.[1,2] In the course of this study, we noted a dramatic difference in the rhodium and iridium systems. As anticipated based on our findings for the mononuclear Rh and Ir compounds, the rhodium chlorido compound reacted with sodium methoxide to yield the corresponding methoxido complex (Fig. 1, left).[3] On the other hand, the iridium congener was cleanly converted to the dicarbonyl dihydrido complex with two formally d^9-configured Ir(0) metal centers (Fig. 1, right). The close proximity of 3 Å in the X-ray crystal structure is between the Ir centers and the PDI planes carrying the spin density explains the antiferromagnetic coupling to a diamagnetic complex. This allowed to fully study the bonding of the dihydrido ligand by NMR spectroscopy. Furthermore, we will present the pathway to the carbonyl dihydrido diiridium complex and will address the distinct outcomes observed for the mononuclear and binuclear Rh and Ir systems.

[1]   W. Dammann, T. Buban, C. Schiller, P. Burger *Dalton Trans.* **2018**, *47*, 12105-12117.
[2]   M. Stephan, W. Dammann, P. Burger *Dalton Trans.* **2022**, *51*, 13396-13404.
[3]   M. Stephan, M. Völker, M. Schreyer, P. Burger *Chemistry* **2023**, *5*, 1961-1989.

Bulk Synthesis and Characterization of Zn-based semiconductors.

A. Malik, G. Thiele*[a]

[a] Institute of Chemistry, Freie Universität Berlin, Germany

asad.malik@fu-berlin.de

Ternary alkali metal chalcogenido zincates with the general formula $A_xZn_yS_z$ (A = Na, K, x = 2, 4, 6, y = 1, 2, 3, and z = 2, 3, 4) show great potential in optoelectronic applications, photocatalytic materials, potential p-type transparent conducting materials due to their moderate band gaps and lack of magnetic interactions. They exhibit a diverse structural chemistry, whereby the anionic moiety comprises either isolated $[ZnS_4]^{6-}$ unit, or more complex 1-, 2- or 3D anionic subunits, formed by edge sharing $[Zn_3S_4]^{2-}$ tetrahedra.[1-6] Several compounds have been predicted to exist but little or less is known about their optoelectronic and physical properties. Herein, we present the bulk synthesis of Na_2ZnS_2 (**1**), K_2ZnS_2 (**2**), $Na_2Zn_2S_3$ (**3**), $K_2Zn_3S_4$ (**4**) (air and moisture stable) and K_6ZnS_4 (**5**) alongside with their crystal structure, dielectric-, and optoelectronic properties.
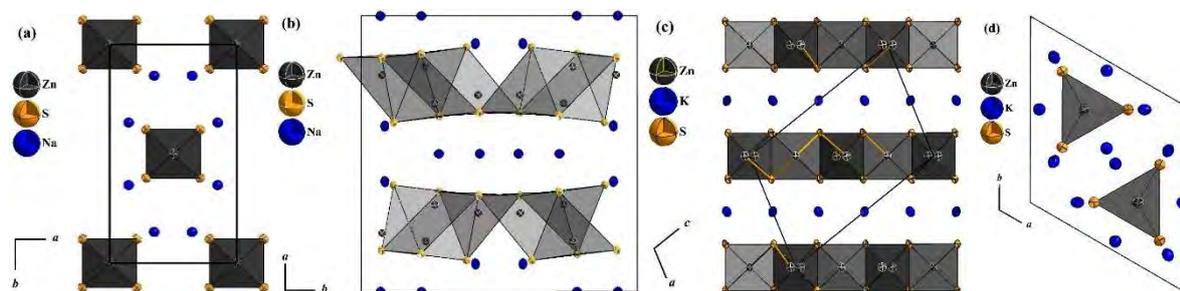
Figure 1. Depiction of the crystal structure of (**1**), (**2**), (**3**), (**4**) and (**5**). **(a)** *Ibam* type (**1**) and (**2**) with 1D connected $[ZnS_4]^{-2}$ anionic sublattice, **(b)** *C*2/*c* type (**3**) with 2D connected $[Zn_2S_3]^{-2}$ anionic sublattice, **(c)** *P*2/*n* type (**4**) with 2D connected $[Zn_3S_4]^{-2}$ anionic sublattice **(d)** *P*6$_3$*mc* type (**5**) with isolated $[ZnS_4]^{-6}$ anionic sublattice.

[1]   Bhutani, A., et al., *New family of anisotropic zinc-based semiconductors in a shallow energy landscape.* Chemistry of Materials, **2019**. **32**(1): p. 326-332.

[2]   Klepp, K. and W. Bronger, *Na₂ZnS₂ und Na₆ZnS₄, zwei neue Thiozinkate.* Revue de chimie minérale, **1983**. **20**(4-5): p. 682-688.

[3]   Lin, J., et al., *Layered Zn-based semiconductors K₂Zn₃S₄ and Rb₂Zn₃Se₄: Crystal growth, structure and potential p-type transparent conductivity.* Journal of Alloys and Compounds, **2022**. **927**: p. 167098.

[4]   Shi, H., et al., *Ternary Chalcogenides Cs₂Zn₃Se₄ and Cs₂Zn₃Te₄: Potential p-Type Transparent Conducting Materials.* Physical Review B, **2014**. **90**(18): p. 184104.

[5]   Wu, E.J. and J.A. Ibers, *Cs₂Mn₃Te₄.* Acta Crystallographica Section C: Crystal Structure Communications, **1997**. **53**(8): p. 993-994.

[6]   Zhang, X., et al., *Prediction of A₂BX₄ metal-chalcogenide compounds via first-principles thermodynamics.* Physical Review B, **2012**. **86**(1): p. 014109.

From Bispentafulvenes and Cumulenes – Synthesis and Reactivity of Mono(pentafulven)titanium Complexes

Marcel Eilers,[a] Tobias Dirksen,[a] Tobias Bötel,[a] Maximilian Beuße,[a] Saskia Bültena,[a] Kevin Schwitalla,[a] Marc Schmidtmann,[a] Malte Fischer,*[b] Rüdiger Beckhaus*[a]

[a] Institut für Chemie, Carl-von-Ossietzky-Universität Oldenburg, Germany. [b] Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Germany.

marcel.eilers@uni-oldenburg.de

Over the past 20 years, pentafulvene complexes have been shown to be effective in activating various H–E bonds (E = H, C, N, O, Hal)[1] as well as multiple bond substrates[1,2] such as ketones or nitriles under mild conditions. While monopentafulvene complexes can be converted selectively,[3] reactions of bispentafulvene complexes resulted in double bond activation or reactions with two equivalents of the substrate regardless of stoichiometry[1,2] (with only a few exceptions[2]). We previously reported the reactions of bis(pentafulvene)titanium complexes **Ti1** with the parent allene propa-1,2-diene, which led to the selective formation of chained titanium-allyl complexes **Ti2**, even with an excess of propa-1,2-diene.[4] Herein, we report further selective reactions of bis(pentafulvene)titanium complexes **Ti1** with cumulenes to generate complexes **Ti3**-**Ti5**, still bearing one remaining fulvene function. This maintains the advantage of enabling additional substrate activation reactions with H–E bonds or multiple bond substrates (see Fig. 1).
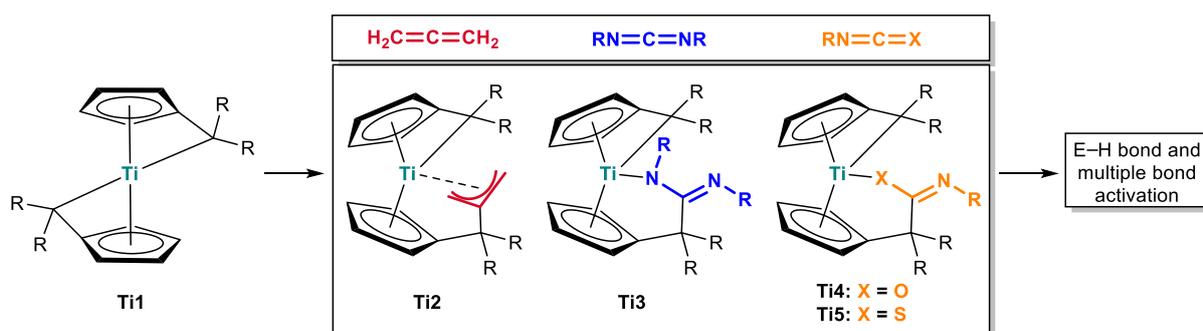
*Figure 1: Reactions of **Ti1** with cumulenes yield mono(pentafulvene)titanium complexes **Ti2**-**Ti5**, which were used for further bond activation reactions, resulting in highly functionalized titanocene complexes.*

[1]   a) R. Beckhaus, *Coord. Chem. Rev.* **2018**, *376*, 467–477; b) S. de Graaff, M. Eilers, J. Buschermöhle, N. Bengen, M. Manßen, A. Dierks, M. Schmidtmann, R. Beckhaus, *Eur. J. Inorg. Chem.* **2023**, *26*, e202200637.

[2]   H. Ebert, V. Timmermann, T. Oswald, W. Saak, M. Schmidtmann, M. Friedemann, D. Haase, R. Beckhaus, *Organometallics* **2014**, *33*, 1440–1452.

[3]   M. Fischer, R. Schaper, M. Jaugstetter, M. Schmidtmann, R. Beckhaus, *Organometallics* **2018**, *37*, 1192–1205.

[4]   M. Eilers, K. Schwitalla, T. Dirksen, M. Schmidtmann, M. Fischer, R. Beckhaus, *Organometallics* **2023**, *42, 11,* 1043–1047.

An Unprecedented Cluster Unit in (BMIm)$_2$[Hf$_9$Cl$_{14}$H$_8$(AlCl$_4$)$_6$]

Jonas Jablonski,[a] Jonas Bresin,[a] Martin Köckerling*[a]

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

Martin.Koeckerling@uni-rostock.de

The reduction of HfCl$_4$ with Li[AlH$_4$] under ionothermal conditions using (BMIm)[AlCl$_4$] as solvent and as reactant[1] gives the compound (BMIm)$_2$[Hf$_9$Cl$_{14}$H$_8$(AlCl$_4$)$_6$] in moderate yield.[2] It contains nona-nuclear metalloid cluster units with an unprecedented arrangement of the metal atoms. This can be described by a polyhedron consisting of two trigonal bipyramids, which are fused in one basal Hf atom. The edges of the Hf$_9$ polyhedron are bridged by Cl atoms and the apical sites Cl-bonded to [AlCl$_4$]$^-$ anions, see Figure 1. These bridge the cluster units into 1D cluster strands, see Figure 2. The metal atom polyhedron can be constructed by a step-wise distortion of a body centred cube. DFT calculations on [Hf$_9$Cl$_{14}$H$_{(8-x)}$(AlCl$_4$)$_6$]$^{2-}$ units for different numbers of hydrogen atoms (x = 8–0) at the UPBE-D3/def2-TZVP level of theory indicate significant metal-metal bonding. These calculations supported strongly the presence of hydridic H atoms bridging triangular faces of the metal atom skeleton. The most stable cluster anion is calculated for eight H atoms present in the cluster unit.
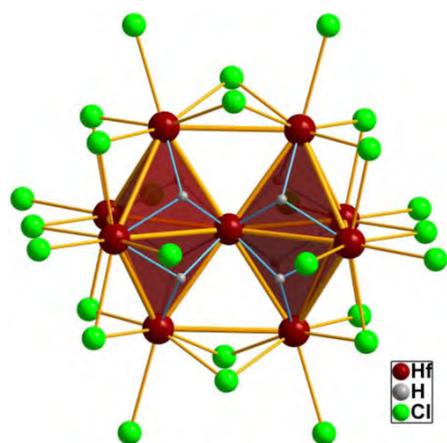
Figure 1: Structure of the chloride surrounded [Hf$_9$H$_8$] cluster core in crystals of (BMIm)$_2$[Hf$_9$Cl$_{14}$H$_8$(AlCl$_4$)$_6$].
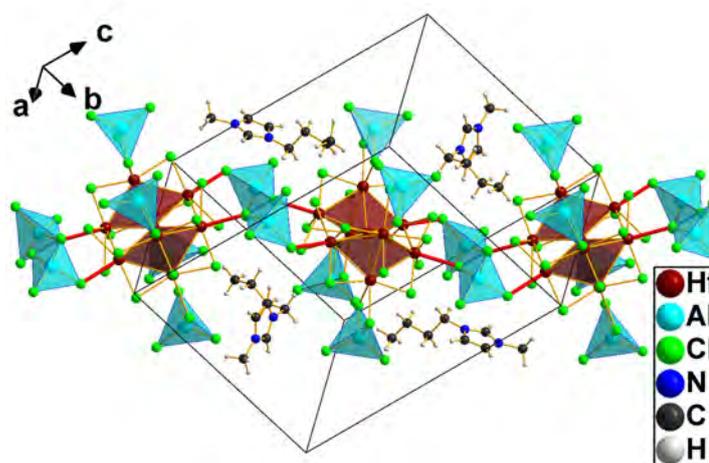
Figure 2: View of one cluster strand with surrounding [BMIm]$^+$ cations in and around the unit cell.

[1]   P. Wasserscheid, T. Welton (edts.), Ionic Liquids in Synthesis, 2nd ed., Wiley, 2007.

[2]   J. Jablonski, J. Bresin, M. Köckerling*, *Eur. J. Inorg. Chem.*, **2021**, 4776–4780.

Triphospha-heteroindanes and Hexaphospha-hetero-*s*-indacenes

Karsten Paul Lüdtke,[a] Lea Schweidt,[a] Edgar Zander,[a] Jonas Bresien,[a] Alexander Villinger,[a] Axel Schulz*[a]

[a] Institut für Chemie, Universität Rostock, Germany.

karsten.luedtke@uni-rostock.de

Recently, in our research group, 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.[1,2] By substituting nitrogen with other elements such as its heavier congeners, the reactivity and biradical character is now being optimized, potentially enabling photo-switchability. The introduction of phosphorus in 2- and 6-position could promote out-of-plane bending and consequently favor a light-induced isomerization to the hausan-type isomer, which hasn't been yet observed for the azadiphospha-derivative.
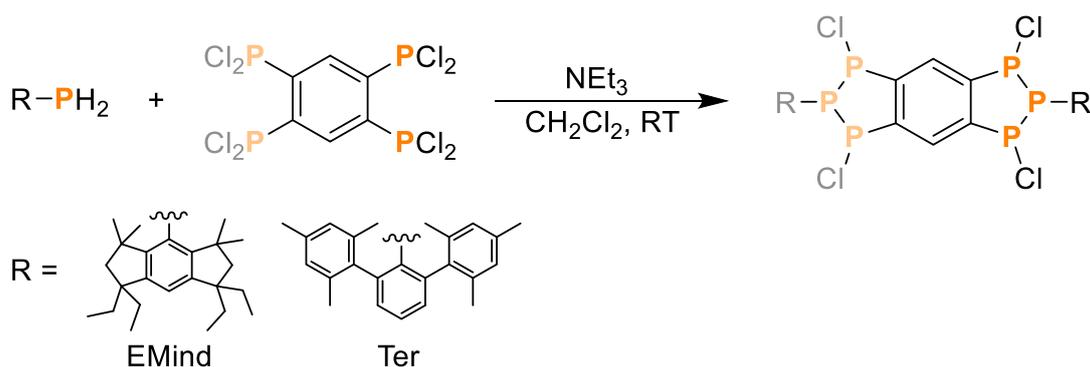
Figure 1: Synthesis of Dichloro-triphosphaheteroindanes and Tetrachloro-hexaphospha-hetreo-s-indacanes with sterically demanding substituents.

To establish the triphospha-heteroindane and hexaphospha-hetero-*s*-indacane framework, the sterically demanding phosphines EMind–PH$_2$[3] and Ter–PH$_2$[4] are reacted with bis(dichlorophosphanyl)-benzene[5] and tetrakis(dichlorophosphanyl)benzene[5] respectively, in the presence of a base. The reduction of these systems is currently under investigation.

[1]   E. Zander, J. Bresien, V. V. Zhivonitko, J. Fessler, A. Villinger, D. Michalik, A. Schulz, *J. Am. Chem. Soc.* **2023**, *145*, 14484–14497.
[2]   J. Bresien, D. Michalik, A. Schulz, A. Villinger, E. Zander, *Angew. Chem. Int. Ed.* **2020**, *133*, 1530–1535.
[3]   B. Li, T. Matsuo, T. Fukunaga, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao, *Organometallics* **2011**, *30*, 3453–3456.
[4]   J. Bresien, C. Hering, A. Schulz, A. Villinger, *Chem. Eur. J.* **2014**, *20*, 12607–12615.
[5]   E. Zander, L. Schweidt, S. Purschke, D. Michalik, A. Villinger, J. Bresien, A. Schulz, *ChemPlusChem* **2023**, *88*, e202300072.

Syntheses of Silyl Acids with Tailer-Made Lewis Acidity

Corinna Girschik[a], Saskia Rathjen[a], Thomas Müller*[a]

[a] Institut of Chemistry, Carl von Ossietzky Universität Oldenburg, Germany

corinna.girschik@uni-oldenburg.de

Herein we report the synthesis and characterisation of acenaphthyl-based, selanyl-substituted dimethylsilyl borates **2**[B(C$_6$F$_5$)$_4$]. Previous studies have shown that the Lewis acidity of these species can be influenced by various factors such as the chalcogenyl centre, the substituents at the silicon and chalcogen atoms, as well as the backbone.[1-3] By introducing a variety of electron-donating and -withdrawing aryl groups at the chalcogen atom this work demonstrates how the fine-tuning of Lewis acids results in tailer-made Lewis acidity. The Lewis acidity of these donor-stabilised silyl cations was estimated by the FBN method.[4]
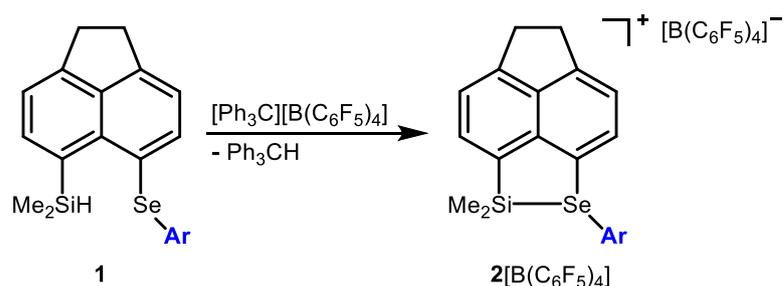
*Scheme 1: Synthesis of silyl cations **2**[B(C$_6$F$_5$)$_4$].*

[1]   N. Kordts, S. Künzler, S. Rathjen, T. Sieling, H. Großekappenberg, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2017**, *23*, 10068–10079.
[2]   S. Rathjen, *Dissertation*, Carl von Ossietzky Universität Oldenburg (Oldenburg) **2021**.
[3]   S. Künzler, *Dissertation*, Carl von Ossietzky Universität Oldenburg (Oldenburg) **2019.**
[4]   S. Künzler, S. Rathjen, A. Merk, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2019**, *25*, 15123–15130.

A new Focus on Mo(VI) Alkylidyne Complexes as Catalysts for Diyne Disproportionation

Angelika Neitzel,[a]   Dirk Bockfeld,[a]   Thomas Bannenberg,[a]   Jonathan Long,[b]   Yann Trolez,[b] Marc Mauduit[b] and Matthias Tamm*[a]

[a] *Institut für Anorganische und Analytische Chemie, TU Braunschweig, Germany.*
[b] *École Nationale Supérieure de Chimie de Rennes, 11 Allée de Beaulieu, 35708 Rennes, France.*

a.neitzel@tu-braunschweig.de

Catalytic alkyne and diyne metathesis have become undeniable for modern synthetic routes towards natural products, polymers and other macromolecules, simplifying the rearrangement of C-C triple bonds. The first tris(siloxy)-supported alkylidyne complexes were independently introduced by TAMM and FÜRSTNER.[1] In collaboration with MAUDUIT, TROLEZ and coworkers, molybdenum(VI) alkylidyne complexes containing mixed fluoroalkoxy-siloxy ligands (see MoSiF9 and MoSi*F9) are highly active catalysts regarding diyne disproportionation of sterically hindered 1,3-conjugated diynes. The reaction proceeds selectively toward the formation of triynes contrary to symmetrically substituted tris(siloxy) systems.[2] Although, siloxide ligands can be nicely tuned in their donor ability[3], design strategies (see Figure 1, A and B) of the past deserve a new perspective regarding their catalytic behaviour. The strongly σ-donating imidazolin-2-iminato ligands, respectively iminato ligands in general, appear to be an interesting alternative to siloxy ligands.[4] In this work, we would like to present a series of catalysts trying to maintain as well as improve the push-pull system by introducing a variety σ-donor ligands and study their performance in diyne disproportionation.
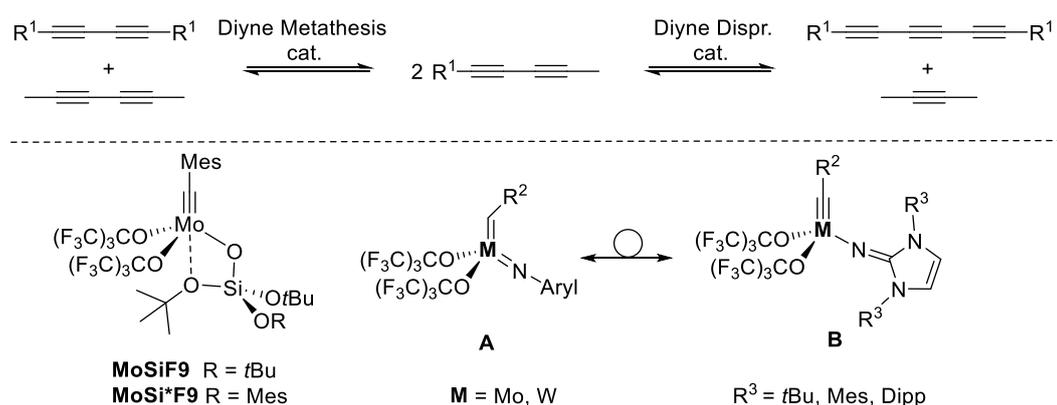
Figure 1: A different perspective of catalyst design strategies for diyne disproportionation.

[1]   Ehrhorn, H.; Tamm, M., *Chem. Eur. J.* **2019**, *25* (13), 3190–3208.
[2]   Zier, M. L.; Colombel-Rouen, S.; Ehrhorn, H.; Bockfeld, D.; Trolez, Y.; Mauduit, M.; Tamm, M., *Organometallics* **2021**, *40* (12), 2008–2015.
[3]   Fürstner, A, *J. Am. Chem. Soc.* **2021**, *143* (38), 15538–15555.
[4]   Beer, S.; Hrib, C. G.; Jones, P. G.; Brandhorst, K.; Grunenberg, J.; Tamm, M., *Angew. Chem. Int. Ed.* **2007**, *46* (46), 8890–8894.

Synthesis and Characterization of novel Alkali Metal Sulfido Silicates

I. S. Dimitrova, G. Thiele[*]

Institute of Chemistry, Freie Universität Berlin, Germany.

irina.dimitrova@fu-berlin.de

Inspired by the family of lithium superionic conductors Thio-LISICON[1] and the sodium ion conductors[2,3] based on the A-Si-S (A = Li, Na) system, we extend the search for solid state electrolytes for all-solid-state batteries to further members of the A-Si-S (A = Li, Na, K, Rb, Cs) family. As only five representatives of this compound class have been reported so far,[1-6] the initial focus lies on the synthesis and crystallization of new ternary alkali metal sulfido silicates. Herein we present the successful synthesis and structural characterization of the *neso*-silicates $A_4[SiS_4]$ (A = Na, K), forming isolated $[SiS_4]^{4-}$ tetrahedra, as well as the *soro*-silicates $A_4[Si_2S_6]$ (A = Na, K), comprising two edge-sharing SiS_4 tetrahedra to form dimeric $[Si_2S_6]^{4-}$ anions. Additionally, we present the crystal structure of the novel quaternary sulfido silicate $Na_4[SiFeS_5]$.
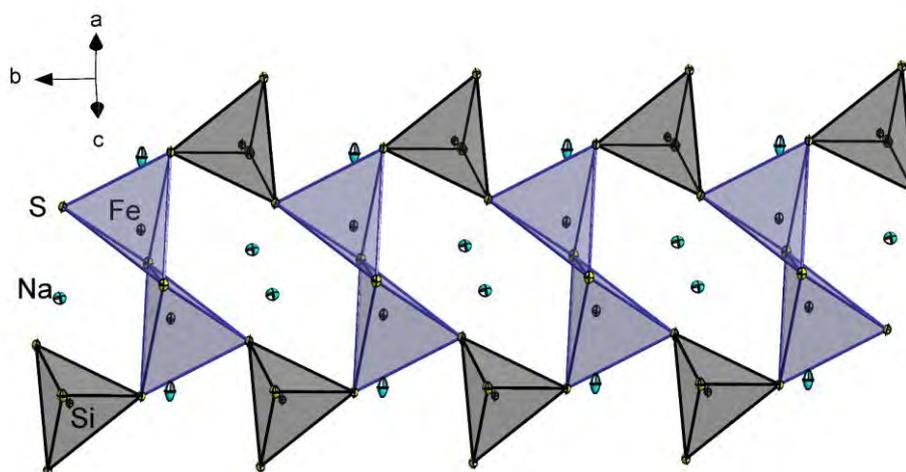
Figure 1: Excerpt of the crystal structure of $Na_4[SiFeS_5]$.

[1] M. Murayama, R. Kanno, M. Irie, S. Ito, T. Hata, N. Sonoyama, Y. Kawamotow, *J. Solid State Chem.* **2002**, *168*, 140.
[2] S. Harm, A.-K. Hatz, C. Schneider, C. Hoefer, C. Hoch, B. V. Lotsch, *Front. Chem.* **2020**, *8*, 1.
[3] N. Tanibata, K. Noi, A. Hayashi, M. Tatsumisago, *RSC Adv.* **2014**, *4*, 17120.
[4] M. Ribes, J. O. Fourcade, E. Philippot, M. Maurin, *J. Solid State Chem.*, **1973**, *8*, 195.
[5] C. Feldmann, H. G. von Schnering, Yu. Grin, *Z. Kristallogr.* **1998**, *213*, 454.
[6] A. Kolb, M. Gollackner; K. O. Klepp, *Z. Kristallogr.* **2004**, *219*, 361−362.

Comparing Ce/U Doped Zirconia: Exploring Similarities and Differences in These Solid Solutions.

Luiza Braga Ferreira dos Santos[a*], Volodymyr Svitlyk[a], Selina Richter[a], Christoph Hennig[a], Nina Huittinen[a,b]

[a]*Helmholtz–Zentrum Dresden–Rossendorf, Dresden, Germany*
[b]*Freie Universität Berlin, Berlin, Germany*

l.braga@hzdr.de

Recent research indicates that crystalline ceramic materials, such as zirconia (ZrO_2), hold great potential as matrices for immobilizing radioactive waste [1]. Zirconia can exist in various crystal structures, including monoclinic (m), tetragonal (t), and cubic (c), as well as several metastable ones (t', t'', κ, and t*), which form in doped zirconia materials[2]. In this study, we synthesized tetravalent Ce- and U-doped zirconia samples, both in the presence and absence of trivalent Y^{3+} as co-dopant. The Ce-doped zirconia samples were prepared with a wide range of cerium concentrations (10-95 mol%) using co-precipitation and calcination methods, while the U-doped samples contained a maximum of 30 mol% U. The trivalent co-dopant concentration was varied between 10 and 20 mol%. All samples underwent thorough characterization using X-ray diffraction and Raman spectroscopy. Despite the close similarity in cation radii between Ce(IV) and U(IV) of only 3%, the resulting zirconia phase compositions were remarkably different for these two tetravalent dopants. The monoclinic phase dominated up to concentrations of 15 mol% in case of Ce and 1 mol% for U doped Zr. Thereafter, t and t'' phases became prominent for Ce(IV) concentrations up to 75 mol%. The identification of the t'' phase relied on Raman data, revealing a defect band at 526.5 cm^{-1} characteristic of metastable phases (Fig 1a). Notably, the t'' phase cannot be distinguished from the cubic phase using only XRD[3]. In contrast, the results for U-doped zirconia with concentration higher than 1 mol%, compositions indicated the formation of orthorhombic and cubic phases. When the trivalent co-dopant (Y^{3+}) was added to the samples, both U- and Ce-doped compositions demonstrated similar behavior. XRD and Raman data revealed that the pure cubic phase was stabilized in both cases when the concentration of Y exceeded 15 mol% (Fig 1b). These findings shed light on the diverse phase behavior of Ce- and U-doped zirconia and the significant influence of co-dopants on the host crystal structure.
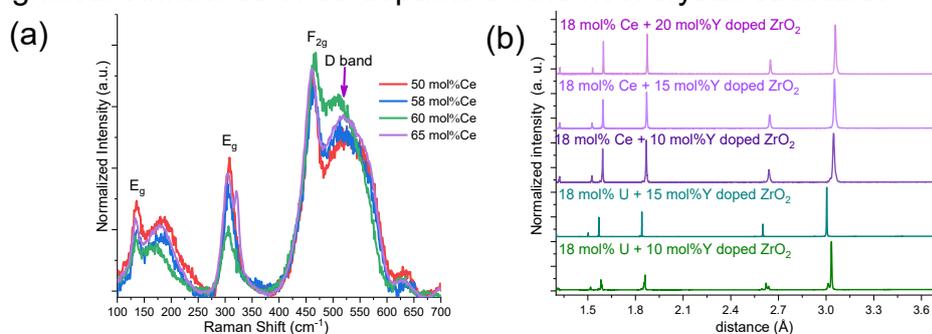
Figure 1: (a) Raman spectra (b) X-ray diffraction for Ce/U-doped zirconia with Y co-doping.

[1]   Kumar, R., et al. (2021). IJPAP, 59(12), p. 811-826.
[2]   Varez, A. et al. (2007). J. Eur. Ceram. Soc. 27, p. 3677-3682.
[3]   Lamas, D. G., et al. (2003). J. Mater. Chem, 13(4),p. 904-910.

Synthesis and Characterization of Organofluorine Derivatives of Polyoxopalladates

Pooja Kulashri, Bassem S. Bassil, and Ulrich Kortz*

School of Science, Constructor University, Campus Ring 1, 28759 Bremen, Germany.

ukortz@constructor.university

Polyoxometalates (POMs) are discrete, anionic, polynuclear transition metal-oxo complexes.[1] POMs exhibit a large variety of shape, size and composition and potential applications ranging from material science to catalysis and biomedicine. Classical POMs are comprised of early *d*-block addenda in high oxidation states, such as W^{VI} or V^{V}. In 2008 the first polynuclear metal-oxo complex of palladium(II) was discovered,[2] and since then this class has been developed further over the years, resulting in almost 100 compounds.[3,4]

Here we report on the first examples of organofluorine derivatives of polyoxopalladates, which were characterized by FT-IR and multinuclear NMR spectroscopy as well as single-crystal/powder X-ray diffraction.

[1] Pope, M. T. *Heteropoly and Isopoly Oxometalates*, *Springer-Verlag*, Berlin, 1983.
[2] Chubarova, E. V.; Dickman, M. H.; Keita, B.; Nadjo, L.; Mifsud, M; Arends, I. W. C.; Kortz, U. *Angew. Chem. Int. Ed.* **2008**, 47, 9542-9546.
[3] Yang, P.; Kortz, U. *Acc. Chem. Res.* **2018**, *51*, 1599-1608.
[4] Yang, P.; Elcheikh Mahmoud, M.; Xiang, Y.; Lin, Z.; Ma, X.; Christian, J. H.; Bindra, J. K.; Kinyon, J. S.; Zhao, Y.; Chen, C.; Nisar, T.; Wagner, V.; Dalal, N. S.; Kortz, U. *Inorg. Chem.* **2022**, *61*, 18524–18535 and references therein.

Synthesis and Characterization of Dimethylarsinate- and Phosphonate-Functionalized Polyoxomolybdates

Vinaya Siby, Bassem S. Bassil, and Ulrich Kortz*

School of Science, Constructor University, Campus Ring 1, 28759 Bremen, Germany.

ukortz@constructor.university

Polyoxometalates (POMs) are discrete, anionic, polynuclear metal-oxo clusters with unparalleled compositional versatility and structural intricacy combined with distinctive physicochemical properties that have unique and potentially useful applications in catalysis, molecular magnetism, material sciences, biotechnology, and medicine.[1] The size, shape, and charge density of POMs render them good candidates for pharmaceutical applications, such as antibacterial, antiviral or anticancer activities. The covalent linkage of organic or organometallic moieties in a controlled fashion can improve the selectivity of POMs towards specific biological targets.[2,3]

Recently we have demonstrated that dimethylarsinate (also known as cacodylate) can be incorporated in polyoxo-platinates and palladates[4a] as well as molybdates.[4b]

Now we tried to further expand the cacodylate-containing polyoxomolybdate family by incorporation of various phosphonate capping groups. Several new compounds could be prepared, which were structurally characterized in the solid state by FT-IR spectroscopy and single-crystal/powder X-ray diffraction and in solution by ^{31}P and ^{13}C NMR spectroscopy as well as ESI-mass spectrometry.

[1] Pope, M. T., *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, 1983.

[2] Barkigia, K. M.; Rajkovic-Blazer, L. M.; Pope, M. T.; Prince, E.; Quicksall, C. O. *Inorg. Chem.* **1980**, *19*, 2531−2537.

[3] Haushalter, R. C.; Lai, F. W. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 743–746.

[4] (a) Zhang, J.; Bhattacharya, S.; Khsara, B. E.; Nisar, T.; Müller, A. B.; Besora, M.; Poblet, J. M.; Wagner, V.; Kuhnert, N.; Kortz, U. *Inorg. Chem.* **2023**, *62*, 33, 13184-13194 and references therein; (b) Sundar, A.; Bhattacharya, S.; Oberstein, J.; Ma, X.; Bassil, B. S.; Nisar, T.; Taffa, D. H.; Wark, M.; Wagner, V.; Kortz, U. *Inorg. Chem.* **2022**, *61*, 11524–11528.

Peroxo-Thorium(IV)-Containing Polyoxometalate: Synthesis and Structural Characterization

<u>Sahar Khandan</u>, Bassem S. Bassil, and Ulrich Kortz*

School of Science, Constructor University, Campus Ring 1, 28759 Bremen, Germany.

ukortz@constructor.university

Polyoxometalates (POMs) represent a distinctive class of discrete, anionic, and soluble polynuclear metal oxides with a broad range of structural and compositional diversities. POMs exhibit intriguing potential for a range of applications, including magnetism, material science, biomedicine, and catalysis.[1,2] The incorporation of peroxo-bridged *d* and *f*-block metal-oxo assemblies into POM structures constitutes a relatively underexplored subarea of POM chemistry, which has garnered attention due to its novelty in terms of both structure and composition.[3-5] Herein, we present the first example of peroxo-thorium(IV)-containing tungstogermanates synthesized through a simple one-pot procedure in aqueous solution. The resulting polyanion was structurally characterized in both the solid state and in solution by various analytical techniques, including single-crystal X-ray diffraction, thermogravimetric analysis, Fourier transform infrared and Raman spectroscopy.

[1]   M. T. Pope, Heteropoly and Isopoly Oxometalates; *Springer*: Berlin, 1983.
[2]   M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.***1991**,*30*, 34−48.
[3]   B. S. Bassil, S. S. Mal, M. H. Dickman, U. Kortz, H. Oelrich, L. Walder, *J. Am. Chem. Soc.* **2008**, *130*, 6696−6697.
[4]   P. Miró, J. Ling, J. Qiu, P. Burns, L. Gagliardi, C. Cramer, *Inorg. Chem*. **2012**, *51*, 8784−8790.
[5]   J. Goura, A. Sundar, B. S. Bassil, G. Ćirić-Marjanović, D. Bajuk-Bogdanović, U. Kortz, *Inorg. Chem*. **2020**, *59*, 16789−16794.

Fluorinated Arylarsonate-containing Polyoxomolybdates: pH-dependent Formation of Mo_6 *vs* Mo_{12} Species

Arun Pal and Ulrich Kortz*

School of Science, Constructor University, Campus Ring 1, 28759 Bremen, Germany.

ukortz@constructor.university

We report on the synthesis and characterization of some novel fluorinated arylarsonate-containing polyoxomolybdates.[1-4] The reaction of different fluoro-arylarsonates with sodium molybdate in aqueous acidic medium resulted in the formation of three polyoxo-6-molybdates (**1-3**) and three polyoxo-12-molydates (**4-6**). These species can be interconverted reversibly as a function of pH. All six polyanions have been characterized by single-crystal X-ray diffraction, infrared spectroscopy, elemental analysis, thermogravimetric analysis (TGA), and multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F).

[1] M. T. Pope, A. Müller, Eds., Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications; Kluwer: Dordrecht, The Netherlands, 2001.
[2] M. T. Pope, *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.
[3] U. Kortz, A. Müller, J. van Slageren, J. Schnack, N. S. Dalal, M. Dressel, *Coord. Chem. Rev.* **2009**, *253*, 2315−2327.
[4] P. Manna, S. Bhattacharya, U. Kortz, *Inorg. Chem.* **2021**, *60*, 7161−7167.

Peroxo-Polyoxometalates for H$_2$O$_2$-based Homogeneous, Heterogeneous, and Biphasic Oxidation Catalysis

Anusree Sundar, Bassem S. Bassil, and Ulrich Kortz*

School of Science, Constructor University, Campus Ring 1, 28759 Bremen, Germany.
ukortz@constructor.university

Polyoxometalates (POMs) are polynuclear metal-oxo complexes which can be synthesized from simple inorganic salts in aqueous, acidic solution by condensation. POMs have many interesting properties such as discrete structure, large size, solution-stability, redox-activity, photo- and chemo-reducibility, that make them attractive candidates in catalysis, magnetism, material science and biomedicine.[1,2] POMs with one or more oxo-bridges replaced by peroxo-groups such as the so-called Venturello ion are of particular interest in green oxidation catalysis as they provide accessible sites for the simultaneous substrate and peroxide activation at the metal centers.[2,3]

Here we present the synthesis of peroxo-zirconium and peroxo-hafnium-containing polyoxotungstates, which were structurally characterized using multiple analytical techniques. Furthermore, these species were shown to be efficient homogeneous as well as heterogeneous catalysts for H$_2$O$_2$-mediated oxidation of alcohols, alkene, *α,β*-unsaturated carbonyl compounds, and thiols.

[1] M. T. Pope, *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.

[2] M. T. Pope, A. Müller, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34−48.C.

[3] C. Venturello, R. D'Aloisio, J. C. J. Bart, M. Ricci, *J. Mol. Cat.* **1985**, *32*, 107-110.

[4] J. M. Brégeault, M. Vennat, L. Salles, J. Y. Piquemal, Y. Mahhaa, E. Briot, P. C. Bakala, A. Atlamsani, R. Thouvenot, *J. Mol. Catal. A: Chem.* **2006**, *250*, 177–189.

Cagefight – Catapinands as mimics for biological anion regognition

Stefan Richter,[a] Carola Schulzke*[a]

[a] Institute of Biochemistry, University of Greifswald, Germany.

stefan.richter@uni-greifswald.de

In biological systems anions often play a crucial role in, e.g. as cofactors, for ion co-transport, as hazards ect.[1] Catapinands are three dimensional supramolecules which can form little pockets inside their cage-like geometry. By serving as a host they can bind with many anions which they then embed as their guests.[1-3]

Several catapinands will be presented, which provide many binding sides similar to those that can be found in proteins, e.g. electron rich oxygen functions, free amines, aliphatic and aromatic binding sites. Our investigations are focused on the binding of and selectivity for the anion in the catapinand.

It was furthermore investigated whether and how easily the anion can change its geometry upon being swallowed by the catapinand, focussing on the examples of molybdate and tungstate, and utilizating of DFT calculations and UV/Vis spectroscopy.[3-4]
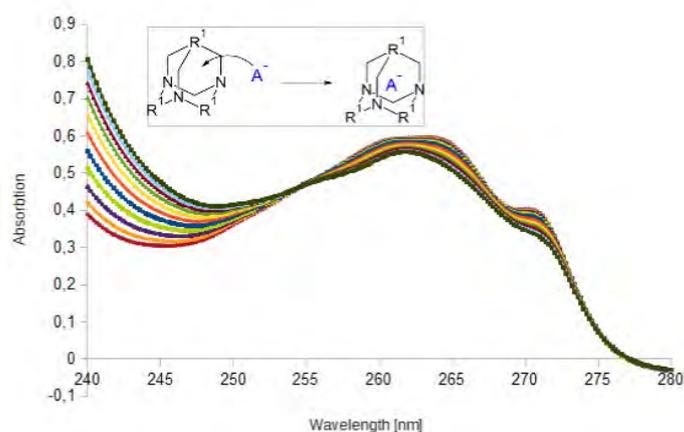
Figure 1: UV/Vis Spectra of Titration from Phosphate with schematic guest molecule

[1]   P. Gamez, T. J. Mooibroek, S. J. Teat, J. Reedijk, *Acc. Chem. Res.* **2007**, *40*, 435-444.
[2]   C. Estrellas, A. Fontera, D. Quinonero, P. M. Deyà, *Angew. Chem.* **2011**, *123*, 435-438
[3]   S. E. Bodman, S. J. Butler, *Chem. Sci.* **2021**, *12*, 2716-2734
[4]   W. R. Hagen, *Molecules* **2023***, 28*, 4017

Manganese thiacorroles with different oxidation states

Nina Schulze,[a] Simon Eulberg,[a] Martin Bröring*[a]

[a] *Institut für Anorganische und Analytische Chemie, Technische Universität, Germany.*

nina.schulze@tu-bs.de

Manganese complexes of porphyrinoids have been studied in detail for a long time. They are used in biological studies because of their similarity to iron porphyrins such as heme.[1] Furthermore manganese corroles and manganese porphyrins show catalytic behaviour for example in C-H halogenation and polymerisation of epoxides.[2,3]

By synthesizing modified porphyrins with altered electronic properties, these processes can be investigated in more detail. 10-Thiacorroles can be considered as the intermediate between porphyrins and corroles. They are dianionic ligands and have a contracted cavity size.[4] Already known complexes of 10-heterocorroles show unusual electronic and magnetic properties[5], so the synthesis of novel manganese complexes of these ligands is of great interest. By varying the axial ligand or using reducing agents, different oxidation states of the manganese can be stabilized.
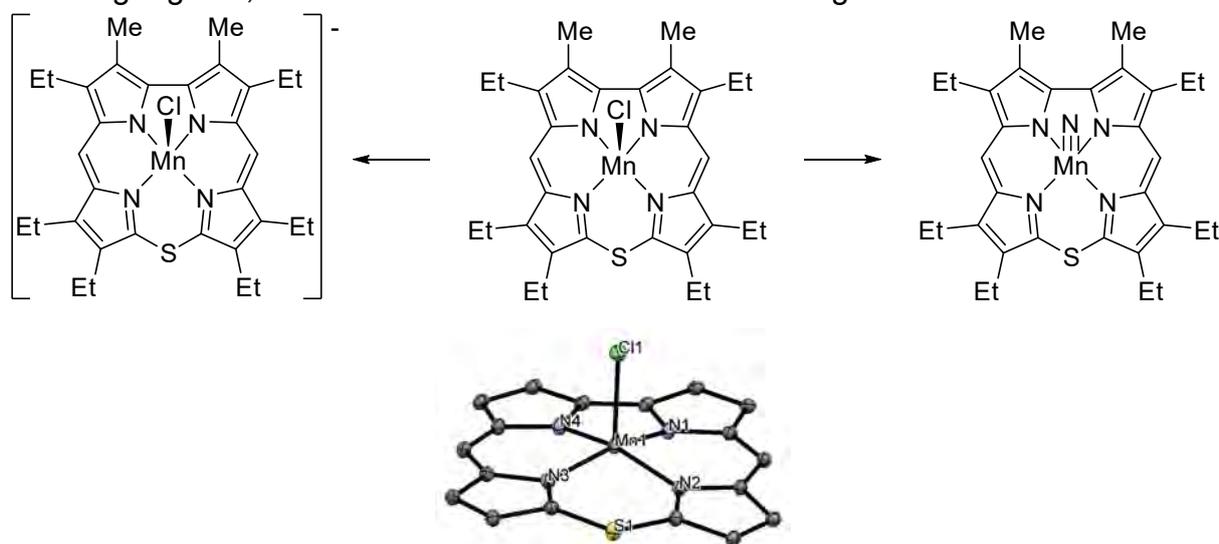
Figure 1: Chlorido manganese thiacorrole (middle) and its reaction to a nitrido manganese thiacorrole (right) and the reduction to anionic chlorido manganese thiacorrole (left). Crystal structure of chlorido manganese thiacorrole (below), cocrystalized solvent, β-substitutions and H omitted for clarity.

[1]   R. A. Baglia, J. P. T. Zaragoza D. P. Goldberg, *Chem. Rev*. **2017**, 117, 21, 13320-13352.
[2]   W. Liu, J. T. Groves, *J. Am. Chem. Soc.* **2010**, 132, 37, 12847-12849.
[3]   C. Robert, T. Ohkawara, K. Nozaki*, Chem. Eur. J.* **2014**, 20, 16, 4789-4795.
[4]   D. Sakow, B. Böker, K. Brandhorst, O. Burghaus, M. Bröring, *Angew. Chem. Int. Ed*. **2013**, 52, 4912-4915.
[5]   D. Sakow, D. Baabe, B. Böker, O. Burghaus, M. Funk, C. Kleeberg, D. Menzel, C. Pietzonka, M. Bröring, *Chem. Eur. J.* **2014**, 20, 2913-2924.

Ventures in Synthesis of Sulfidolanthanidates (II) Salts

Islam Ramadan,[a] Günther Thiele[a]

[a] Inorganic Chemistry, Institute of Chemistry and Biochemistry, Department of Biology, Chemistry, and Pharmacy, Free University Berlin, Germany.

islam.ramadan@fu-berlin.de

While some sulfidometalates such as $K_2Fe_3S_4$ and $Na_2Fe_3S_4$ exhibit extraordinary ionic conductivity, and dielectric properties, exploring potential isotypic structures of sulfidolanthanidates can provide new candidates for electronic applications.[1] Although the lanthanides series possesses interesting characteristics because of *f*-orbital interactions, only $A[LnS_2]$ is known in literature (A = alkali metal & Ln = lanthanoid) with a noticeable absence of any ternary sulfidolanthanidates (II), and sulfidolanthanidates possessing an organic cation. While lanthanoids are known to exist in the divalent state on the molecular level, their existence beyond binary systems on a network solid level is still a matter of question.[2] In order to achieve the goal beforehand , two synthesis approaches were employed: solid state synthesis, and wet chemistry synthesis such as ligands substitution reactions in solvents starting from $(cation)_3[LnCl_6]$ (III) species followed by further reduction.

Pursuing wet chemistry synthesis approach starting from hexahalidolanthanidates (III) species, synthesis of $(cation)_3[LnCl_6]$ species was improved, leading to synthesis of a series of novel compounds possessing aliphatic ammonium-based or an imidazolium-based cation. Ligands substitution reactions were attempted on the $(cation)_3[LnCl_6]$ salts with A_2S in coordinating solvents such as ethane-1,2-diamine (*en*) and triethylene glycol (*TEG*) at 150 °C. This attempt yielded a series of novel compounds possessing formulas $[Ln(en)_xCl_y]Cl_z$ and $[Ln(TEG)_xCl_y]Cl_z$, variations in x, y, and z follow the pattern seen in lanthanides contraction. The coordinating nature of these solvents interfered with the targeted synthesis, for that, further attempts are planned to take place in non-coordinating solvents. Different attempts in solid-state synthesis yielded only the literature known $A[LnS_2]$, (Ln = Ce, Eu, Sm), even with targeting quaternary stoichiometries such as $K_2[Fe_2LnS_4]$, mixed phases of $K_3[Fe_2S_4]$ and $K[LnS_2]$ were obtained. Obtained compounds were characterized by means of X-Ray diffraction and investigated for optical properties and reduction potential.

[1]   Mohammad R. Ghazanfari, Archa Santhosh, Johannes C. Vrijmoed, Konrad Siemensmeyer, Bertram Peters, Stefanie Dehnen, Paul Jerabek, Günther Thiele, Large-scale synthesis of mixed valence K 3 [Fe 2 S 4] with high dielectric and ferrimagnetic characteristics , RSC Advances, 10.1039/D2RA05200H, 12, 47, (30514-30521), (2022)

[2]   Nicholas, H.M. and Mills, D.P. (2017). Lanthanides: Divalent Organometallic Chemistry. In Encyclopedia of Inorganic and Bioinorganic Chemistry, R.A. Scott (Ed.). https://doi.org/10.1002/9781119951438.eibc2453

Arsenic Corroles

<u>Hendrik Peters</u>,[a] Martin Bröring*[a]

[a] IAAC, TU Braunschweig, Germany.

hendrik.peters@tu-braunschweig.de

Corrole macrocycles have aroused research interest as part of porphyrinoid chemistry. Due to the 18 π-system and tri-ionic 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
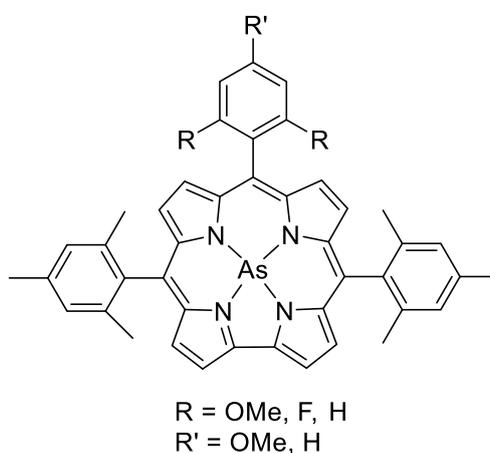
Figure 1: Arsenic corroles with oxidation state of +3

[1]   J. F. B. Barata, M. G. P. M. S. Neves, M. A. F. Faustino, A. C. Tomé, J. A. S. Cavaleiro, *Chem. Rev.* **2017**, *117*, 3192–3253.
[2]   S. Eulberg, N. Schulze, J. Krumsieck, N. Klein, M. Bröring, *Angew. Chem.* **2023**, *135*.
[3]   L. M. Reith, M. Stiftinger, U. Monkowius, G. Knör, W. Schoefberger, *Inorg. Chem.* **2011**, *50*, 6788–6797.
[4]   K. M. Kadish, C. Erben, Z. Ou, V. A. Adamian, S. Will, E. Vogel, *Inorg. Chem.* **2000**, *39*, 3312–3319.

Exploring Novel Phosphaalkene based Monoanionic P,N,P Ligands for Coordination Chemistry to Early Transition Metals

Kushik, Christian Hering-Junghans*, Torsten Beweries*.

Leibniz-Institut für Katalyse e.V. (LIKAT)*, Albert-Einstein-Str. 29a, 18059 Rostock (Germany).*

kushik.kushik@catalysis.de

Phosphinopyridine P,N and pyridineimine N,N ligands have been ubiquitously used in coordination chemistry and their widespread application in catalytic processes has been demonstrated.[1] In contrast, reports on related pyridinephosphaalkene P,N ligands and their applications in coordination chemistry and catalysis are still rather limited. Apart from Geoffroy's studies of a pyridine-based phosphaalkene P,N Cu complex,[2] only a series of Ru P,N complexes were reported by Cain and co-workers lately.[3] Our group has recently demonstrated the synthesis of π-extended P,N phosphaalkene ligands using the phospha-Wittig reagent Mes*−P(PMe$_3$) and 2-quinolinecarboxaldehyde.[4] When coordinated to Rh(I)[5] and Ir(I),[6] these ligands showed a diverse coordination chemistry, ranging from simple twofold coordination to C−H bond activation at the o-*t*Bu group of the Mes*-substituted phosphaalkenes in case of Rh. The Ir(I) complexes have been shown to be good pre-catalysts for the Guerbet-type upgrading of EtOH to iso-butanol.

(a) PNP   (b) PN$_4$
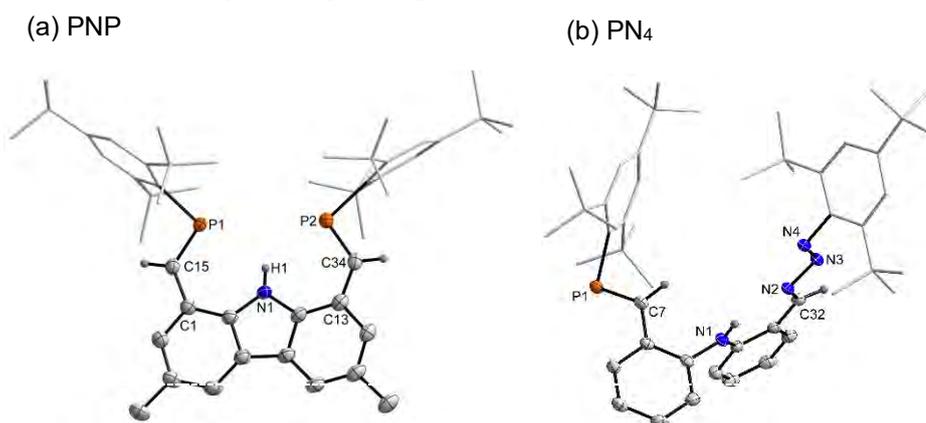
Figure 1: (a). PNP – derived from a carbazole dialdehyde backbone; (b). PN$_4$ – derived from a diphenylamine dialdehyde backbone.

To further extend the library of P,N,P type phosphaalkenes, we have been interested to use carbazole and diarylamine backbones, which would give monoanionic P,N,P type ligands. In this realm we have optimised the synthesis of carbazole and diarylamine based dialdehydes and have used these dialdehydes for the synthesis of novel bisphosphaalkenes and mono-phosphaalkene ligands respectively. In case of mono-phosphaalkene ligands the second aldehyde position is available for further functionalisation. Whereas monoanionic P,N,P type ligands are accessible in case of P,N,P ligand derived from a carbazole dialdehyde backbone using mild base. Preliminary studies show coordination to Ti(IV).

[1]   Speiser, F.; Braunstein, P.; Saussine, L. *Organometallics* **2004,** *23*, 2633.
[2]   Jouaiti, A.; Geoffroy, M.; Bernardinelli, G. *J. Chem. Soc., Dalton Trans.* **1994**, 1685.
[3]   Nakashige, M. L.; Loristo, J. I. P.; Wong, L. S.; Gurr, J. R.; O'Donnell, T. J.; Yoshida, W. Y.; Rheingold, A. L.; Hughes, R. P.; Cain, M. F. *Organometallics* **2019**, *38*, 3338.
[4]   Gupta, P.; Siewert, J.-E.; Wellnitz, T.; Fischer, M.; Baumann, W.; Beweries, T.; Hering-Junghans, C. *Dalton Trans.* **2021,** *50*, 1838.
[5]   Gupta, P.; Täufer, T.; Siewert, J.-E.; Reiß, F.; Drexler, H.-J.; Beweries, T.; Hering-Junghans, C. *Inorg. Chem.* **2022**, *61*, 11639.
[6]   Gupta, P.; Drexler, H.-J., Wingad, R.; Wass, D.; Baráth, E.; Beweries, T.; Hering-Junghans, C. *Inorg. Chem. Front.* **2023**,*10*, 2285.

Silole and germole anions substituted with stabilized silylenes

Chenghuan Liu,[a] Thomas Müller*[a]

[a] *Institute of Chemistry, Carl von Ossietzky University Oldenburg, Carl von Ossietzky-Str. 9-11, 26129 Oldenburg, Germany, European Union*

thomas.mueller@uni-oldenburg.de

Tri-coordinated Si(II) compounds such as silole anions **1** and derivatives of Roesky's silylene **2** are isolobal to phospholes and phosphanes and show favorable properties for coordination chemistry and small molecule activation.[1] In this work, we combine both structural motifs in one compound to study possible cooperative phenomena. We report here the synthesis of potassium salts of the silylene-substituted silole anion [**3**]⁻ and discuss its electronic properties. Interestingly, the silylene substituted germole anion [**4**]⁻ cannot be isolated but it rearranges to the cyclic germenyl anion [**5**]⁻. First results on the reactivity of K[**3**] and K[**5**] will be reported.
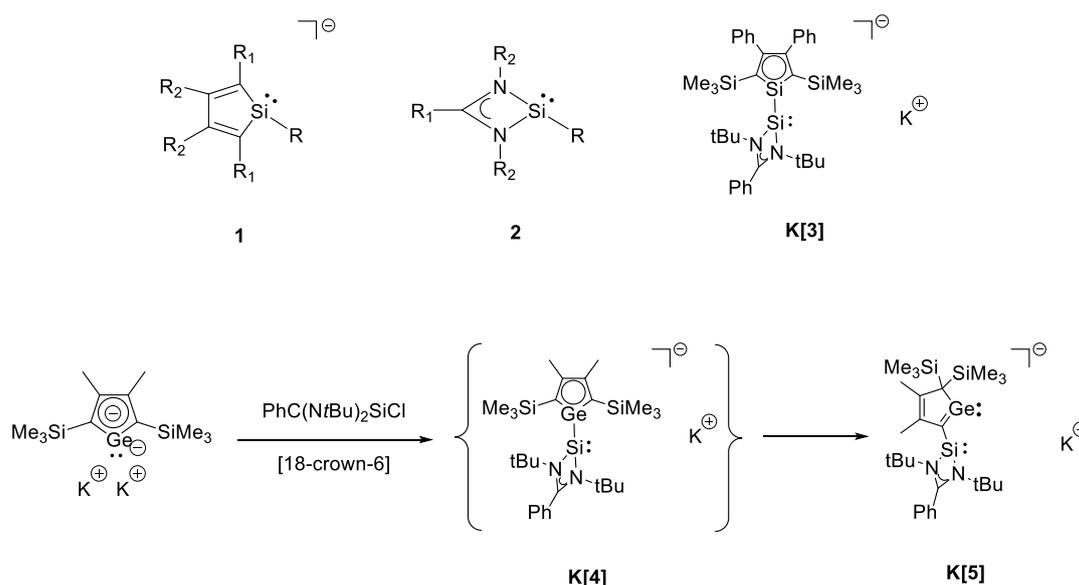
*Figure 1: Tri-coordinated Silylene **1,2** and the synthesis of **K[3]**, **K[4]**, **K[5]**.*

[1]   a) Saito, M. *Coord. Chem. Rev*. **2012**, *256*, 627-636; b) Dong, Z.; Albers, L.; Müller, T. *Acc of Chem Res.* **2020,** *53*, 532-543; c) Wang, L.; Li, Y.; Li, Z.; Kira, M. *Coord. Chem. Rev.* **2022**, *457*, 214413-214441.

New Perfluorinated Silver(I) Alcoholates - Versatile Transfer Reagents

P. Golz, *M. Balizs, H. Kemmler, M. Kleoff, K. Shakeri, L. Maas, P. Voßnacker, S. Riedel*
a

a Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 14195 Berlin; E-mail: p.golz@fu-berlin.de

p.golz@fu-berlin.de

The perfluorinated alkoxy groups like OCF_3 and OC_2F_5 can be used as a tool for tuning the properties of bio active agents as the group is lipophilic and thermally and chemically stable.[1] The temperature sensitive Silver(I) alcoholate $AgOCF_3$, is known as versatile reagent to incorporate this group into organic molecules. Starting from Lewis acidic carbonyl fluoride, perfluorinated carboxylic acid fluorides, or ketones the silver(I) alcoholates can be synthesized via the reaction with silverfluoride. $AgOCF_3$[2], $AgOC_2F_5$ and the higher alcoholates can be used as stable acetonitrile solutions.

$$R = F, CF_3, C_2F_5, C_7F_{15}$$
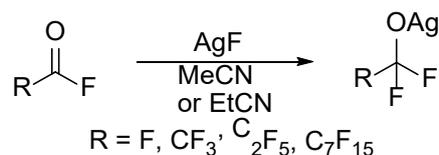
Via metathesis the corresponding copper(I) alcoholates $CuOCF_3$ and $CuOC_2F_5$ can be synthesized. Crystallization of these species showed that in the silver compounds the OCF_3 groups serve as bridging ligands connecting silver(I) moieties while the analogous copper compound forms isolated F_3CO^- and $[Cu(MeCN)_4]^+$ ions. Further experiments focus on the application of these reagents in organic synthesis and coordination chemistry.
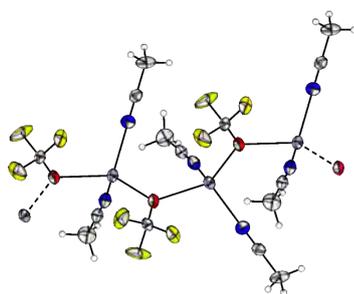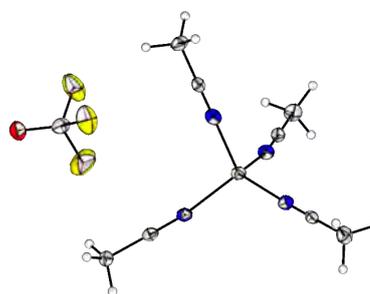
[Ag(MeCN)2(OCF3)]n   [Cu(MeCN)4][OCF3]

[1]   T. Besset, P. Jubault, X. Pannecoucke, T. Poisson, *Org. Chem. Front.* 2016, *3*, 1004; F. R. Leroux, B. Manteau, J.-P. Vors, S. Pazenok, *Beilstein J. Org. Chem.* 2008, *4*, 13.

[2]   A. Turksoy, T. Scattolin, S. Bouayad-Gervais, F. Schoenebeck, *Chem: Eur. J.* 2020, *26*, 2183.

Gaining new insights into the synthesis of low valent group 6 complexes with dithiooxamide ligands

Anna-Lena Land, Christian Fischer*

Institut für Biochemie, Universität Greifswald, Germany.

anna-lena.land@stud.uni-greifswald.de

Research on low valent molybdenum and tungsten complexes with dithiooxamide type ligands peaked during the late last century.[1-4] We think that these complexes have a high potential to be active for small molecule activation catalysis as they possess the most wanted attributes, such as low valency, a wide redox potential range, solubility in polar organic solvents, and proton-switching capabilities.

In 1984 tom Dieck and Form[3] were the first to describe a synthetic procedure starting with $[Mo(CO)_3(CH_3CN)_3]$. The complexes were synthesized by substituting the acetonitrile ligands with triphenylphosphine and dithiooxamide in methanol. However, the analysis of all compounds was restricted to IR-spectroscopy and elemental analysis. Our poster presents an improved procedure for this complex type and the first molecule structures of its kind. Additionally, inevitable side products and a mechanistic explanation for their formation are shown.
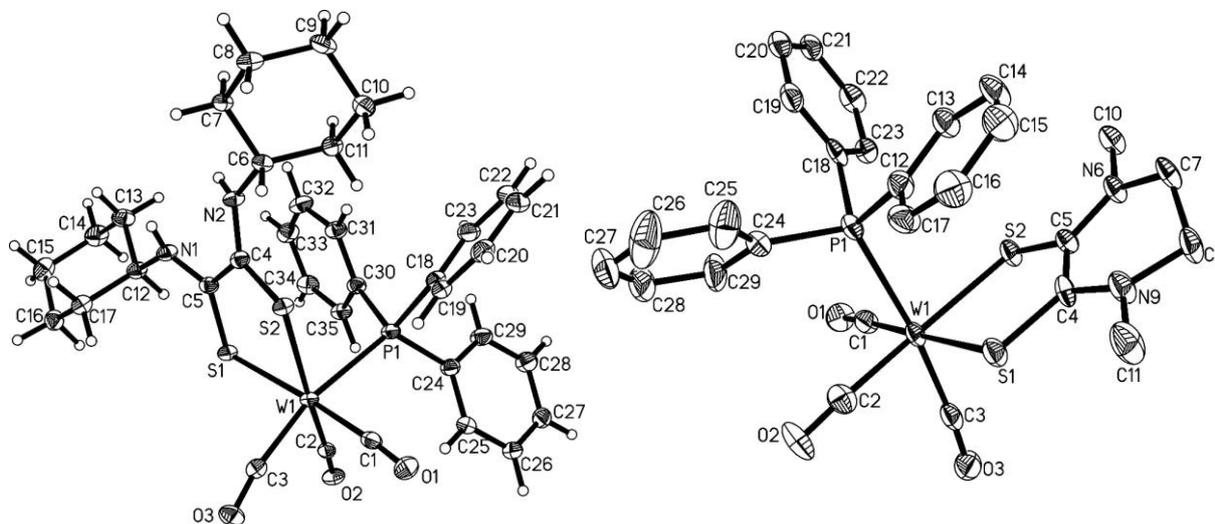
Figure 1: Molecule structures of $[W(CO)_3(PPh_3)(cycdto)]$ and $[W(CO)_3(PPh_3)(me_2pipdt)]$ (cycdto = N,N'-Dicyclohexyldithiooxamide, me_2pipdt = 1,4-dimethylpiperazine-2,3-dithione).

[1] H. tom Dieck, H. Friedel, *Journal of the Chemical Society D: Chemical Communications* **1969**, 411.
[2] H. tom Dieck, F. Hohmann, M. Form, T. Mack, I. W. Renk, *Journal of the Less Common Metals* **1977**, *54*, 221-231.
[3] H. tom Dieck, M. Form, *Zeitschrift für anorganische und allgemeine Chemie* **1984**, *515*, 19-35.
[4] K. R. Bernard, A. G. Wedd, E. R. T. Tiekink, *Inorganic chemistry* **1990**, *29*, 891-892

A visible light-mediated double photoswitch: Combining biradicals with azobenzenes

Yannic Pilopp,[a] Jonas Bresien,[a] Dirk Michalik,[a,b] Alexander Villinger,[a] Axel Schulz*[a,b]

[a] *Institute of Chemistry, University of Rostock, Germany.* [b] *Leibniz Institute for Catalysis, Germany.*

yannic.pilopp@uni-rostock.de

Molecular switches containing multiple switchable units have become the subject of intense investigations in recent time to get insights into their use as e.g. molecular motors.[1,2] We now introduce a molecular switch that combines both biradical and azobenzene motifs to perform visible-light induced constitutional and stereo isomerization within the same molecule. The insertion of functionalized azobenzenes into already established four-membered biradical [•P(μ-N-Ter)$_2$P•] represents a straight-forward method to generate the desired double switches (e.g. **1**) in excellent yields (>90%). The switching properties were demonstrated with fluorinated species **1** and, interestingly, can be done either gradually or simultaneously, depending on the order in which the sample is irradiated with red and/or green light (Figure 1).
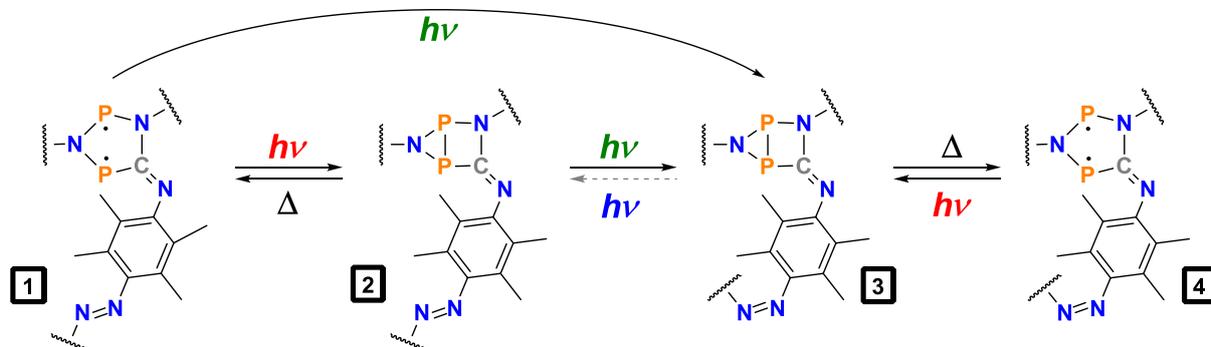
Figure 1: A molecular switch undergoing either constitutional or stereo isomerization upon irradiation with visible light as a combination of biradicals with azobenzenes.

All possible isomerization reactions, i.e. housane formation and *E/Z* isomerization at the azobenzene, were successfully carried out and the reaction products **2**, **3** and **4** (when performing the thermal reverse reaction in the dark) were identified using ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy. Results from quantum chemical calculations contributed to the understanding and visualization of the different conformers of each of the observed compounds (**1** to **4**) caused by the unique structure of the double switches.

[1]   D. Bléger, S. Hecht, *Angew. Chem. Int. Ed.* **2015**, *54*, 11338–11349.
[2]   A. Gerwien, B. Jehle, M. Irmler, P. Mayer, H. Dube, *J. Am. Chem. Soc.* **2022**, *144*, 3029–3038.

A stable tetraradical and its reactivity towards small molecules

Edgar Zander,[a,b] Jonas Bresien,*[a] Vladimir V. Zhivonitko,[c] Johannes Fessler,[b] Alexander Villinger,[a] Dirk Michalik,[a,b] Axel Schulz*[a,b]

[a] Institute of Chemistry, University of Rostock, Germany. [b] Leibniz-Institut für Katalyse e.V., Rostock, Germany. [c] NMR Research Unit, University of Oulu, Finland.

edgar.zander@uni-rostock.de

Pnictogen centered, cyclic biradicals have been in the focus of our research over the last decade. They have been used as molecular switches or for the activation of small molecules.[1] One approach to increase the number of reactive centers is to link several (cyclic) biradical units. Thus, tetraradicals can be synthesized by connecting two biradicals with completely[2] or partially[3] conjugated linkers. Here, a P-centered tetraradical (**1**) is presented in which all radical centers are localized in a single annulated and aromatic ring system (Figure 1).[4]
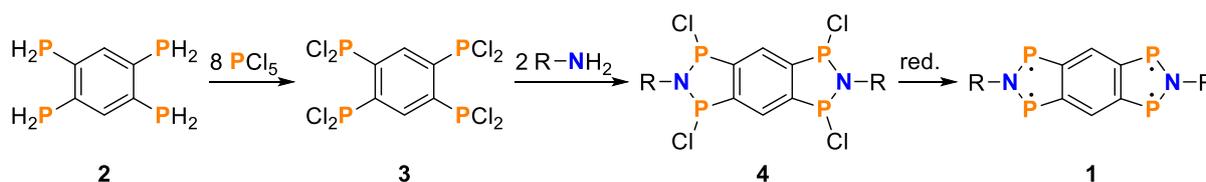
*Figure 1: Synthesis of the tetraradical **1** starting from 1,2,4,5-tetraphosphinobenzene (**2**).*[4,5]

Starting from 1,2,4,5-tetraphosphinobenzene (**2**),[6] 1,2,4,5-tetrakis(dichlorophosphi-no)benzene (**3**) was prepared.[5] By reaction with sterically demanding primary amines, diaza-tetraphospha-*s*-hydrindacenes (**4**) can be synthesized. Tetraradicals (**1**) were obtained by reduction of (**3**).[4]

It will be shown that the stability of **1** depends on the sterical demand of the substituent R: In case of insufficient stabilization, dimerization occurs, which can be prevented by the use of trapping reagents. Finally, first examples for the reactivity of the tetraradical towards small molecules will be shown.

[1] J. Bresien, L. Eickhoff, A. Schulz, E. Zander, in *Comprehensive Inorganic Chemistry III* (Eds.: J. Reedijk, K.R. Poeppelmeier), Elsevier, **2023**, pp. 165–233.

[2] A. Rodriguez, F. S. Tham, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2004**, *43*, 4876–4880.

[3] A. Hinz, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2015**, *137*, 9953–9962.

[4] E. Zander, J. Bresien, V. V. Zhivonitko, J. Fessler, A. Villinger, D. Michalik, A. Schulz, *J. Am. Chem. Soc.* **2023**, *145*, 14484–14497.

[5] E. Zander, L. Schweidt, S. Purschke, D. Michalik, A. Villinger, J. Bresien, A. Schulz, *ChemPlusChem* **2023**, *88*, e2023000.

[6] M. A. Fox, D. A. Chandler, *Adv. Mater.* **1991**, *3*, 381–385.

Hybrid Ligand Systems in the Coordination Chemistry of Low-Valent Uranium Complexes

Christian Urbank,[ab] Lisa Vondung [a]

[a] *Institute of Inorganic and Applied Chemistry, University of Hamburg, Germany*
[b] *Institute for Inorganic Chemistry, University of Göttingen, Tammannstraße 4, 37077 Göttingen*

christian.urbank@uni-hamburg.de

In the past two decades, actinide coordination chemistry has experienced a significant renaissance, with uranium being the core and centre of most research efforts.[1] The rich redox and coordination chemistry of this metal has shown promising potential for activating small molecules such as CO_2 or CO. The predominantly low-valent U(III) compounds involved exhibit high reduction potentials and oxophilicity, which enables their reactivity towards CO_2 or CO, but also often hinders the closing of catalytic cycles. In most activation products, the U-O bond formed is far too stable for product release and regeneration of active species.[2]

One approach to overcome these limitations and to further improve the reactivity of low-valent uranium coordination compounds is to employ hybrid ligand systems combining different donor sites.[3] In this work we designed hybrid ligands based on selectively functionalised 2-picolylamin derivatives and investigated their coordination chemistry with uranium and the reactivity of the resulting complex. The hereby generated insights could help to realise a real catalytic turnover in a uranium-mediated small molecule activation.
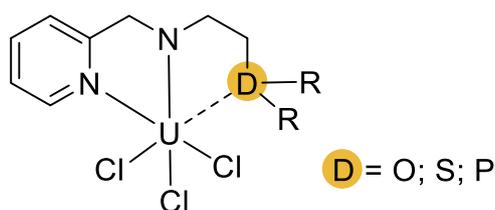
Figure 1: Structural motive of the investigated hybrid ligand uranium complexes.

[1] S. T. Liddle, *Angew. Chemie Int. Ed.* **2015**; *54*; 8604–8641.
[2] K. Meyer, *JACS Au* **2021**, *1*, 698–709.
[3] P. Braunstein, *Angew. Chemie Int. Ed*. **2001**, *40*, 680–699.

Macrocyclic ligands for the deposition of transition-metal complexes on surfaces

Küpra Yildiz,[a] Kai Uwe Clausen,[a] Dr. Thomas Strunskus,[b] Prof. Dr. Felix Tuczek[a]

[a] *Institute of Inorganic Chemistry, University of Kiel, Germany.* [b] *Institute of Materials Science, University of Kiel, Germany.*

kyildiz@ac.uni-kiel.de

The activation of small molecules by deposition of transition metal complexes on metallic surfaces is a novel approach to combine the advantages of homogeneous and heterogeneous catalysis. By adsorption of metal-organic complexes the electronic properties of the transition metal are changed due to interactions between the substrate surface and the adsorbate.[1] Previous work showed that the distance from the transition metal to the surface and the conjugation in the spacer can have a significant impact on this interaction.[2-4] A new approach is to deposit organometallic complexes with tridentate dome-shaped ligands directly on the substrate surface. The electronic influence of metal surfaces on dome-shaped complexes has not been studied yet.

R = p-Tolyl, n-Octyl
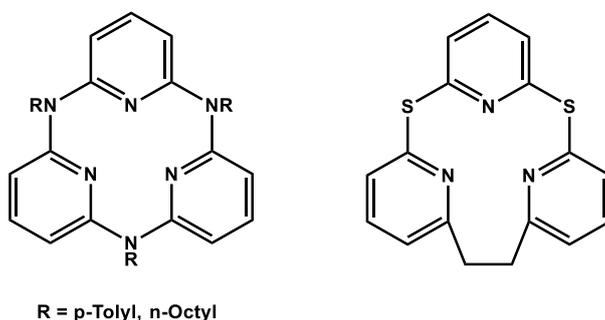
Figure 1: Dome-shaped ligands which were subsequently complexed and studied.

The ligands were complexed and physisorbed on Au(111) by deposition from solution and were investigated using a variety of surface-spectroscopic methods. The ability to activate small molecules was assessed by determining the IR vibrational frequencies of bound CO-ligands with the help of infrared reflection absorption spectroscopy (IRRAS). Moreover, X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) were used to determine the purity of the monolayers and the orientation of the molecules on the surface.

[1]   R. Otero, A. L. Vazquez de Parga, J. M. Gallego, *Surf. Sci. Rep.* **2017**, *72*, 105-145.
[2]   H. Jacob, K. Kathirvel, F. Petersen, T. Strunskus, A. Bannwarth, S. Meyer, F. Tuczek, *Langmuir* **2013**, *29*, 8534–8543.
[3]   A. Schlimm, N. Stucke, B. M. Flöser, T. Rusch, J. Krahmer, C. Näther, T. Strunskus, O. M. Magnussen, F. Tuczek, *Chem. Eur. J.* **2018**, *24*, 10732– 10744.
[4]   F. Petersen, I. Lautenschläger, A. Schlimm, B. M. Flöser, H. Jacob, R. Amirbeigiarab, T. Rusch, T. Strunskus, O. M. Magnussen, F. Tuczek, *Dalton Trans.* **2021**, *50*, 1042-1052.

[Xe(OTeF$_5$)(py^F)]$^+$: Xenonium(II) Teflate Cation Stabilized by N-Donor Bases

Ahmet N. Toraman,[a] Lukas Fischer,[a] Alberto Pérez-Bitrián,[a,b] Kurt F. Hoffmann,[a] Sebastian Riedel*[a]

[a] *Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany*
[b] *Department of Chemistry, Humboldt-Universität zu Berlin, Germany*

ahmet.toraman@fu-berlin.de

The pentafluoroorthotellurate group (teflate, –OTeF$_5$) resembles fluoride as it is also highly electronegative, but with a higher steric bulkiness, enabling the stabilization of a variety of reactive species, as for example noble-gas compounds.[1] The strong oxidizing [XeF]$^+$ cation has been extensively studied and is known to readily form Lewis acid-base adducts.[2] In contrast, the [XeOTeF$_5$]$^+$ analogue is known to exist as the solvent adduct [Xe(OTeF$_5$)·SO$_2$ClF]$^+$ in the solid state,[3] but its chemistry has not been developed so far.

Herein we report on the adduct formation between the [XeOTeF$_5$]$^+$ cation with fluorinated pyridines to yield [Xe(OTeF$_5$)(py^F)][Al(OTeF$_5$)$_4$] (py^F = C$_5$F$_5$N, C$_5$H$_3$F$_2$N), which entail an unprecedented motif in xenon-teflate chemistry, while at the same time represent the first xenonium cations stabilized by the weakly coordinating [Al(OTeF$_5$)$_4$]$^-$ anion. The Lewis superacid Al(OTeF$_5$)$_3$ is able to abstract one teflate group from Xe(OTeF$_5$)$_2$, resulting in the formation of a xenonium(II) cation species, whose characterization is possible upon subsequent coordination of oxidation-resistant N-bases. Additionally, the analogous synthesis of the related [Sb(OTeF$_5$)$_6$]$^-$ salts, has enabled the characterization of the [Xe(OTeF$_5$)(NC$_5$F$_5$)]$^+$ cation in the solid state by single-crystal X-ray diffraction (Figure 1).
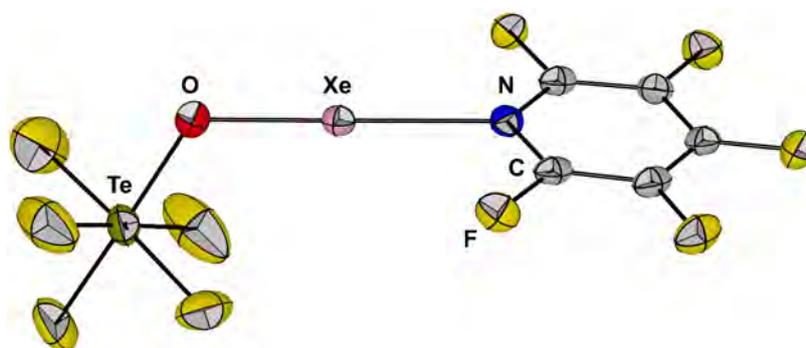
Figure 1: Molecular structure in the solid state of the [Xe(OTeF$_5$)(NC$_5$F$_5$)]$^+$ cationic adduct. The anion [Sb(OTeF$_5$)$_6$]$^-$ is omitted for clarity.

[1]   K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 877–956.
[2]   A. A. A. Emara, G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.* **1987**, *21*, 1644–1646.
[3]   (a) P. Ulferts, K. Seppelt, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1589–1593. (b) H. P. A. Mercier, M. D. Moran, J. C. P. Sanders, G. J. Schrobilgen, R. J. Suontamo, *Inorg. Chem.* **2005**, *44*, 49–60.

Mononuclear Rhodium complexes with redox active ligands

Tobias Greven[a], Jarl Ivar van der Vlugt[a]

Bioinspired Coordination Chemistry & Catalysis Group, Institute of Chemistry, Carl von Ossietzky University Oldenburg, Germany

Tobias.greven@uni-oldenburg.de

Combining a redox-active ligand with a transition metal often result in novel unique properties of the ensuing mononuclear complex. Of particular note is the access to new reaction pathways for the selective preparation of a broad spectrum of synthetically useful compounds *via* ligand-centered one-electron transfer reactivity.[1] Our group published *inter alia* Pd[II] species with tridentate redox-active PNO[H2] or NNO[H2] platforms that are competent for the homolytic bond activation of disulfides or the aminocyclization of organic azides, respectively.[2,3] Inspired by these results we currently focus on the synthesis of suitable rhodium based complexes for olefine functionalizations, including model complexes for evaluation of their intrinsic redox chemistry. We will report on the synthesis and characterization of several new species using multinuclear NMR spectroscopy, UV absorption spectroscopy, cyclovoltammetry, EPR and XRD analysis supported by DFT calculations.
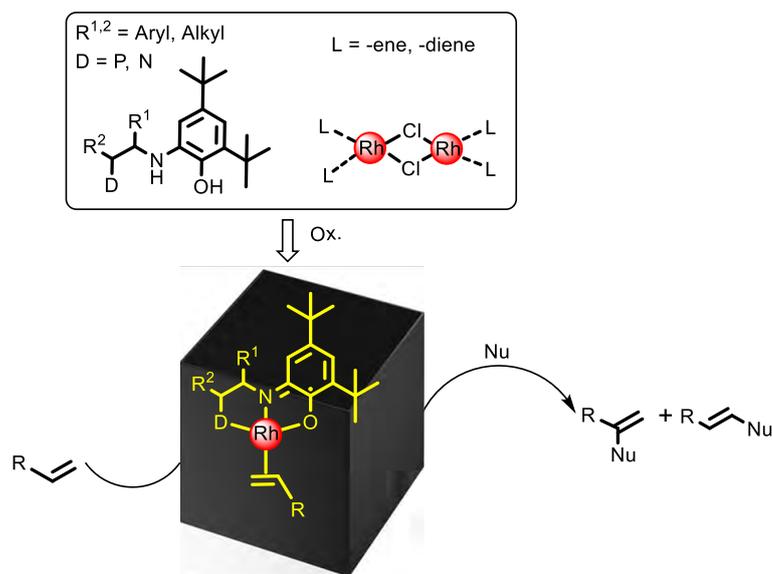
[1] K. Singh, A. Kundu, D. Adhikari, *ACS Catal.* **2022**, 12, *20*, 13075–13107

[2] D. L. J. Broere, L. L. Metz, B. de Bruin, J. N. H. Reek, M. A. Siegler, J. I. van der Vlugt, *Angew. Chem. Int. Ed.* **2015**, *54*, 1516-1520.

[3] D. L. J. Broere, B. de Bruin, J. N. H. Reek, M. Lutz, S. Dechert, J. I. van der Vlugt, *J. Am. Chem. Soc.* **2014**, *136*, 11574–11577.

Synthesis and characterization of a [Mo(CO)₃(PPP)]-complex covalently attached to Au-electrodes for small-molecule activation

Niels Michaelis,[a] Dr. Tobias A. Engesser,[a] Dr. Thomas Strunskus,[b] Dr. Nicolas LePoul,[c] Prof. Dr. Felix Tuczek*[a]

[a] Institute of Inorganic Chemistry, University of Kiel, Germany. [b] Institute of Materials Science, University of Kiel, Germany. [c] UMR CNRS UMR 6521, Université de Bretagne Occidentale, France.

nmichaelis@ac.uni-kiel.de

Catalysts based on low-valent molybdenum complexes bearing phosphine ligands are of critical interest in synthetic nitrogen fixation, possessing remarkable catalytic activities in solution.[1-3] Current research is slowly progressing towards electrochemical NH_3 production.[4-6] One approach is the covalent attachment of homogenous catalysts onto electrode surfaces. As a model for such a functionalized electrode we are currently investigating the covalent attachment of [Mo(CO)₃(etPP^PhH^P)] onto an azide-terminated Au-surface *via* CuAAC.[7] The functionalized surfaces are investigated by XPS, NEXAFS, IRRAS and CV to determine the chemical composition, surface-orientation, CO-activation and redox-potentials.
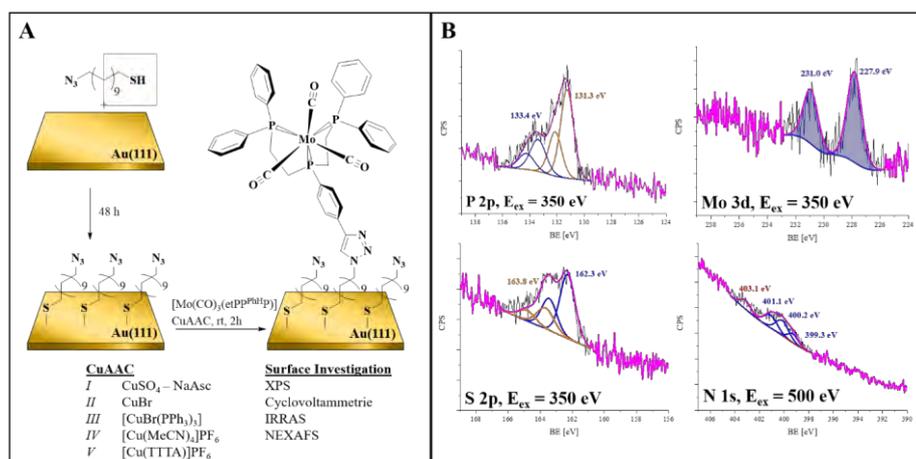
Figure 1: A: Schematic depiction of the surface functionalization process on Au(111). B: XP Spectra of an functionalized SAM with [Mo(CO)₃(etPP^PhH^P)] via CuAAC using [Cu(MeCN)₄]PF₆ and 2,6-lutidine.

[1]　T. A. Engesser, A. Kindjajev, J. Junge, J. Krahmer, F. Tuczek, *Chem. Eur. J.* **2020**, *26*, 14807–14812.
[2]　Y. Ashida, T. Mizushima, K. Arashiba, A. Egi, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *Nature Synthesis,* **2023**, *2*, 635-644.
[3]　A. Eizawa, K. Arashiba, H. Tanaka, S. Kuriyama, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Nature Comm.*, **2017**, *8*, 14874-14886.
[4]　Q. J. Bruch, S. Malakar, A. S. Goldman, A. J. M. Miller, *Inorg. Chem.,* **2022**, *61*, 2307-2318.
[5]　L. Merakeb, S. Bennaamane, J. De Freitas, E. Clot, N. Mezailles, M. Robert, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202209899.
[6]　M. J. Chalkley, P. Garrido-Barros, J. C. Peters, *Science,* **2020**, *369*, 850-854.
[7]　D. Evrard, F. Lambert, C. Policar, V. Balland, B. Limoges, *Chem. Eur. J.*, **2008**, *14,* 9286 – 9291.

Reactivity of Germacyclopentadienediides towards Group 13 Halides

Lukas Bührmann[a], Thomas Müller*[a]

[a] *Institute of Chemistry, Carl von Ossietzky University Oldenburg, Germany.*

lukas.buehrmann@uni-oldenburg.de

In recent years, several studies on the synthetic potential of the dipotassium salts of germacyclopentadienediides, also known as germole dianions, K$_2$[**1**], towards element dihalides have been carried out by our group. Starting from the idea of obtaining heteropentafulvenes with polarized multiple bonds, mostly the resulting compounds underwent a rearrangement reaction.[1,2] For example, reactions of dipotassium germole dianion K$_2$[**1**] and amino-substituted dichloroboranes led to η^5-borole complexes of Ge(II) (**2**).[3] In contrast, the reaction of K$_2$[**1**] with the Cp*-substituted dichloroalane resulted in the formation of a novel germaaluminocene (**3**).[2]

Further investigations on the reaction of dipotassium germacyclopentadienediides K$_2$[**1**] towards Group 13 halides showed that the outcome of the rearrangement reaction is affected by the choice of the Group 13 element as well as its substituent resulting either in Group 13 heterole complexes of Ge(II) (**2**) or in germole complexes of Group 13 elements (**3**).
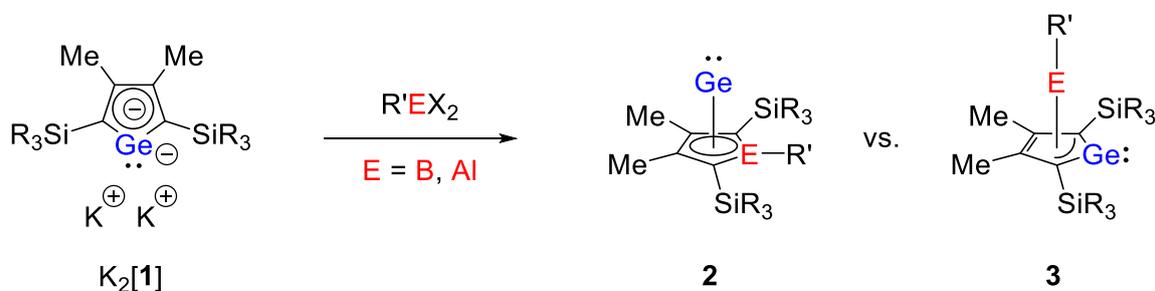
*Figure 1: Synthesis of Group 13 heterole complexes of Ge(II) (**2**) or germole complexes of Group 13 elements (**3**) after reaction of dipotassium salts of germacyclopentadienediides K$_2$[**1**] with Group 13 halides.*

[1]   Z. Dong, L. Albers, T. Müller *Acc. Chem. Res.* **2020**, *53*, 532-543.
[2]   L. Albers, P. Tholen, M. Schmidtmann, T. Müller *Chem. Sci.* **2020**, *11*, 2982-2986.
[3]   P. Tholen, Z. Dong, M. Schmidtmann, L. Albers, T. Müller, *Angew. Chem. Int. Ed.* **2018**, *57*, 13319-13324.

Mixed Oxy-Hydride Materials as PCET Reagents

Yasaman Sheidaei[1], Thorsten M. Gesing[2,3], Inke Siewert[1]

1. University of Göttingen, Institute for Inorganic Chemistry, Tammannstraße 4, D-37077, Göttingen, Germany.

2. University of Bremen, Institute for Inorganic Chemistry and Crystallography, Leobener Straße 7, D-28359, Bremen, Germany.

3. University of Bremen, MAPEX Center for Materials and Processes, Bibliothekstraße 1, D-28359 Bremen, Germany.

yasaman.sheidaei@uni-goettingen.de

Proton-coupled electron transfer (PCET) reactions are of utmost importance in chemical energy conversion reactions. In such energy conversion reactions, electrons that are generated in the oxygen evolution reaction are used to reduce small molecules, e.g., protons, N_2, CO_2. While PCET reactions at molecular complexes have been investigated intensively for these reactions, extensive literature on water splitting by materials was focused on electron transfer at the interface of surface species [1]. For instance, Mayer and co-workers [1] showed that TiO_2 nanoparticles react as PCET reagents in interfacial reactions. Initial research of PCET reactions at the interface of solid materials and solutions focused on carbon and oxide materials with hydroxy (M−OH) groups that form oxo (MO) surface species upon oxidation [2]. Materials with hydridic H-atoms have been rarely investigated so far, although such surface M−H species are key intermediates in energy conversion reactions, e.g., HER, or the hydrogenation of (polar) double bonds. This prompted us to investigate Perovskite-type oxides (ABO_3) that are doped with hydride anions as PCET reagents. The material $BaTiO_{3-x}H_x$ is synthesized in topotactical solid state synthesis. The anionic sublattice is comprised of both O^{2-} and H^- anions around Ti cations existing in a mixed Ⅳ/Ⅲ oxidation (Fig. 1) [2]. The material has been characterized thoroughly and initial studies on the PCET are under way.
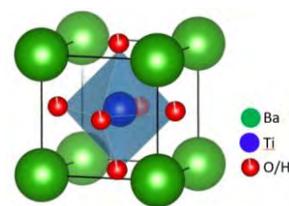
Figure 1. *Crystal structure of $BaTiO_{2.81}H_{0.19}$ showing cubic structure.*

[1] a) S. Ardo, G. J. Meyer, Chem. Soc. Rev. 2009, 38, 115-164; b) Roubelakis, M. M.; Bediako, D. K.; Dogutan, D. K.; Nocera, Energy Environ. Sci. 2012, 5(7), 7737−7740; c) J. M. Mayer, J. Am. Chem. Soc. 2023, 145(13), 7050-7064, d) J.N. Schrauben, R. Hayoun, C.N. Valdez, M. Braten, L. Fridley, J.M. Mayer, Science, 2012, 336, 1298-1301; e) C.N. Valdez, M. Braten, A. Soria, D.R. Gamelin, J.M. Mayer, J. Am. Chem. Soc., 2013, 135, 8492-8495.

[2] M.N. Jackson.; M.L. Pegis, Y. Surendranath, ACS Cent. Sci. 2019, 5, 831-841; C. F. Wise, J.M. Mayer, J. Am. Chem. Soc., 2019, 141, 14971-14975, b) C. Eklöf-Österberg., R. Nedumkandathil., and et. Al., Journal of Phys. Chem. C. 2019, 123 (4), 2019-2030.

Air-Stable Teflate Derivatives for the Synthesis of Strong Lewis Acids

D. Wegener,[a] A. Pérez-Bitrián,[a] K. F. Hoffmann[a] and S. Riedel[a]

[a]Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 14195 Berlin, Germany.

daniel.wegener@fu-berlin.de

The pentafluoroorthotellurate group (teflate, $OTeF_5$) provides access to a variety of weakly coordinating anions (WCAs) and strong Lewis acids, as well as highly reactive species.[1] Nevertheless, the teflate group presents some drawbacks, such as its sensitivity to hydrolysis and the complex synthesis of the starting material $HOTeF_5$. This severely limits its potential field of application and requires working under strictly inert conditions. Due to the higher stability of organotellurium compounds,[2] we envisioned the substitution of some of the fluorine atoms in the $OTeF_5$ group by (perfluoro)aryl groups to improve some of the properties of this ligand.

Herein we present two air-stable derivatives of the pentafluoroorthotellurate group containing fluorinated and non-fluorinated aryl substituents,[3] whose precursors can be prepared through easy fluorination of aryl tellurides using the TCICA/KF oxidation system.[4] The outstanding properties of the pentafluorophenyl derivative $trans$-$(C_6F_5)_2TeF_3OH$ in comparison to the non-fluorinated cis-$PhTeF_4OH$, prompted us to explore the use of the former for the synthesis of a new family of Lewis acids with sterically demanding ligands. The synthesis, properties and reactivity of the boron- and aluminium-based compounds will be dis
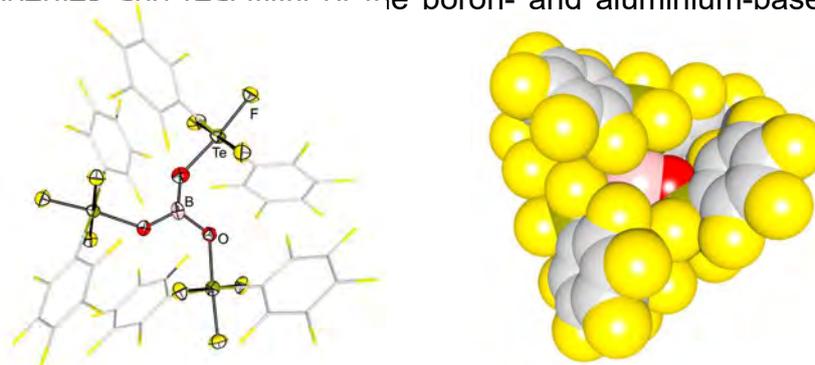
Figure 1: Molecular structure in the solid state (left) and space filling model (right) of $B[OTeF_3(C_6F_5)_2]_3$.

[1] K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 877-888.

[2] K. Grollier, A. Taponard, T. Billard, *Eur. J. Org. Chem.* **2020**, 6943-6954.

[3] D. Wegener, K. F. Hoffmann, A. Pérez-Bitrián, I. Bayindir, A. N. Hadi, A. Wiesner, S. Riedel, *Chem. Commun.* **2022**, *58*, 9694-9697.

[4] Y. Kraemer, E. N. Bergman, A. Togni and C. R. Pitts, *Angew. Chem. Int. Ed.* **2022**, *61*, e202205088.

Trichloride Salts as Efficient Chlorine Storage Media and Useful Chlorination Reagents

P. Voßnacker,[a] A. Wüst,[a] T. Keilhack,[a] N. Schwarze,[a] M. Kleoff,[a] S. Riedel*[a]

[a] Institut für Chemie und Biochemie, Freie Universität Berlin, Germany.

patrick.vossnacker@fu-berlin.de (Arial 12 pt)

Organic chloride salts react with gaseous Cl_2 to form trichlorides and can thereby bind up to 0.8 g chlorine per gram storage material at atmospheric pressure and room temperature.[1] The formed trichlorides exist either as solids or low viscous room temperature ionic liquids and show a high long-term stability. Chlorine can either be released from the trichloride (by vacuum, heat, or addition of H_2O) or the trichloride can directly be used as an easy-to-handle chlorination reagent (Figure 1, left). This was demonstrated by the use of $[NEt_3Me][Cl_3]$ for the chlorination of CO to form the intermediate chemical phosgene at room temperature and atmospheric pressure.[2] Additionally, the reaction of $[NEt_3Me][Cl_3]$ with sulfur resulted in the formation and stabilization of the hitherto unprecedented $[SCl_6]^{2-}$ anion which was characterized by single crystal XRD and Raman spectroscopy (Figure 1, right).[3] Overall, we present trichlorides as promising candidates for a safer chlorine storage which can also be directly used as chlorination reagents for the synthesis of industrial important chemicals (e.g., phosgene) and unprecedented molecules ($[SCl_6]^{2-}$).
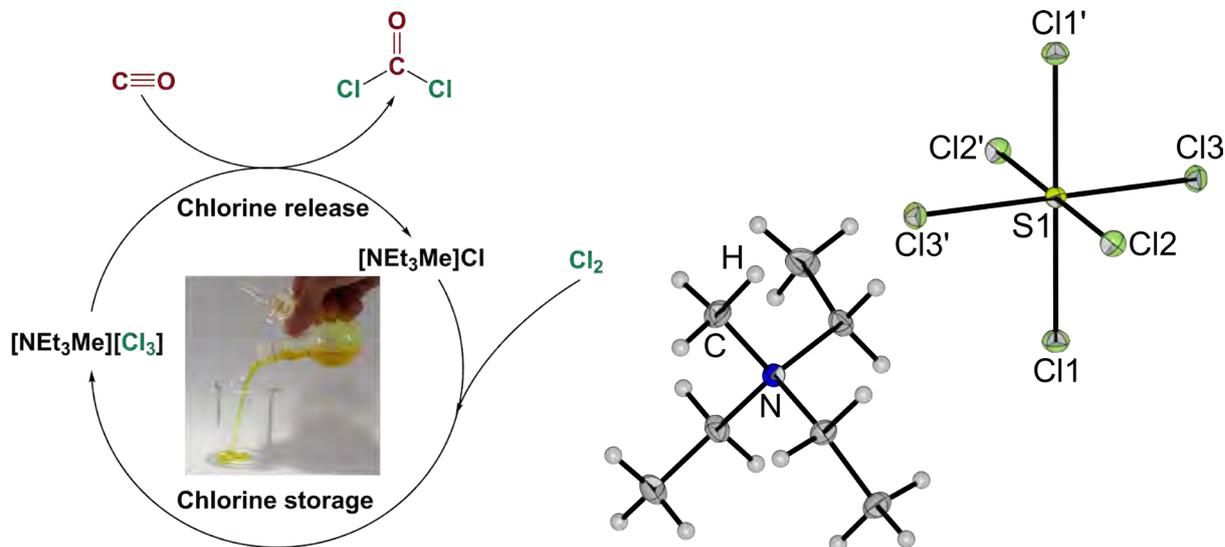
Figure 1. Proposed cycle for chlorine storage and release (left) and molecular structure in the solid state of $[NEt_3Me]_2[SCl_6]$ with thermal ellipsoids shown at 50% probability (right).

[1] P. Voßnacker, N. Schwarze, T. Keilhack, M. Kleoff, S. Steinhauer, Y. Schiesser, M. Paven, S. Yogendra, R. Weber, S. Riedel, *ACS Sustainable Chem. Eng.* **2022**, *10*, 9525.

[2] P. Voßnacker, A. Wüst, T. Keilhack, C. Müller, S. Steinhauer, H. Beckers, S. Yogendra, Y. Schiesser, R. Weber, M. Reimann, R. Müller, M. Kaupp, S. Riedel, *Sci. Adv.* **2021**, *7*, eabj5186.

[3] P. Voßnacker, A. Wüst, C. Müller, M. Kleoff, S. Riedel *Angew. Chem. Int. Ed.* **2022**, e202209684.

Introducing the Perfluorinated Cp* Ligand into Coordination Chemistry

Robin Sievers,[a] Malte Sellin,[b] Susanne M. Rupf,[a] Joshua Parche,[a] Nico G. Kub,[a] Tim Streit,[a] Moritz Malischewski*[a]

[a] *Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.* [b] *Institute of Inorganic and Analytical Chemistry, Albert-Ludwigs Universität Freiburg, Germany.*

robin.sievers@fu-berlin.de

The perfluorinated Cp* $[C_5(CF_3)_5]^-$ (figure 1) resembles an extremely electron deficient analogue of the well known Cp*, showing significantly deviating ligand properties and was consequently never coordinated, since its first synthesis in 1980.[1] However, more than four decades later, the reaction of $AgBF_4$ and $[Rh(COD)Cl]_2$ in presence of $[NEt_4][C_5(CF_3)_5]$ afforded the fluorocarbon soluble complex $[Rh(COD)(C_5(CF_3)_5)]$ by salt metathesis, representing the first example for a successful coordination of the weakly basic $[C_5(CF_3)_5]^-$ ligand.[2,3] The subsequent quantitative reversible substitution of the $[C_5(CF_3)_5]^-$ ligand in $[Rh(COD)(C_5(CF_3)_5)]$ by coordinating solvents, converting it into a WCA, experimentally proved the extraordinary weak bonding interaction.[4] Furthermore, a series of rare and unusually stable group 11 cyclopentadienyl complexes,[5] as well as a mixed ferrocene with extreme redox properties have been prepared.[6]
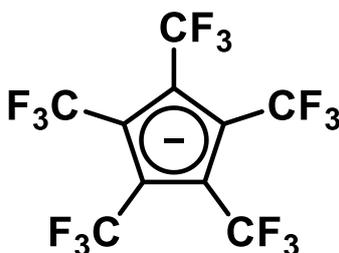
Figure 1: The perfluorinated Cp* $[C_5(CF_3)_5]^-$ as an extremely electron deficient ligand for organometallic coordination chemistry.

[1]   E. D. Laganis, D. M. Lemal, *J. Am. Chem. Soc.* **1980**, *102*, 6633–6634.
[2]   R. Sievers, M. Sellin, S. M. Rupf, J. Parche, M. Malischewski, *Angew. Chem. Int. Ed.* **2022, 61,** e202211147.
[3]   R. Sievers, J. Parche, N. G. Kub, M. Malischewski, *Synlett*, **2023**, *34*, 1079–1086.
[4]   J. Parche, S. M. Rupf, R. Sievers, M. Malischewski, *Dalton Trans.* **2023**, *52*, 5496–5502.
[5]   R. Sievers, N. G. Kub, S. M. Rupf, M. Malischewski, *manuscript in preparation*.
[6]   R. Sievers, T. Streit, M. Malischewski, *manuscript in preparation*.

Rational design of a Phosporus-centered disbiradical

Jan Rosenboom,[a] Florian Taube,[a] Jonas Bresien,[a] Alexander Villinger,[a] Björn Corzilius,*[a] Axel Schulz*[a]

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

jan.rosenboom@uni-rostock.de

Biradicals are molecular entities with an even number of electrons with two (possibly delocalized) radical centres.[1] They can be characterized by the interaction of the two electron spins with each other. The term disbiradical has been suggested for a molecule where the two unpaired electrons show little to no interaction, while in a biradical(oid) there is a considerable interaction.[2,3] The singlet biradical [P(μ-NTer)]$_2$ [1] (Ter = 2,6-dimesitylphenyl), which was first synthesized in our group in 2011, has since been shown to activate a great variety of small molecules and its reactive behavior ranges between classic closed-shell and radical reactivity. [4–7] By using the biradical-bromoalkane route towards asymmetrically substituted cyclo-1,3-diphospha-2,4-diazanes recently established by our group,[6] it was now possible to link two N$_2$P$_2$ ring systems with a dibromoalkane [2] allowing for the synthesis of a disbiradical [3] which has been extensively studied by EPR spectroscopy.

1   2   3
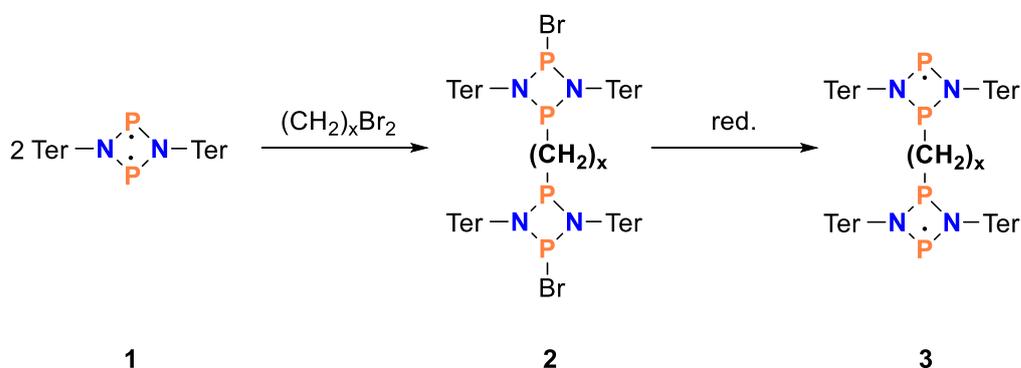
[1]   M. Abe, *Chem. Rev.* **2013**, *113*, 7011–7088.

[2]   J. Bresien, L. Eickhoff, A. Schulz, E. Zander, in *Comprehensive Inorganic Chemistry III* (Eds.: J. Reedijk, K.R. Poeppelmeier), Elsevier, **2023**, pp. 165–233.

[3]   A. Schulz, *Dalton Trans.* **2018**, *47*, 12827–12837.

[4]   T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2011**, *50*, 8974–8978.

[5]   A. Hinz, A. Schulz, *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 578–581.

[6]   J. Rosenboom, L. Chojetzki, T. Suhrbier, J. Rabeah, A. Villinger, R. Wustrack, J. Bresien, A. Schulz, *Chem. Eur. J.* **2022**, *28*, e202200624.

[7]   A. Hinz, J. Bresien, F. Breher, A. Schulz, *Chem. Rev.* **2023**, *123*, 10468–10526.

Heterobimetallic mediators for electrocatalytical hydrogenation

Friederike M. Hamann,[a,b] Alexander Villinger,[a] Robert Francke,[b] Wolfram Seidel*[a,b]

[a] Institute of Chemistry, University of Rostock, Germany. [b] Leibniz Institute for Catalysis, Rostock, Germany

friederike.hamann@uni-rostock.de

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 trait in 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.
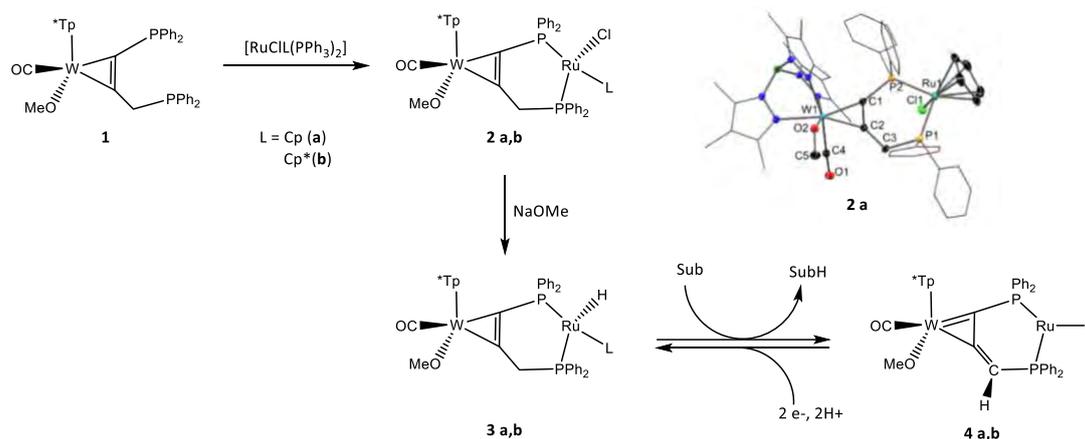
Figure 1: Reaction scheme of intended catalysed hydrogenation.

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. 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.

[1] Stephan Ludwig, Friederike M. Hamann, Kai Helmdach, Alexander Villinger, Wolfram W. Seidel, Dalton Trans., 2023, 52, 326.

Iron catalyzed Suzuki cross coupling

Constanze von Meyenn,[a] Tim-Oliver Kindler,[a] Axel-Jacobi von Wangelin*[a]

[a] Dept. of Chemistry, University of Hamburg, Germany.

constanze.meyenn@uni-hamburg.de

Iron-catalyzed cross-coupling reactions have become a valuable method for C-C bond formation in recent years. However, reactivity patterns and mechanisms are not yet fully understood, which means that other and hitherto unknown manipulations of the catalysis activity by substrate effects are to be expected.[1,2]. The iron catalyzed Suzuki biaryl couplings remained problematic in several publications[3] and to best of our knowledge there is only one known example of the Bedford group.[4]

Fig. 1 shows the studied iron-catalyzed sp^2-sp^2 suzuki cross-coupling. Here, an imine acts as the directing group for the linkage of the phenyl borinate at the position of the leaving group Y (Y = Hal, OMe). In contrast to the previous work,[4] this reaction proceeds under mild reaction conditions, with a small excess of the borinate. Crucial appears to be a pre-coordination of the iron catalyst to the imine donor function, leading to a dramatic acceleration of the elementary steps of the cross-coupling (oxidative addition, transmetallation, reductive elimination), while the thermodynamically favored direct addition of the organometallic species to the electrophilic carbonyl derivative function is suppressed. As a result, a broad substrate scope with a high functional group tolerance is achieved.
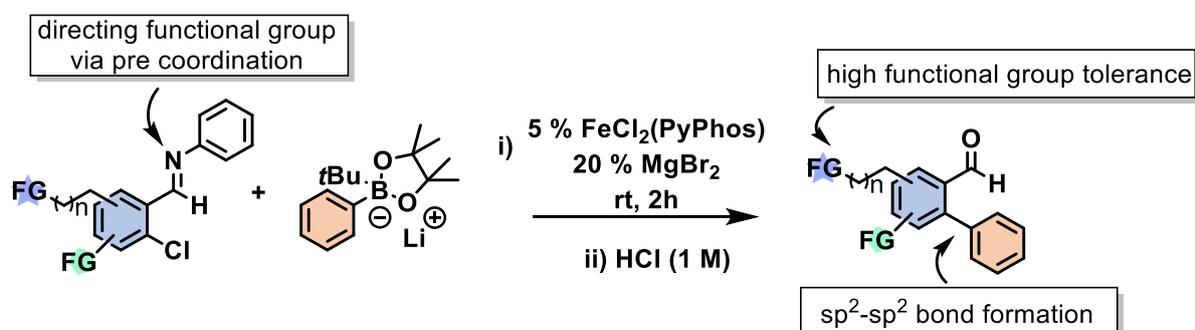
Figure 1: reaction equation of the studied iron-catalyzed sp^2-sp^2 suzuki cross-coupling

[1]   Bedford, R. *Acc. Chem. Res.* **2015**, 48, 5, 1485–1493.
[2]   Wu, G., Jacobi von Wangelin*, A. *Nat. Catal.* **2018**, **1**, 377–378.
[3]   a) Crockett M. et al., Angew. Chem. Int. Ed. 2020, 59, 5392 –5397; b) Iwamoto T. et al. Chem. Commun., 2019, 55, 1128-1131; c) Daifuku S. et al. J. Am. Chem. Soc. 2015, 137, 11432−11444; d) Bedford et al. Synthesis 2015, 47, 1761–1765 and more
[4]   O'Brien, H., Manzotti M., Abrams R., Elorriaga D., Sparkes H., Davis S., Bedford R.*, *Nat. Catal.* **2018**, 1, 429–437.

Synthesis, characterization and structure-property relations in Pb2(Pb1-xSnx)O4

Christopher S. Reuter[1], M. Mangir Murshed[1,2], Michael Fischer[2,3,4], Thorsten. M. Gesing[1,2]

[1]*University of Bremen, Institute of Inorganic Chemistry and Crystallography, Leobener Straße 7, D-28359 Bremen, Germany*

[2]*University of Bremen, MAPEX Center for Materials and Processes, Bibliothekstraße 1, D-28359 Bremen, Germany*

[3]*University of Bremen, Crystallography, Faculty of Geosciences, Klagenfurter Straße 2-4, D-28359 Bremen, Germany*

[4]*University of Bremen, BCCMS Bremen Center for Computational Materials Science, Am Fallturm 1, D-28359 Bremen, Germany*

christopher.reuter@uni-bremen.de

Both Pb_2PbO_4 (Pb_3O_4) and Pb_2SnO_4 are members of the mullite-type family. At ambient condition Pb_2PbO_4 and Pb_2SnO_4 crystallize in space group *P4₂/mbc* and *Pbam*, respectively. At what extend the crystal structure prefers either of the space groups would be an excellent playground for a respective $Pb_2(Pb_{1-x}Sn_x)O_4$ solid solution. Several members of this series have been prepared by solid-state reactions in sealed quartz tubes. X-ray powder diffraction data Rietveld refinements confirm the structures of the red-orange Pb_2PbO_4 and yellow-beige Pb_2SnO_4 phases. Since the Pb^{4+} cation is about 10 pm larger than Sn^{4+}, the MO_6

Figure 1: Crystal structure of Pb2(Pb1-xSnx)O4 with M = Pb4+, Sn4+

polyhedral volume decreases linearly with increasing Sn content in the compounds. Moreover, the MO_6 contraction needs more space for the stereo-chemical activity of the $6s^2$ lone electron pairs (LEPs) of the Pb^{2+} cations resulting in symmetry reduction. As such, the Wang-Liebau eccentricity (WLE) [1] parameter, which is a measure of the distortion of a cation coordination including the associated deformation of the LEP electron density [2], increases with increasing tin in the solid solution. The gradual global blue shift of the Raman mode frequencies can be explained from the contraction of the metric parameters, which is as well supported by the lattice dynamical calculations. The indirect band-gap energy calculated by the RATD method [3] linearly increases from 2.1(1) eV (x = 0) to a maximum value of 2.5(1) eV (x = 0.8) followed by a sharp drop for x > 0.8.

[1] X. Wang, F. Liebau, Z Kristallogr. 211 (1996) 437.
[2] M. Curti et al., Z. Kristallogr. 228 (2013) 629.
[3] Th. M. Gesing et al., J. Mater. Sci. 57 (2022) 19280.

Reactivity of Pacman Phosphanes

Liesa Eickhoff,[a] Jonas Bresien,[a] Alexander Villinger,[a] Axel Schulz*[a,b]

[a] Institute of Chemistry, University of Rostock, Germany. [b] Leibniz Institute for Catalysis, Rostock, Germany.

liesa.eickhoff@uni-rostock.de

Cooperativity of two reactive centres is a common motif in the field of small-molecule activation, e.g. in FLPs or biradicals.[1] Following the same intention, already in 1983 Pacman complexes were developed, enforcing spatial proximity of two coordinated metal centres for possibly cooperative catalytic processes.[2]

Replacing the metal centres by P atoms, we intend to transfer the concept to non-metal chemistry and bring two reactive P centres in close proximity. The introduction of two PCl units into a Pacman ligand leads to the *endo-exo*-orientated Pacman phosphane **1Cl** which represents a precursor for the formation of different reactive molecules.[3]
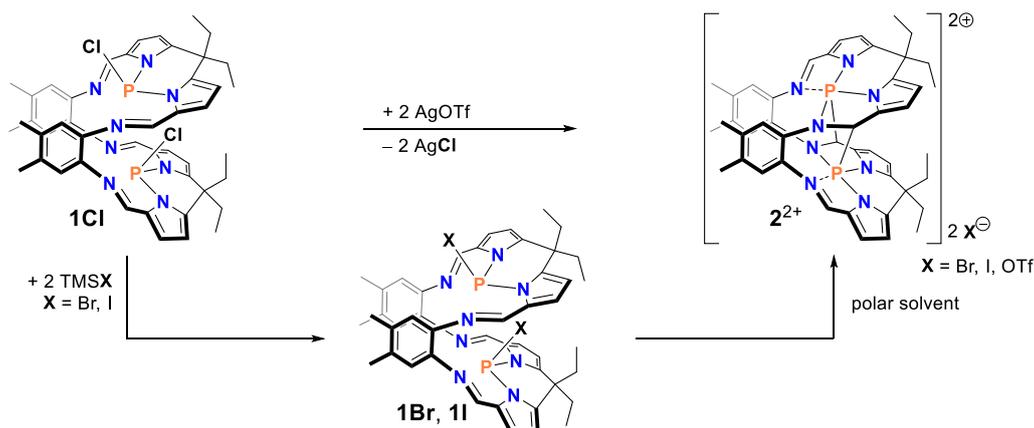
*Figure 1: First Pacman phosphane **1Cl** and its reaction pathways to [**2**][X]$_2$.*

As one example, the dication **2**$^{2+}$ is accessible *via* chloride abstraction from **1Cl** using AgOTf or by halogen exchange to **1Br** or **1I** which both isomerise to [**2**][X]$_2$ in polar solvents.[3] Due to an intramolecular redox reaction of the P centres which cooperatively attack adjacent C=N double bonds, the dicationic **2**$^{2+}$ forms a cage compound. Currently, the reactivity of **2**$^{2+}$ towards different substrates is investigated.

[1]   J. A. R. Jupp, D. W. Stephan, *Trends Chem.* **2019**, *1*, 35–48; J. Bresien, L. Eickhoff, A. Schulz, E. Zander, in *Comprehensive Inorganic Chemistry III* (Eds.: J. Reedijk, K. Poeppelmeier), Elsevier, **2023**, pp. 165–233.

[2]   C. K. Chang, I. Abdalmuhdi, *J. Org. Chem.* **1983**, *48*, 5388–5390; P. Lang, M. Schwalbe, *Chem. Eur. J.* **2017**, *23*, 17398–17412.

[3]   L. Eickhoff, L. Ohms, J. Bresien, A. Villinger, D. Michalik, A. Schulz, *Chem. Eur. J.* **2022**, *28*, e202103983; L. Eickhoff, P. Kramer, J. Bresien, D. Michalik, A. Villinger, A. Schulz, *Inorganic Chemistry* **2023**, *62*, 6768–6778.

Coinage metal complexes of multidentate Pacman phosphane ligands

Leon Ohms[a], Liesa Eickhoff[a], Pascal Kramer[a], Alexander Villinger[a], Jonas Bresien[a] and Axel Schulz*[a]

[a] _Institut für Chemie, Universität Rostock, Germany._

leon.ohms@uni-rostock.de

Cofacial and so-called Pacman ligands have been used as model systems to study the catalytic processes in enzymes, such as chlorophyll, due to their structural similarity.[1–3] We were able to introduce phosphorus into such Pacman ligands,[4] which leads to a new kind of bidentate phosphane ligands. We refer to such compounds as Pacman phosphanes. These Pacman phosphanes form a cavity, in which metals can be coordinated in various ways.
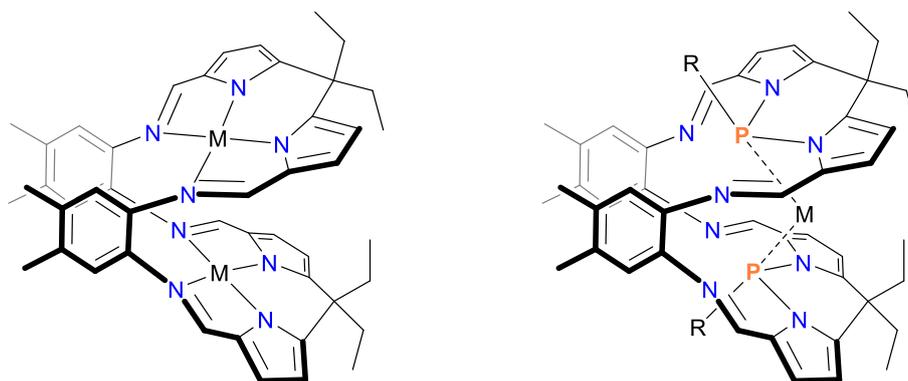
Figure 1: Pacman complex (left)[3] and a Pacman phosphane-metal complex (right).

As prove of concept, we synthesized two Pacman phosphanes bearing either phenyl or diisopropylamine substituents on the phosphorus atoms and reacted them with coinage metals. In the resulting cationic complexes, the metal is located inside the cavity formed by the ligand. Under the influence of the phosphorus and iminic nitrogen atoms, different coordination environments at the metal reaching from linear over trigonal planar to a "see-saw" type of coordination, can be realized. Due to the special structure of these complexes, interesting catalytic properties are expected.[5]

[1] C. K. Chang, M. -S Kuo, C. -B Wang, _J. Heterocycl. Chem._ **1977**, _14_, 943–945.
[2] F. P. Schwarz, M. Gouterman, Z. Muljiani, D. H. Dolphin, _Bioinorg. Chem._ **1972**, _2_, 1–32.
[3] J. W. Leeland, F. J. White, J. B. Love, _J. Am. Chem. Soc._ **2011**, _133_, 7320–7323.
[4] L. Eickhoff, L. Ohms, J. Bresien, A. Villinger, D. Michalik, A. Schulz, _Chem. - Eur. J._ **2022**, _28_, e202103983.
[5] L. Ohms, L. Eickhoff, P. Kramer, A. Villinger, J. Bresien, A. Schulz, _Chem. Commun._ **2023**, _59_, 5245–5248.

Electrophilic Aromatic Substitution Reaction of Lewis Acid Stabilized Ketenimine

J. Surkau,[a] K. Bläsing,[a] J. Bresien,[a] D. Michalik,[a] A. Villinger,[a] A. Schulz*[a]

a Institute of Chemistry, University of Rostock, Germany.

jonas.surkau@uni-rostock.de

Electrophilic aromatic substitution (EAS) can provide a straightforward approach to the efficient synthesis of functionalized complex aromatic molecules. In general, Lewis acids (LA) serve as beneficial stimulus for the formation of a Wheland complex. In presence of the strong LA $B(C_6F_5)_3$[1] tricyanomethane $HC(CN)_3$ (**1a**)[2] is activated leading to an unusual type of EAS. Thereby, the LA causes the isomerization of **1a** to the ketenimine, $HN=C=C(CN)_2$, which directly attacks the aromatic species in the EAS, with simultaneous proton migration forming an amino group instead of elimination. Amino-malononitrile-substituted aromatic compounds (**2Ar**·2**B**) are built in one step.
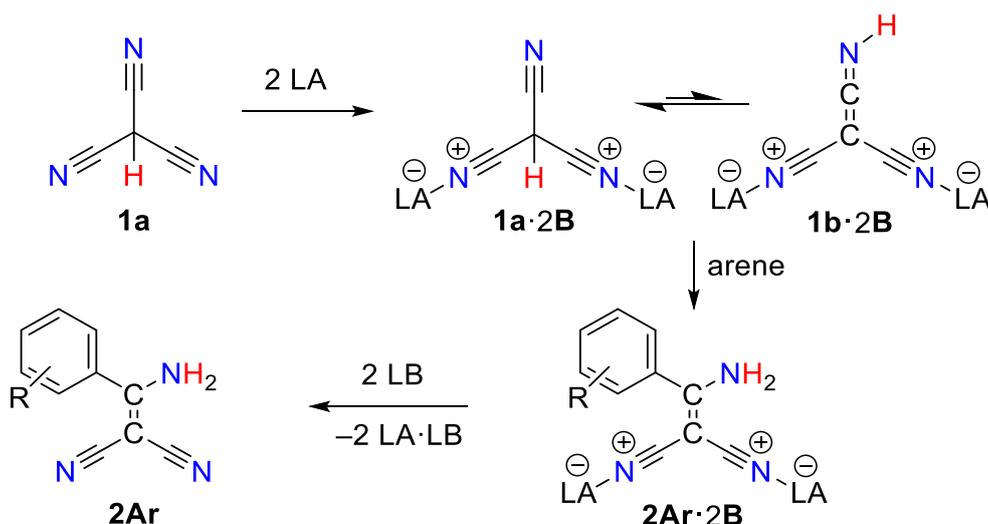
*Figure 1: EAS reaction of aromatic compounds (**Ar** = Ph, pTol, Xyl, Mes, Dur) in presence of $B(C_6F_5)_3$.*

When a solution of **1a** with two equivalents of $B(C_6F_5)_3$ (**B**) in CH_2Cl_2 is concentrated, an orange solid (**1**·2**B**) is obtained. The isolated **1**·2**B** with arenes such as benzene or methylated aromatics led always to di-borane adducts of type **2Ar**·2**B** in an EAS reaction. In presence of H_3CCN the LA is stereoselectively removed in (*E*)-position, whereas water leads to the uncoordinated product **2Ar**.[3]

[1] M. Kuprat, M. Lehmann, A. Schulz, A. Villinger, *Organometallics* **2010**, *29*, 1421–1427.
[2] K. Banert, M. Chityala, M. Hagedorn, H. Beckers, T. Stüker, S. Riedel, T. Rüffer, H. Lang, *Angew. Chem. Int. Ed.* **2017**, *56*, 9582–9586.
[3] J. Surkau, K. Bläsing, J. Bresien, D. Michalik, A. Villinger, A. Schulz, *Chem. – Eur. J.* **2022**, *28*, e202201905.

Nitrogen centered aqueous oxygenation of an iridium(V) nitrido complex

Philipp A. Wieser,[a] Sven Schneider*[a]

[a] *Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Germany.*

philipp.wieser@uni-goettingen.de

Ammonia oxygenation is an industrially and biologically important process for the synthesis of high-valent nitrogenous compounds.[1] Early homogeneous models demonstrated the oxidation of coordinated ammonia in aqueous media to nitrosyl, and ultimately all the way to nitrate.[2] Terminal nitrido complexes were proposed as intermediates, but not isolated.[3] While the oxygenation of electrophilic nitrido ligands with O-atom transfer reagents is well known,[4] the use of water as oxygen source is rare and mechanistically not well examined.[5]

We here describe the N-centered oxygenation of an iridium(V) nitrido complex[6] upon oxidation in aqueous hydroxide solution (Scheme 1). The mechanism of N–O bond formation and associated proton-coupled electron transfer steps are discussed.
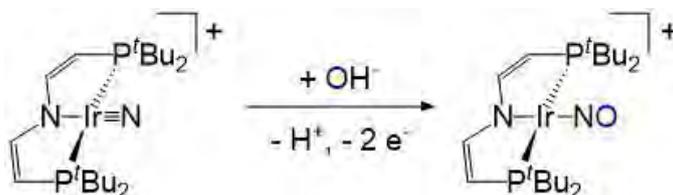
Scheme 1: Conversion of an iridium(V) nitride to the corresponding nitrosyl complex.

[1]   J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, *Science* **2018**, 360.
[2]   M. S. Thompson, T. J. Meyer, *J. Am. Chem. Soc.* **1981**, *103*, 5577.
[3]   W. R. Murphy Jr., K. Takeuchi, M. H. Barley, T. J. Meyer, *Inorg. Chem.* **1986**, 25, *7*, 1041.
[4]   J. M. Smith, *Progr. Inorg. Chem.* **2014**, *58*, 417.
[5]   A. Wu, A. Dehestani, E. Saganic, T. J. Crevier, W. Kaminsky, D. E. Cohen, J. M. Mayer *Inorg. Chim. Acta* **2006**, *359*, 2842.
[6]   M. G. Scheibel, B. Askevold, F. W. Heinemann, E. J. Reijerse, B. de Bruin, S. Schneider, *Nat. Chem.* **2012**, *4*, 552.

Planar Corrole Dimers: Synthetic Approaches to di-topic non-innocent Ligands

Sebastian Günther,[a] Martin Bröring*[a]

[a] IAAC, Technical University of Brunswick, Germany.

Sebastian.guenther@tu-bs.de

The research on polymers of porphyrinoids emerged in recent years as a promising new field in the already well established area of the chemically, biologically and medicinally important tetrapyrroles.[1-5] Fusing these porpyrinoids to oligomers drastically increases the molecular complexity and potential applications. This complexity is advantageous if the synthetic approach is highly selective. This poster will provide insight into the process of developing synthesis strategies to obtain di-topic molecules, showcasing several different possible approaches.[6-9]
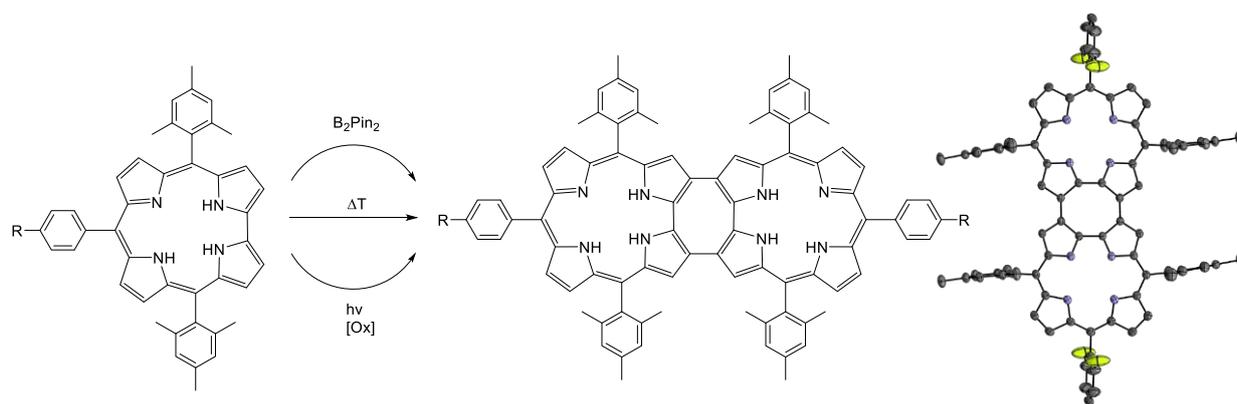
Figure 1: Synthetic pathways to planar corrole dimers with obtained crystal structure of the target molecule on the right.

[1]   S. Ooi, K. Ueta, T. Tanaka. A. Osuka, *ChemPlusChem* **2019**, *84*, 578-588.
[2]   P.S.S. Lacerda, M. Bartolomeu, A.T.P.C. Gomes, A.S. Duarte, A. Almeida, M.A.F. Faustino, M.G.P.M.S. Neves, J.F.B. Barata, *Microorganisms* **2022**, *10*, 1167.
[3]   W. Sinha, A. Mahammed, N. Fridman, Z. Gross, *ACS Catal.* **2020**, *10*, 3764-3772.
[4]   W. Sinha, A. Mahammed, N. Fridman, Z. Gross, *Isr. J. Chem*. **2023**, e202300036.
[5]   A. Kumar, D. Kim, S. Kumar, A. Mahammed, D.G. Chrchill, Z. Gross, *Chem. Soc. Rev.*, **2023**, *52*, 573-600.
[6]   J.F.B. Barata, A.M.G. Silva, M.G.P.M.S. Neves, A.C. Tomé, A.M.S. Silva, J.A.S. Cavaleiro, *Tetrahedron Letters*, **2006**, *47*, 8171-8174.
[7]   S. Hiroto, K. Furukawa, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 12380-12381.
[8]   J.F.B. Barata, M.G.P.M.S. Neves, A.C. Tomé, M.A.F. Faustino, A.M.S. Silva, J.A.S. Cavaleiro, *Tetrahedron Letters*, **2010**, *51*, 1537-1540.
[9]   S. Hirabayashi, M. Omote, N. Aratani, A. Osuka, *Bull. Chem. Soc. Jpn*. **2012**, *85*, 558-562.

Synthesis and Magnetic Properties of Low-Coordinate Iron(II) and Iron(I) Pogo Stick Complexes

Katharina Münster,[a] Dirk Baabe,[a] Benjamin Kintzel,[b] Michael Böhme,[b] Winfried Plass,[*b] Jan Raeder,[a] Marc D. Walter[*a]

[a] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Germany. [b] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Germany.

k.muenster@tu-bs.de

The magnetic properties of organo-iron species have recently attracted growing interest because of their possible application as single-molecule magnets.[1] [{Cp'Fe(μ-I)}$_2$] (Cp' = 1,2,4-tri-*tert*-butylcyclopentadienyl) reacts with lithium amides to the quasi-linear high-spin Fe(II) half-sandwich complexes **Fe-tms**, **Fe-^{t}Bu** and **Fe-dipp**,[2] which in two cases can also be reduced to Fe(I) compounds.
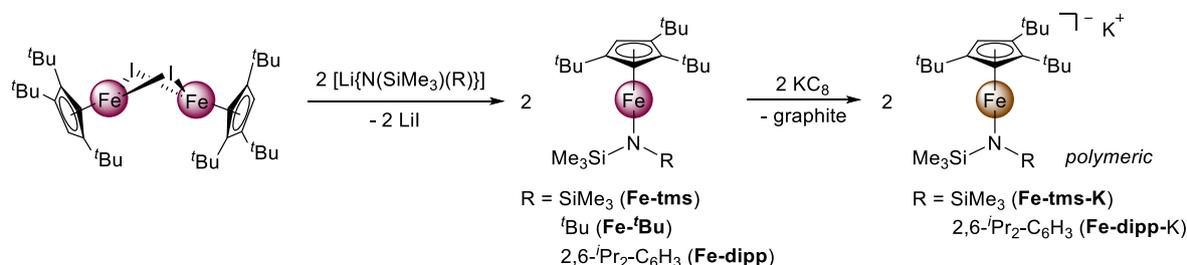
Figure 1: Synthesis of Fe(II) and Fe(I) amido half-sandwich complexes starting from [{Cp'Fe(μ-I)}$_2$].

The zero-field ^{57}Fe Mößbauer spectra of the Fe(II) complexes at T > 20 K feature asymmetrically broadened singlets representative of slow paramagnetic relaxation. At lower temperatures, the well-resolved six-line spectra indicate large internal magnetic hyperfine fields at the ^{57}Fe nuclei. Magnetic measurements supported by computations suggest significant axial zero-field splitting. Slow relaxation of magnetization is detected in the absence of a static magnetic field for compound **Fe-^{t}Bu**.[2]
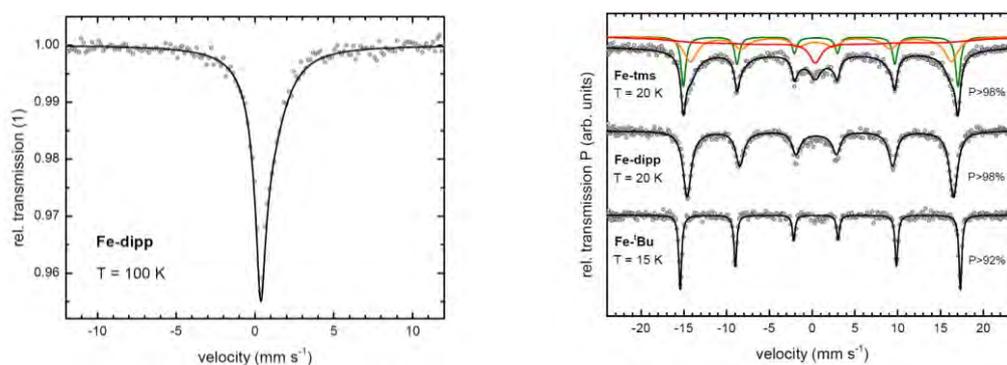
*Figure 2: Zero-field ^{57}Fe Mößbauer spectra of **Fe-dipp** at T = 100 K (left) and the Fe(II) amido complexes at T = 15 and 20 K (right). Black dots are experimental data, lines represent the fit based on the Blume-Tjon model.[2,3]*

[1]   M. Feng, M.-L. Tong, *Chem. Eur. J.* **2018**, *24*, 7574–7594.
[2]   K. Münster, D. Baabe, B. Kintzel, M. Böhme, W. Plass, J. Raeder, M. D. Walter, *Inorg. Chem.* **2023**, 61, 18883–18898.
[3]   M. Blume, J. A. Tjon, *Phys. Rev.* **1968**, *165*, 2, 446–456.

Neutral Trigonal Cu(I) Complexes with Anionic *N*-Heterocyclic Carbenes

<u>Lucie J. Groth</u>,[a] Philipp R. Meinhold,[a] Lars E. Burmeister,[b] Stefanie Tschierlei,[b] Matthias Tamm*[a]

[a] *Institut für Anorganische und Analytische Chemie, TU Braunschweig, Germany*
[b] *Institut für Physikalische und Theoretische Chemie, TU Braunschweig, Germany*

lucie.groth@tu-braunschweig.de

Trigonal *N*-heterocyclic carbene (NHC)-Cu(I) complexes have gained attention due to their capability to emit blue light with high quantum yields.[1] Whereas multiple examples of cationic complexes have been reported, only a limited number of neutral complexes with an anionic *N,N'*-ligand are known.[2-3] We want to expand the scope with Cu(I) complexes containing an anionic NHC and neutral *N,N'*-ligands by preparation of a novel series of neutral emissive Cu(I) complexes.

The well established carbene transfer agent **1** is known to form in a reaction with CuCl the toluene solvate **2**, which we deemed an excellent starting point.[4] The targeted complex **3** can be obtained by combination with the corresponding *N,N'*-ligand, which easily replaces the coordinated toluene. The blue luminescence in related complexes is mainly optimized by tailoring the *N,N'*-ligand, which makes this variation the most versatile.[2] Complex **3** showed a bright blue luminescence in the solid state, which is currently examined further.
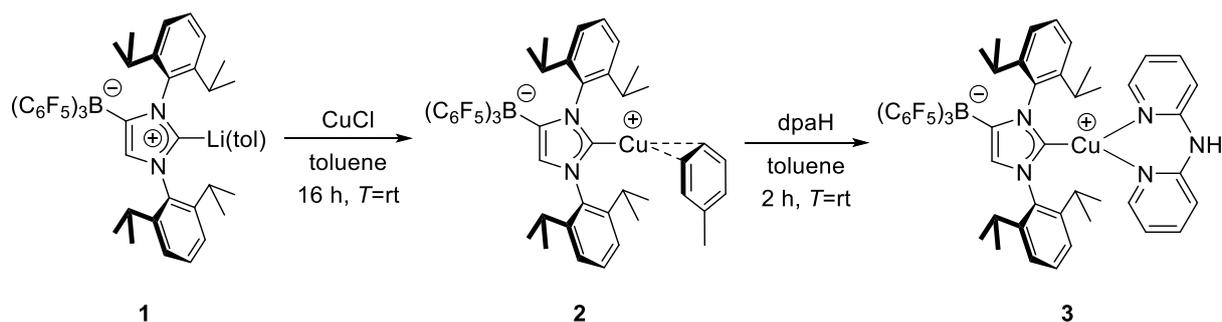
*Scheme 1: Representative synthethic aproach towards targeted Cu(I) complexes of type **3**.*

[1] C. E. Housecroft, E. C. Constable, *J. Mater. Chem. C* **2022**, *10*, 4456–4482.
[2] a) V. A. Krylova, P. I. Djurovich, M. T. Whited, M. E. Thompson, *Chem. Commun.* **2010**, *46*, 6696–6698. b) R. Marion, F. Sguerra, F. Di Meo, E. Sauvageot, J.-F. Lohier, R. Daniellou, J.-L. Renaud, M. Linares, M. Hamel, S. Gaillard, *Inorg. Chem* **2014**, *53*, 9181–9191.
[3] V. A. Krylova, P. I. Djurovich, B. L. Conley, R. Haiges, M. T. Whited, T. J. Williams, M. E. Thompson, *Chem. Commun.* **2014**, *50*, 7176–7179.
[4] S. Planer, J. Frosch, M. Koneczny, D. Trzybiński, K. Woźniak, K. Grela, M. Tamm, *Chem. Eur. J.* **2021**, *27*, 15218–15226.

Rhodium(I) PNN pincer complexes with proton-responsive ligands: synthesis, characterisation, and catalytic dehydrocoupling of amine boranes

Mirko Rippke,[a] Hans-Joachim Drexler,[a] Torsten Beweries*[a]

[a] *Leibniz Institute for Catalysis, Albert-Einstein-Str. 29a, 18059 Rostock, Germany.*

Mirko.rippke@catalysis.de

Cooperative ligands, which activate the substrate in concert with the transition metal show a high activity for a variety of catalytic reactions.[1] One example is the dehydropolymerisation of amine boranes $H_3B \cdot NMe_nH_{3-n}$ (n = 0-2), commonly referred to as isoelectronic main group analogues of alkanes with great potential for the construction of oligomeric, polymeric and heterogeneous B-N materials.[2][3] We synthesised Rh(I) complexes with the potentially cooperative pyridine-pyrazole PNN(H) ligand, first reported by Caulton and co-workers and used this system for the dehydropolymerisation of amine boranes.[4]
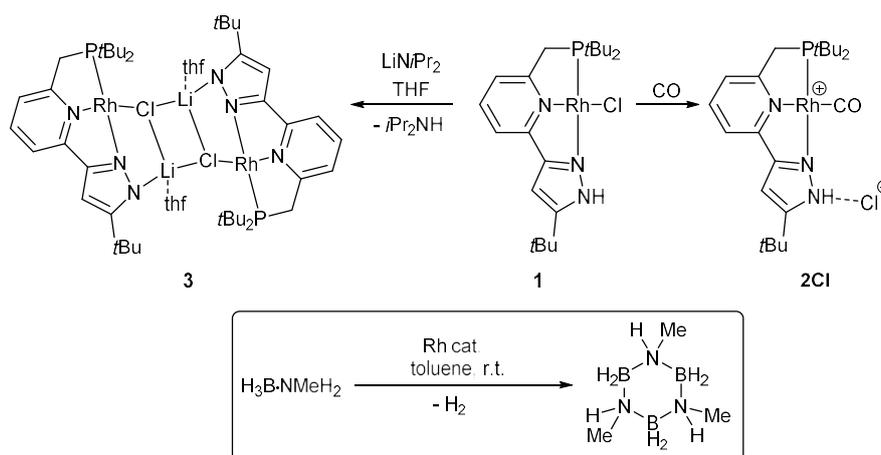
Figure 1: Synthesis of new Rh(I)) PNN complexes and catalytic oligomerisation of methylamine borane.

Starting from the Rh chloride complex **1** a cationic complex **2Cl** was created by addition of CO. The deprotonation of **1** was achieved with Li(N*i*Pr$_2$) and furnished a bimetallic complex **3**. All three complexes were tested as precatalysts for the dehydrocoupling of amine boranes, producing mainly *N*-methylcyclotriborazane $(H_2BNMeH)_3$.

[1]   Selected overviews: a) H. Li, B. Zheng, K.-W. Huang, *Coord. Chem. Rev.* **2015**, *293-294*, 116-138; b) T. Zell, D. Milstein, *Acc. Chem. Res.* **2015**, *48*, 1979-1994; c) S. Schneider, J. Meiners, B. Askevold, *Eur. J. Inorg. Chem.* **2012**, 412-429.

[2]   a) D. Han, F. Anke, M. Trose, T. Beweries, *Coord. Chem. Rev.* **2019**, *380*, 260-286; b) A. L. Colebatch, A. S. Weller, *Chem. Eur. J.* **2019**, *25*, 1379-1390.

[3]   a) T. Beweries, H. Helten, in *Encyclopedia of Inorganic and Bioinorganic Chemistry* **2020**, pp. 1-25; b) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023–4078.

[4]   A. V. Polezhaev, C.-H. Chen, Y. Losovyj, K. G. Caulton, *Chem. Eur. J.* **2017**, *23*, 8039-8050.

Synthesis, Characterization and Follow-Up Chemistry of Superoxides and Ozonides with Organic Cations

Jonas R. Schmid, [a] Oliver R. H. Rennefeld,[a] Prof. Dr. Dr. hc. M. Jansen,[b] Prof. Dr. S. Riedel [a]

[a] *Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.*
[b] *Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany.*

jonas.schmid@fu-berlin.de

Alkaline superoxides have been investigated thoroughly by x-ray as well as neutron diffraction studies, but no reliable O–O bond distances could be determined, due to multiple structural phase transitions and disorder of the anion.[1] Therefore, organic cations have been chosen to force the $[O_2]^-$ groups in ordered positions.[1c] So far, only six examples are known and analyzed via single crystal x-ray diffraction, from which five include crystallized ammonia.[1c,2] We were able to obtain a second crystal structure without crystallized ammonia in combination with the shortest O–O bond in any reported organic superoxide (1-propyl-1-methylpyrrolidin-1-ium superoxide, [PMP][O_2]), as shown in **Figure 1**.
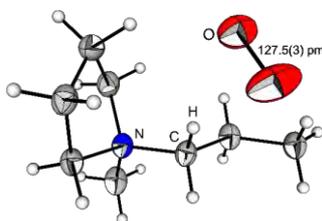
Figure 1: Crystal structure of [PMP][O2]. Thermal ellipsoids are set to 50% probability.

As a result of the high reactivity and the limited scope of suitable solvents, metalorganic or complex chemistry of ozonides is rather undiscovered.[3] Therefore, we investigated asymmetric ammonium-based cations for the synthesis of new ozonide salts, which are now available as highly soluble synthons.[4] Based on these results, we were able to explore new reaction pathways.

[1]   a) O. Sikora, D. Gotfryd, A. Ptok, M. Sternik, K. Wohlfeld, A. M. Oleś, P. Piekarz, *Phys. Rev. B* **2020**, *102*, 085129;
       b) W. Hesse, M. Jansen, W. Schnick, *Prog. Solid State Chem.* **1989**, *19*, 47;
       c) H. Seyeda, M. Jansen, *J. Chem. Soc., Dalton Trans.* **1998**, 875.
[2]   a) P. D. C. Dietzel, R. K. Kremer, M. Jansen, *Chem. Asian J.* **2007**, *2*, 66;
       b) P. D. C. Dietzel, R. K. Kremer, M. Jansen, *J. Am. Chem. Soc.* **2004**, *126*, 4689.
[3]   M. Jansen, H. Nuss, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1307.
[4]   J. R. Schmid, P. Voßnacker, M. Jansen, S. Riedel, *Z. Anorg. Allg. Chem.* **2022**, *648*, e202200225.

N–H bond activation by a strictly T-shaped phosphine

Sotirios Pavlidis,[a] Josh Abbenseth*[a]

[a] *Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin*

sotirios.pavlidis@gmx.de

The activation of polar small molecules to synthesize value-added chemicals has long captivated the realm of transition metal chemistry. Transition metal complexes exhibit catalytic prowess in converting diverse small molecules through E–H bond cleavage. However, ammonia (NH_3) has posed a persistent challenge due to its proclivity for forming Werner-type complexes, leading to unfavorable coordination/activation equilibria.[1] Pincer-type phosphines have emerged as an intriguing avenue for N–H bond activation reactions. The geometric pertubation of the phosphorus center results in Lewis-acidic reactivity enabled by an unoccupied p-orbital centered at the P atom.[2] While rare redox-neutral and more common oxidative addition of ammonia have been documented, the subsequent transfer to organic substrates has remained enigmatic.[3]

Here we report the reactivity of the strictly T-shaped phosphine **I**[4] towards amines. Cooperative N–H bond scission along a flanking P–N bond proceeds under retention of the phosphorus redox state. Mechanistic intricacies are illuminated through NMR experiments. Additionally, we delve into the electronic structure of **I**, particularly the interplay between the planarized phosphorus center and the redox non-innocent acridane derived NNN pincer ligand.[5] These insights enrich our understanding of compound **I**'s reactivity and its future potential in metal free catalysis.
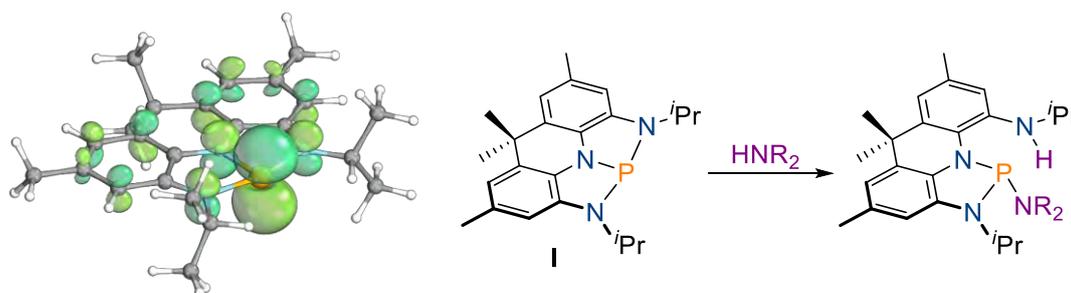
*Figure 1: LUMO of **I** (left); reactivity of **I** with amines (right).*

[1]   S. Streiff, F. Jerôme, *Chem. Soc. Rev.* **2021**, *50*, 1512–1521.
[2]   Recent review: J. Abbenseth, J. M. Goicoechea, *Chem. Commun.* **2020**, *11*, 9728–9740.
[3]   a) S. M. McCarthy, Y.-C. Lin, D. Devarajan, J. W. Chang, H. P. Yennawar, R. M. Rioux, D. H. Ess, A. T. Radosevich, *J. Am. Chem. Soc.* **2014**, *136*, 4640–4650; b) J. Ciu, Y. Li, R. Ganguly, A. Inthirarajah, H. Hirao, R. Kinjo, *J. Am. Chem. Soc.* **2014**, *136*, 16764–16767; c) T. P. Robinson, D. M. De Rosa, S. Aldridge, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2015**, *54*, 13758–13763; d) J. Abbenseth, O. P. E. Townrow, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2021**, *60*, 23625–23629
[4]   A. J. King, J. Abbenseth, J. M. Goicoechea, *Chem. Eur. J.* **2023**, *29*, e202300818.
[5]   J. Underhill, E. S. Yang, T. Schmidt-Räntsch, W. K. Myers, J. M. Goicoechea, J. Abbenseth, *Chem. Eur. J.* **2023**, *29*, e202203266.

Relativistic Effects on the Thermochemistry of Proton-Coupled Electron Transfer at a Rhenium Complex

Sandipan Maji[a], Daniel Delony[a], Martin Diefenbach[b], Serhiy Demeshko[a], Max C. Holthausen[c], Sven Schneider[*a]

ᵃ Georg-August Universität Göttingen, Germany. ᵇ Technische Universität Darmstadt, Germany, ᶜ Department of Chemistry, Goethe-Universität Frankfurt, Germany.

sandipan.maji@stud.uni-goettingen.de

The magnetic and spectroscopic properties of heavy metal complexes are heavily determined by spin-orbit coupling (SOC).[1] In contrast, the impact of relativistic effects on reaction thermochemistry is less well examined. Computations by Kývala et al. predicted that the SOC-induced splitting of the $^2T_{2g}$ ground states of O_h-symmetric $[M(H_2O)_6]^{3+}$ (M = Ru, Os) significantly shifts the M^{III}/M^{II} redox potentials by $\Delta E° = -190$ mV (Ru) and $\Delta E° = -390$ mV (Os), respectively.[2] However, such large effects might be quenched in lower molecular symmetry. Furthermore, absolute computations of redox potentials are challenging due to inherent difficulties to adequately describe solvation.

We therefore moved to a net charge neutral proton-coupled electron transfer (PCET) reaction of the heavy metal rhenium (Figure 1). The thermochemical parameters were derived by calorimetry and through the square-scheme formalism and compared with multireference computations using perturbational treatment of SOC. Our results reveal a SOC contribution to the PCET reaction energetics around $\Delta E_{SOC} = 28.1$ kJ/mol (X=Cl), thus, confirming a large SOC effect in low symmetry (C_{2v}). This is attributed to the nearly degenerate S=1 ground state of the rhenium(III) amine complex.

Figure 1: Proton-coupled electron transfer reaction of the examined rhenium complex.

[1]   J. Chatt, G. J. Leigh, D. M. P. Mingos, *J. Chem. Soc. A* **1969**, 1674–1680
[2]   M. Srnec, J. Chalupsky, M. Fojta, L. Zendlova, L. Havran, M. Hocek, M. Kyvala, L. Rulisek, *J. Am. Chem. Soc.* **2008**, *130*, 10947–10954

Investigation of Bichloride Ionic Liquids as Hydrogen Chloride Storage

G. Dreyhsig,[a] P. Voßnacker,[a] Dr. M. Kleoff,[a] Prof. Dr. S. Riedel*[a]

[a] *Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany.*

gesa.dreyhsig@fu-berlin.de

Organic ammonium chloride salts can form bichlorides when reacting with gaseous hydrogen chloride (**Scheme 1**). This reactivity is already known for the lighter halogen fluorine due to its ability to form bifluorides, considered as a stabilized, less-volatile type of gaseous hydrogen fluoride.[1] The bichlorides exist either as ionic liquids or as solids at room temperature, depending on the organic groups of the ammonium cation.[2]

$$[NR_3Me]Cl \quad + \quad n\,HCl \quad \longrightarrow \quad [NR_3Me][Cl(HCl)_n]$$
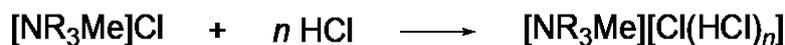
Scheme 1: Reaction of organic ammonium chloride ionic liquids (R = Me, Et, Pr, Bu) with n equivalents of hydrogen chloride to form bichloride salts.

Since hydrogen chloride is produced in various large-scale processes as a side-product, the industry must deal with its corrosive behavior as a gas, or even worse, as an aqueous solution.[3] The possibility to store hydrogen chloride as an ionic liquid or as a solid would help to prevent corrosion and could also lead to a safer method for handling it. In our work, we characterize different properties of four different bichlorides to investigate their possible industrial application (**Figure 1**).
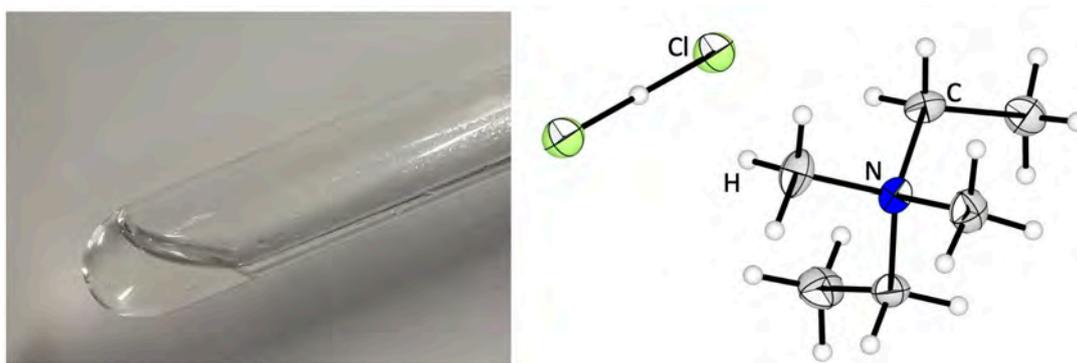
Figure 1: Picture of the ionic liquid [NEt$_3$Me][Cl(HCl)] (left) and the molecular structure in the solid state of [NEt$_2$Me$_2$][Cl(HCl)], with thermal ellipsoids shown at 50% probability (right).

[1]   G. A. Olah, J. T. Welch, Y. D. Vankar, M. Nojima, I. Kerekes, J. A. Olah, *J. Org. Chem.* **1979**, *44*, 3872.
[2]   S. Riedel, P. Voßnacker, WO2023020942 A1, *Storage medium for storing hydrogen chloride and method for separating and storing hydrogen chloride HCl from HCl containing gas*, **2023**.
[3]   M. Bertau, A. Müller, P. Fröhlich, M. Katzberg, *Industrielle Anorganische Chemie*, 4. ed., Wiley-VCH, Weinheim, **2013**.

Re-discovering Silicon Teflates

Friederike Oesten,[a] Sebastian Riedel[a]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Germany*

friederike.oesten@fu-berlin.de

Among the few silicon compounds containing the pentafluoroorthotellurate group ($OTeF_5$, teflate) that have been reported, $Me_3SiOTeF_5$ is the only one that has been fully characterised.[1] On the contrary, $Si(OTeF_5)_4$ was only briefly mentioned in the literature and its characterization is limited to its melting point.[2] With the aim of eventually isolating and characterizing unambiguously this compound, we envisioned a stepwise Cl/$OTeF_5$ substitution of different organosilicon chlorides towards silicon compounds with an increasing teflate content.

Inspired by the synthesis of $Me_3SiOTeF_5$, several other $R_3SiOTeF_5$ (R = alkyl, aryl) compounds like $Ph_3SiOTeF_5$ could be obtained by reacting $HOTeF_5$ and the corresponding R_3SiCl. Based on these results, the synthesis of $R_2Si(OTeF_5)_2$ species (R = Me, Et, ^iPr, Ph) was tackled. However, for the introduction of two teflate groups, $AgOTeF_5$ has to be used as an $OTeF_5$-transfer reagent. Similar attempts towards silicon compounds with a higher teflate content look currently promising. Moreover, the Lewis acidity of silicon teflates $R_xSi(OTeF_5)_{4-x}$ (x = 3–0, R = aryl, alkyl) is also investigated.
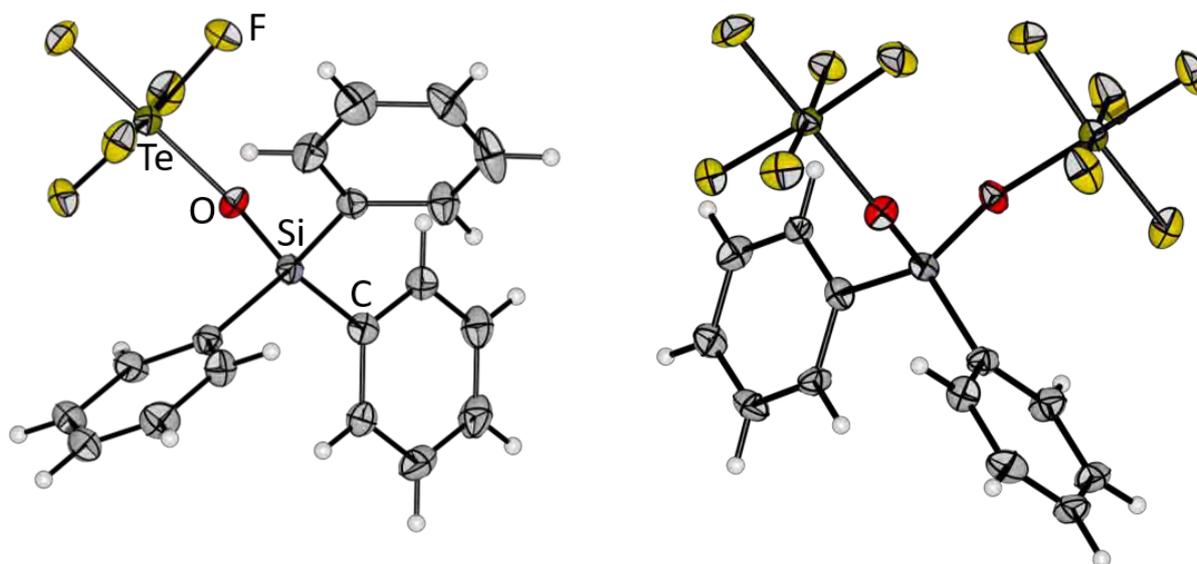
Figure 1: Molecular structure of $Ph_3SiOTeF_5$ and $Ph_2Si(OTeF_5)_2$ in the solid state. Thermal ellipsoids are set at 50% probability.

[1]   M. A. Ellwanger, C. von Randow, S. Steinhauer, Y. Zhou, A. Wiesner, H. Beckers, T. Braun, S. Riedel, *Chem. Commun.* **2018**, *54*, 9301.
[2]   F. Sladky, H. Kropshofer, *J. Chem. Soc., Chem. Comm.* **1973**, 600.

Introducing a New Aluminum-based Lewis Superacid: Aluminum Tris(fluorosulfate)

Johanna Schlögl,[a] Simon Steinhauer,[a] Sebastian Riedel*[a]

[a] Freie Universität Berlin, Institute of Chemistry and Biochemistry – Inorganic Chemistry, Fabeckstraße 34/36, 14195 Berlin, Germany.

schjo@zedat.fu-berlin.de

Lewis acids, whose strength surpasses that of monomeric SbF_5 in the gas phase, are commonly known as Lewis superacids.[1] These species play a major role not only in fundamental research, but also in applied chemistry. The quest for the strongest, most easily accessible and most stable Lewis superacid is of increasing scientific interest.

Herein we present a new aluminum-based Lewis superacid, $Al(SO_3F)_3$. It is the first fluorosulfate-based Lewis superacid and its remarkably easy synthesis directly from commercially available starting materials distinguishes it from other aluminum-based representatives. Its full characterization as a Lewis superacid will be reported.
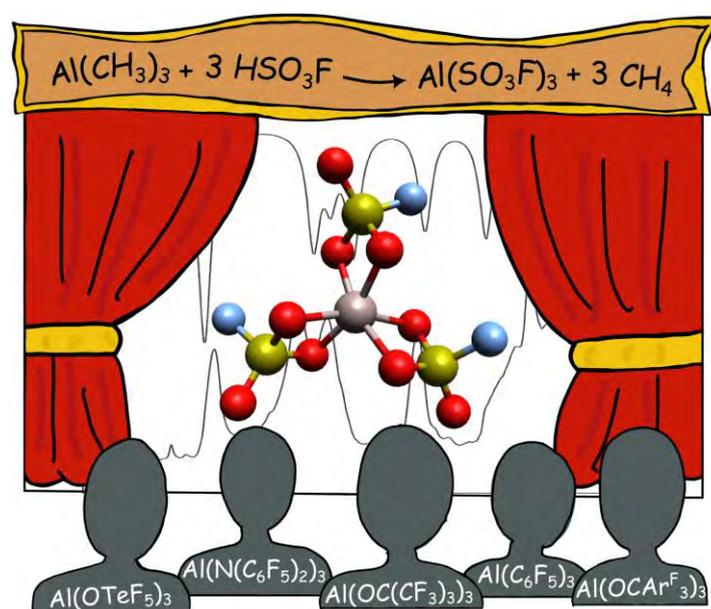
Figure 1: Introducing a new aluminum-based Lewis superacid: Aluminum tris(fluorosulfate). In the background the experimental and calculated IR spectra show a clear conformity (B3LYP-D3(BJ)/def2-TZVPP).

[1]   L. O. Müller, D. Himmel, J. Stauffer, G. Steinfeld, J. Slattery, G. Santiso-Quiñones, V. Brecht, I. Krossing, *Angew. Chem. Int. Ed.* **2008**, *47*, 7659 -7663.

Sequence selective terpolymerisation of Elemental Sulfur with Propylene oxide and Carbon Disulfide: Scope, Mechanism and Crosslinking

Cesare Gallizioli,[a] David Battke, [a] Peter Deglmann,[b] Alex J. Plajer [a],*

a Institute für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34-36, 14195 Berlin;. b BASF SE, Carl-Bosch-Strasse 38, 67056 Ludwigshafen am Rhein, Germany.
plajer@zedat.fu-berlin.de

Elemental sulfur, a cheap by-product of the oil refinement process, represents a promising synthetic opportunity for the synthesis of new functional, recyclable, and degradable materials. Controlled anionic polymerisations to access thermoplastic polysulfide from S_8 however depend on thiolate intermediates generated through expensive comonomers and catalysts to facilitate S_8 ring-opening[1][2]. We show that simple lithiumalkoxides facilitate the polymerisation of elemental sulfur S_8 with industrially relevant propylene oxide (PO) and CS_2, a sulfur base chemical sourced from waste S_8 itself. A rare sequence selective ring-opening terpolymerisation (ROTERP) forming poly(monothiocarbonate-alt-S_x) in an unusual heat-to-head-alt-tail-to-tail selectivity is observed allowing to control the rank of the polysulfide links S_x and the ROTERP of a range of monosubstituted and alicyclic epoxides. A combined experimental and computational elucidation of the mechanism reveals kinetic S_8 over CS_2 selection by in-situ formed lithium thiolate intermediate which are formed by a central O/S exchange step to be key in the reaction mechanism. The Sulfur centres of the starting S_8 building blocks get distributed by thermodynamically controlled reshuffling involving intermolecular attack of R-S_x-R links by thiolate chain-ends and back-biting pathways at R-S_x-Li chain ends. The polymers can be crosslinked in-situ with multifunctional thiols to yield thermally reporcessable and nucleophilically degradable networks with improved solvent resistance. Our report demonstrates how mechanistic understanding allows S_8 waste utilization with inexpensive components to yield a broad palette of reprocessable and degradable materials.
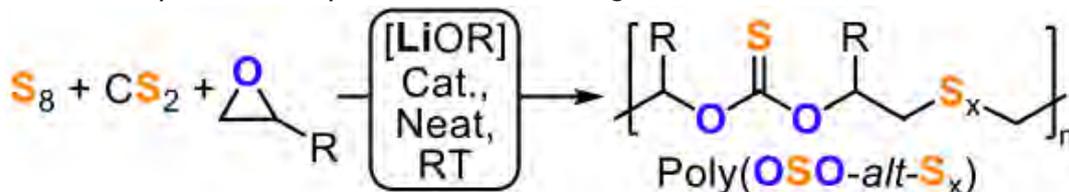
Figure 1: Ring opening copolymerization (ROCOP) between elemental sulfur, propylene oxide and carbon disulfide to make polysulfides-alt-monothiocarbonate containing materials.

[1] Chao, J., Yue, T., & Ren, W. (2022). *Angewandte Chemie International Edition*, *61*(16).

[2] Andrzej Duda, Stanislaw Penczek (1982) *Macromolecules,* 15, 36-40

An Unsymmetrical Diborane(4) as a Facile Precursor to PBP Boryl Pincer Complexes

Philipp Rutz[a], Jörg Grunenberg[b], Christian Kleeberg[a]*

[a] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Germany.*
 [b] *Institut für Organische Chemie, Technische Universität Braunschweig, Germany.*

p.rutz@tu-bs.de

The synthesis of PBP aminoboryl pincer complexes introduced in 2009 by Yamashita and Nozaki et al. has thus far been restricted to B-H oxidative addition of diaminoborane ligand precursors to transition metal precursors.[1] This limitation has hindered the field's progress. Consequently, we developed a new process to access PBP boryl pincer complexes *via* an unsymmetrical diborane(4), a class of compounds established as boryl ligand precursors.[2]

The unsymmetrical diborane(4), $d(CH_2P(iPr)_2)abB–Bpin$ (pin = $(OCMe_2)_2$; $d(R)ab$ = $1,2-(RN)_2(C_6H_4)$), was obtained by reacting a copper(I) boryl complex (boron nucleophile) with a boron electrophile, the borane $d(CH_2P(iPr)_2)abB–H$; a protocol we established as a general route to unsymmetrical diborane(4) derivatives.[3]

This diborane(4) precursor can be used as a precursor to prepare PBP boryl pincer complexes. The versatility of this method was demonstrated by preparing copper and platinum complexes, $[(d(CH_2P(iPr)_2)abB)Cu]_2$ and *trans*-$[(d(CH_2P(iPr)_2)abB)Pt–Bpin]$, as well as a series of group nine boryl complexes with the general formula $(d(CH_2P(iPr)_2)abB)M(PMe_3)_n$ (n = 1, 2).[4,5]
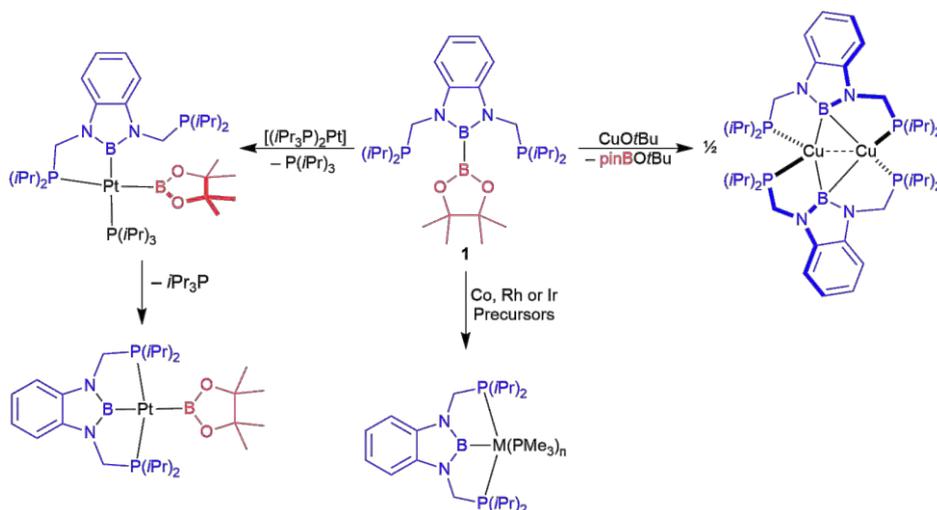
Scheme 1: Reactions of $d(CH_2P(iPr)_2)abB–Bpin$ with transition metal precursors.

[1] Y. Segawa, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 9201.
[2] (a) C. Borner, C. Kleeberg, *Eur. J. Inorg. Chem.* **2014**, *2014*, 2486. (b) C. Borner, M. T. Wiecha, C. Kleeberg, *Eur. J. Inorg. Chem.* **2017**, *2017*, 4485.
[3] W. Oschmann, C. Borner und C. Kleeberg, *Dalton Trans.* **2018**, 47, 5318.
[4] P. M. Rutz, J. Grunenberg, C. Kleeberg, *Organometallics* **2022**, *41*, 3044.
[5] P. M. Rutz, J. Grunenberg, C. Kleeberg, *under review*.

Teilnehmende des NDDK 2023

Freie Universität Berlin

Prof. Dr. Müller

Lea Dettling

Samantha Frank

Moritz Ernst

Richard Kopp

Dr. Kuldeep Singh

Dorian Reich

Markus Peschke

Daniela Doppelstein

Prof. Dr. Hasenstab-Riedel

Johanna Schlögl

Friederike Oesten

Gesa Dreyhsig

Lukas Fischer

Jonas Schmid

Patrick Voßnacker

Daniel Wegener

Ahmet Toraman

Paul Golz

Yan Lu

Xiya Xia

Marlon Winter

Dr. Merlin Kleoff

Mei Wen

Lilian Maria Maas

Johanna Sturm

Thomas Drews

Elisabeth Schlaß

Dr. Anja Wiesner

Dr. Nina Huittinen

Dr. Mathias Ellwanger

Jacqueline Grewe

Dr. Susanne Rupf

Dr. Moritz Malischewski

Amina Moshtaha

Tim-Niclas Streit

Robin Sievers

Joshua Parche

Liam Griffin

Dr. Alex Plajer
Cesare Gallizioli
Christoph Fornacon-Wood
Bhargav Rampura
Manjunatha

Dr. Günther Thiele
Friederike Fuß
Mohammadreza Ghazanfari
Islam Ramadan
Irina Savova Dimitrova
Asad Malik

Prof. Dr. Dieter Lentz

Humbolt Universität
Dr. Josh Abbenseth
Sotirios Pavlidis

Dr. Alberto Pérez-Bitrián

Universität Potsdam
Prof. Dr. Nora Kulak
Olga Verbitsky
Julian Heinrich
Dr. Beatrice Battistella
Victoria Chua

Bundesanstalt für Materialforschung
Dr. Asad Mehmood
Luise Sander
Juliane Scholl
Simon Dietzmann
Shu-Han Wu

Technische Universität Braunschweig
Prof. Dr. Matthias Tamm
Lukas Körner
Lucie Groth
Angelika Neitzel

Prof. Dr. Marc Walter
Katharina Münster
Simon Eulberg
Sebastian Günther
Nina Schulze
Hendrik Peters

Philipp Rutz

Leibnitz Institut für Katalyse Rostock
Prof. Dr. Torsten Beweries
Alexander Linke
Mirko Rippke
Kushik Kushik

Dr. Christian Hering-Junghans
Jan-Erik Siewert

Universität Rostock
Prof. Dr. Axel Schulz
Peter Fritz
Jonas Surkau
Leon Ohms
Liesa Eickhoff
Jonas Bresien
Jan Rosenboom
Edgar Zander
Yannic Pilopp
Karsten Lüdtke

Prof. Dr. Wolfram W. Seidel
Malte Reihwald
Friederike Marie Hamann

Prof. Dr. Martin Köckerling

Universität Bremen
Prof. Dr. Thorsten Gesing
Sarah Wittmann
Christopher Reuter

Constructor University Bremen
 <u>Prof. Dr. Ulrich Kortz</u>
 Anusree Sundar
 Sahar Khandan
 Vinaya Siby
 Pooja Kulashri
 Arun Pal
 Mahmoud Elcheikh-Mahmoud
Universität Greifswald
 <u>Prof. Dr. Carola Schulzke</u>
 Stefan Richter
 <u>Dr. Christian Fischer</u>
 Anna-Lena Land
 Sebastian Pätsch

Universität Göttingen
 <u>Prof. Dr. Sven Schneider</u>
 Sandipan Maji
 Philipp Wieser
 Marc Neben

 <u>Prof. Dr. Inke Siewert</u>
 Yasaman Sheidaei

 <u>Jun.-Prof. Malte Fischer</u>

 Christian Urbank

Universität Oldenburg
 <u>Prof. Dr. Thomas Müller</u>
 Lukas Bührmann
 Cheng-Huan Liu
 Corinna Girschik
 Nadeschda Geibel
 Marie Sophie Würdemann

 Marcel Eilers
 Kevin Schwitalla

 <u>Prof. Dr. Jarl Ivar van der Vlugt</u>
 Niklas Breims
 Tobias Greven

Universität Hamburg
Prof. Dr. Axel Jacobi von Wangelin
Christopher Reuter
Roderich Meißner

Prof. Dr. Lisa Vondung
Christian Urbank

Prof. Dr. Peter Burger
Thomas Marx

Universität Kiel
Prof. Dr. Felix Tuczek
Anna-Marlene Vogt
Niels Michaelis
Küpra Yildiz

Magritek	Dr. Sanel Suljić
M. Braun	Dr. Plinio de Paula Furtat
Thermo Fischer	Norman Fischer
Bruker	Dr. Tony Stüker