Universität
Münster

KCT
2025
Münster
Germany

Programme &
Book of Abstracts

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Contents

Welcome to Münster

Welcome Message of the Organizing Committee

Dear Participants,

it is with great pleasure that we welcome you to the **19th Koordinationschemietreffen (KCT 2025)**, hosted at the **University of Münster** from **February 24th to 26th, 2025**. We invite you to immerse yourself in the world of **fundamental science** with **technological perspectives** while engaging with **cutting-edge research** in your favorite field of **chemistry**, all within the historic and inspiring atmosphere of the **Münsterland in Westphalia**.

Since its inception in **2005**, the **KCT** has evolved into a highly regarded **international conference**, fostering **collaboration** and **knowledge exchange** among more than **200 researchers**—primarily from **Germany, Switzerland, and Austria**. The event embraces a broad spectrum of topics, from **fundamental coordination chemistry** to advancements in **molecular magnetism, photophysics, medicinal chemistry, structure-property relationships, and biotechnological applications**. At its core, **KCT** is not only a **networking platform** for **independent researchers** but also a significant stepping stone for **early-career academics** to present their work and establish themselves in the field.

Staying true to the **Koordinationschemietreffen tradition**, all **talks** are delivered by **graduate students**, with each **research group** contributing **one talk** and up to **two poster presentations**. We also warmly encourage the participation of additional **group members**, fostering a dynamic **exchange of interdisciplinary ideas**.

Beyond the conference, we invite you to explore the **historic city of Münster**, a place shaped by over **1200 years of history**. Münster is internationally recognized for its **Peace of Westphalia (1648)**, which ended the infamous **Thirty Years' War**, and for its resilience through the tragedies of **World War II**, after which it was meticulously rebuilt. Today, Münster is a **vibrant scientific and economic hub**, home to over **300,000 residents** and a thriving **academic community**, with the **University of Münster** and the **University of Applied Sciences** educating more than **60,000 students** across **180 disciplines**. Its unique blend of **medieval charm** and **modern innovation** makes Münster an ideal setting for **intellectual exchange** and **scientific inspiration**.

We wish you a **stimulating and fruitful conference** filled with **engaging discussions, new collaborations, and inspiring scientific discoveries**. Enjoy **KCT 2025**, and **welcome to Münster!**

The Organizing Committee

Marian Hebenbrock **Mareike Jahnke**

Beate Jasper-Peter **Marcus Layh**

Jens Müller **Cristian A. Strassert**

Nina Zwingmann

A **BIG THANK YOU** to:

Aleksandra Brik, Victoria Cappellari, Julian Fischer, Kirsten Hagelschur, Nele Konrad, Joschua Lüke, Ivan Maisuls, Luca Mensing, Noah Neumann, Thaison Nguyen, Silpa Padmakumar, Benjamin Pauls, Julian Polle, Rafael Probst, Tim Schäfer, Victoria Seiffert & Ali Tonkul.

Sponsor List

We gratefully thank the following sponsors for their financial support of KCT 2025.

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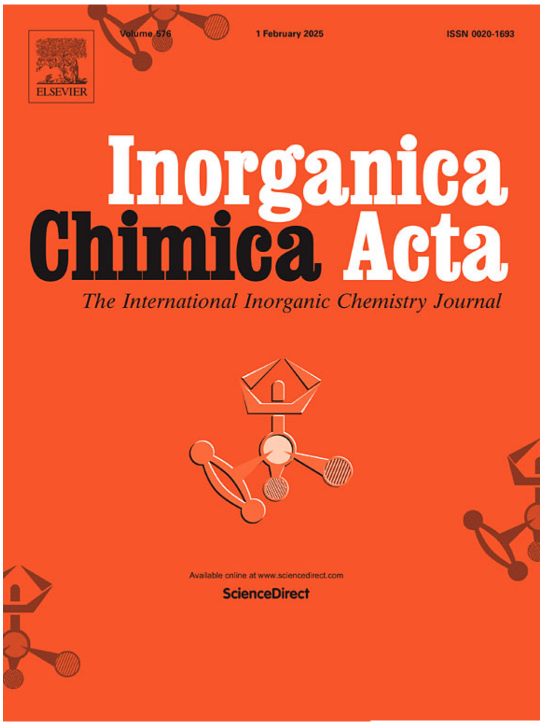

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General Information

Date

The conference takes place from Monday, February 24th, until Wednesday, February 26th, 2025.

Conference Office & Registration Desk

Opening hours:

Monday	11:00 – 16:30
Tuesday	08:30 – 12:45

Badges

Access to the conference venue is restricted to registered persons. All participants are thus kindly asked to wear their badges at all times.

Talks

The lecture hall is equipped with a projector and a PC (suitable file formats are pptx or pdf). Remote control and laser pointer will be provided. All speakers are kindly requested to strictly stay within their time slot of 15 min, which already includes 3 min for Q&A.

Uploading Your Presentation

Presentations must be uploaded on the computer in the Lecture Hall during the coffee breaks. Please make sure that your talk is uploaded at least in the coffee break ahead of your scheduled session.

Poster Presentations

Posters should be prepared in portrait format with a maximum size of A0 (118.9 cm x 84.1 cm). Poster Sessions will take place on Monday (18.45 – 20.15) and Tuesday evenings from (17.30 – 19.00). All posters will be on display until Tuesday evening. Please make sure your poster is ready by Monday at 14:00 and is taken down at the latest on Wednesday at 11:00. Presenters with odd-numbered posters are asked to present their posters during the Monday session, while presenters with even-numbered posters should present on Tuesday.

Awards

Poster awards and an award for the best talk will determined by attendee´s vote. The winners will be announced during the closing ceremony on Wednesday.

Coffee Breaks

Coffee, tea, and beverages as well as some snacks will be provided during the coffee breaks.

Lunch Break

You will receive a lunch voucher together with your badge, valid on Tuesday for the Mensa am Ring. You have a choice between different meals including side dishes, or salad buffet, or the special offer, as well as a soft drink. The food counter in the Mensa closes at 14:00. An English version of the menu is available online (https://muenster.my-mensa.de/chooser.php?v=14357942&hyp=1&mensa=all&lang=en#ring_tage).

For doctoral students: please present also your student ID card, when you pay your lunch with the voucher.

Public Transport

Welcome! Ticket Münster: With the “Welcome! Ticket Münster” you can use public transport within the municipal area of Münster free of charge for the duration of the conference.

Luggage Storage

On Monday and Wednesday, there is the possibility to store luggage in seminar room 85. The organizers or staff members assume no liability for the stored luggage.

WLAN

WLAN is accessible throughout the conference venue. Access to the eduroam network is possible, if you have the respective authentication from your institution.

Conference Dinner

The Conference Dinner will take place on Tuesday evening, starting at 19:15 in the Mensa am Ring. You will need to show your dinner ticket at the entrance to the venue.

Public transport runs from the bus stop “Coesfelder Kreuz” to the city centre (for taking a bus to the city centre or train station you have to cross the street and go the bus stop on the side opposite the Mensa). Be aware that in the evening hours (after 20:00) there is a reduced number of buses operating as line N80, which follow the same route than line 11 (daily hours) to the train station. Until 22:46 the bus N80 runs every half hour, then it switches to hourly operation times (23:46). The last bus (N80) will run to the train station at 00:46! Also regional bus line R64 runs hourly (21:13, 22:13, 23:13) to the train station following a different route than line N80. Alternatively, you can phone a taxi by calling +49 251 60011 (Taxizentrale Münster e.G.) or +49 251 25500 (Taxiruf Münster).

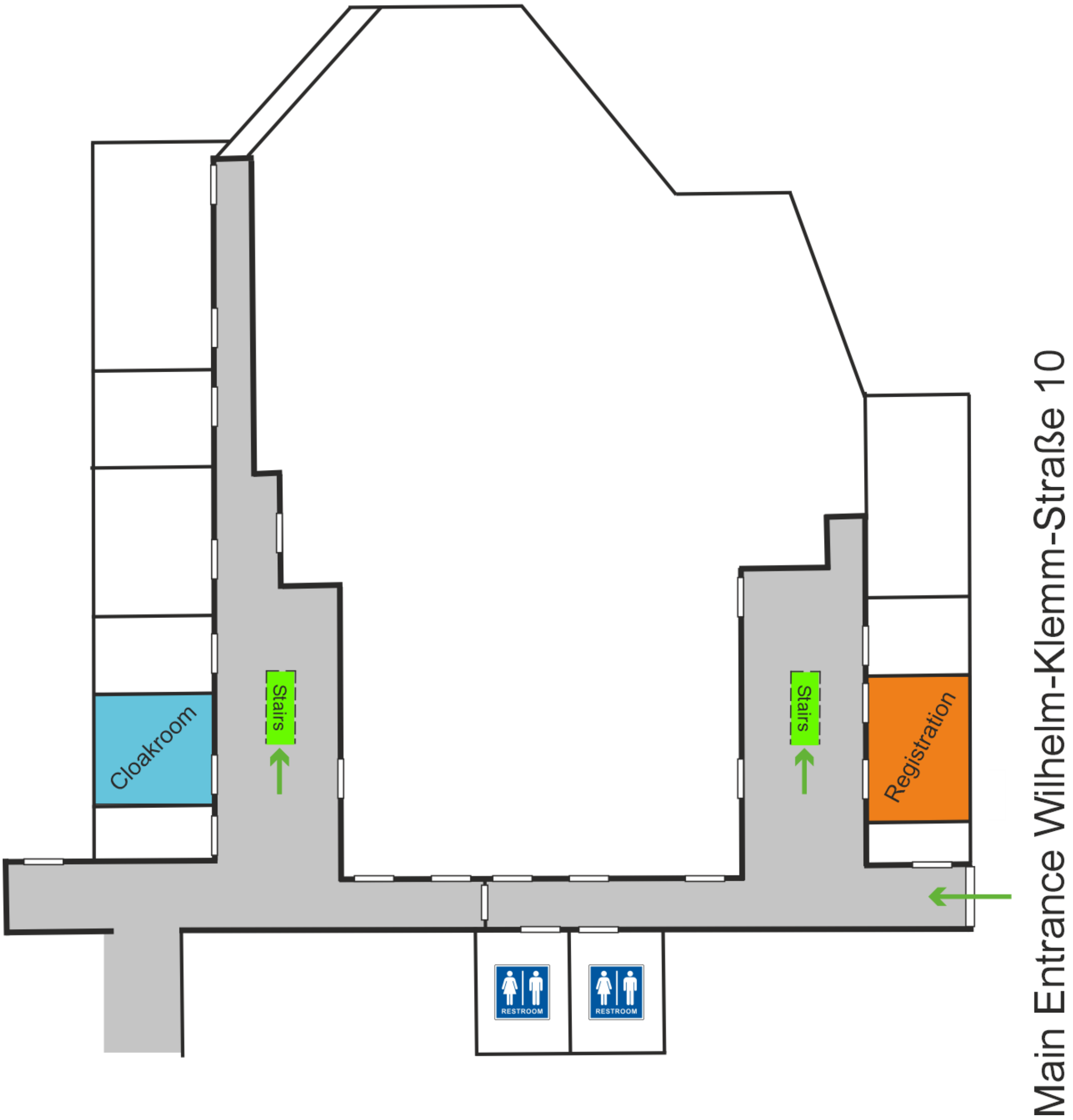
Venue Information

The conference will be held at the natural sciences campus of the University of Münster. All lectures will be presented in lecture hall **HS1** in the physics building (Wilhelm-Klemm-Str. 10). Coffee breaks, poster sessions and vendor exhibitions will take place on the first floor in front of the lecture hall **HS1**. The registration desk is located on the ground floor close to the main entrance. The cloak room for luggage storage on Monday or Wednesday can also be found on the ground level.
A parking garage free of charge is located close to the venue (Opening hours: Mo-Fr 06:00 to 24:00; overnight parking is not permitted).

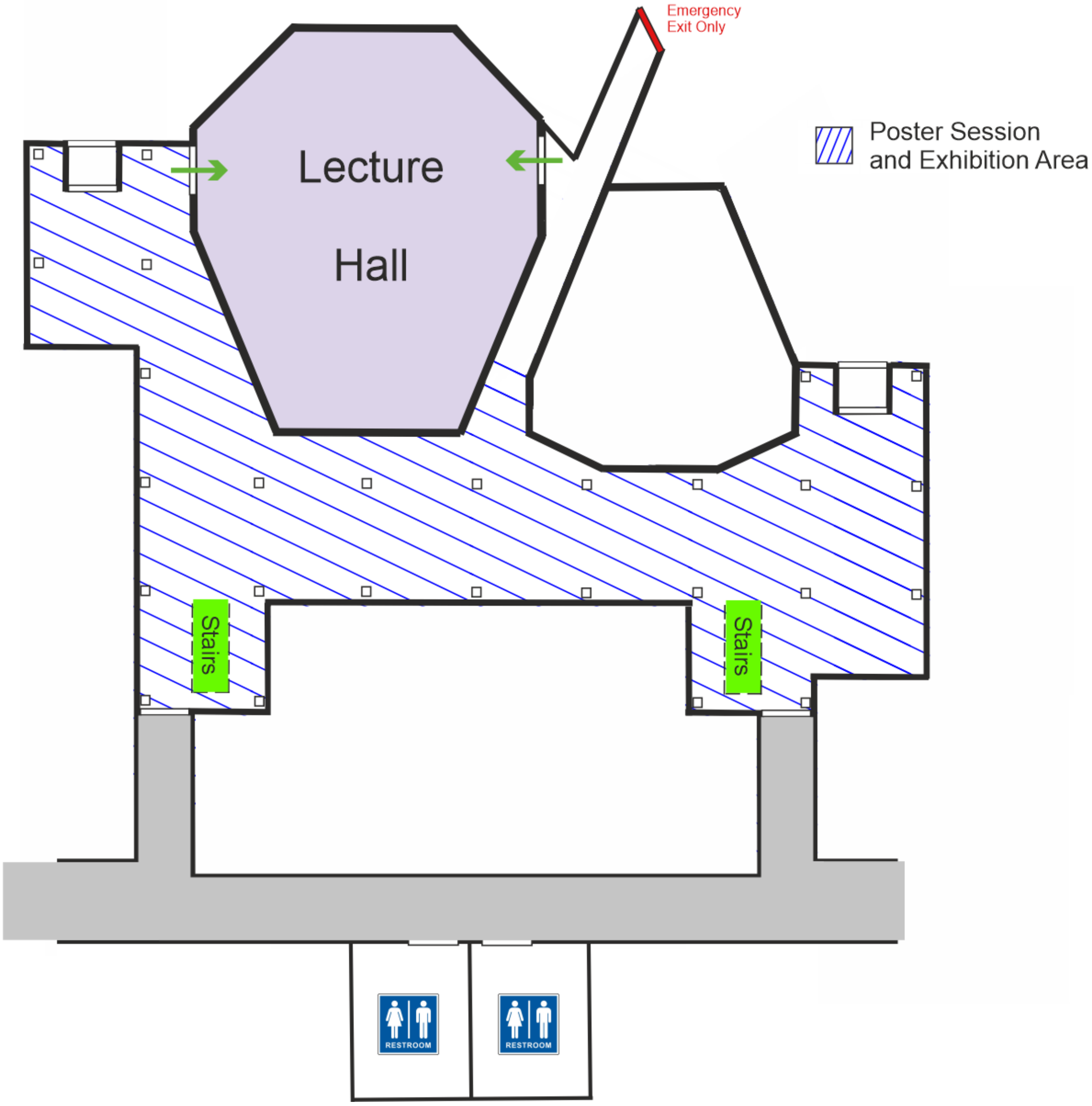
Near to the venue is the bus stop “Coesfelder Kreuz”. It is served by the urban bus lines 1, 2, 5, 11, 12 and the regional bus line R63.

The dinner takes place in the Mensa am Ring, next to the bus stop “Coesfelder Kreuz” and the parking garage.

Ground Floor



First Floor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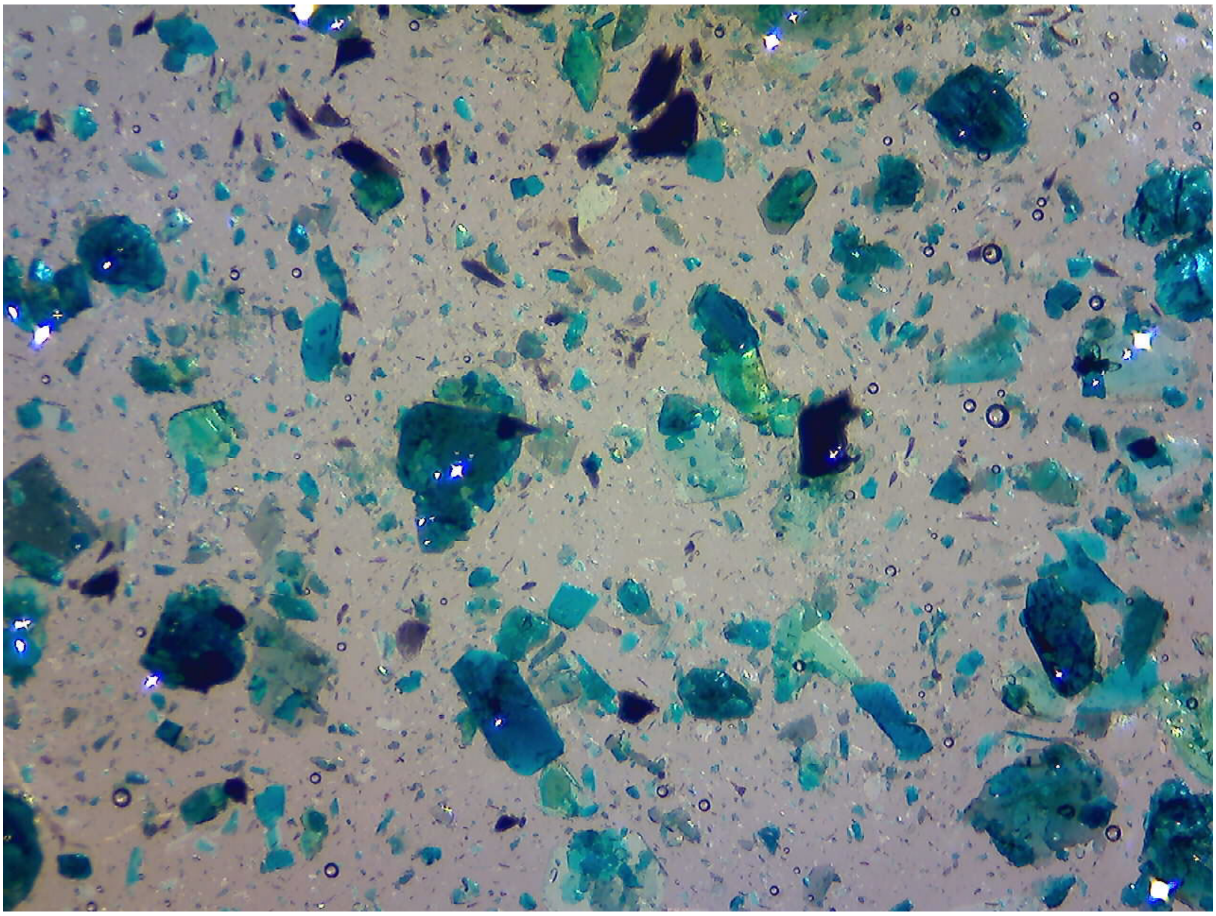
RESTROOM

Scientific Programme



Monday, 24.02.2025

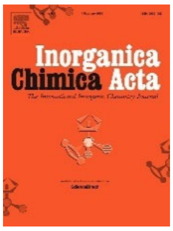
11:00 – 12:45		**Arrival & Registration**
12:45 – 13:00		**Welcome by the Organizers**
13:00 – 14:30		**1st Session “Photochemistry I / Supramolecular Chemistry”** **Chair: Dominik Moreth** (AK Schatzschneider, JMU Würzburg)
13:00	**O1**	**Björn Schmidt** (AK Clever, Technische Universität Dortmund) Transformation of a Lantern-shaped Tröger’s Base Pd_2L_4 Cage into a Unique Pd_4L_6 Species
13:15	**O2**	**Malavika Gamgadharan Kalarikkal** (AK Van Craen, Technische Universität Dortmund) Anion Recognition and Chiroptical Sensing with Charge-Neutral L_2Zn_2 Helicates
13:30	**O3**	**Nicole Winterholler** (AK Kreidt, Technische Universität Dortmund) Photoswitching lanthanoid luminescence with diazocines
13:45	**O4**	**Indranil Sen** (AK Steffen, Technische Universität Dortmund) Conformation Dependent Emission and Circularly Polarized TADF in Linear CDP Copper(I) Complexes
14:00	**O5**	**Maximilian Henning** (AK Bauer, Universität Paderborn) Low-Temperature Emission of Cyclometalated Cobalt(III) Complexes Linked to Organic Chromophores
14:15	**O6**	**Liliana Capulín Flores** (AK Klein, Rijksuniversiteit Groningen) Light-driven oxidation of weak X-H bonds by a dinuclear Au(II) carboxylate complex
14:30 – 15:00		**Coffee Break**
15:00 – 16:45		**2nd Session “Coordination Chemistry I”** **Chair: Tim Schäfer** (AK Müller, Universität Münster)
15:00	**O7**	**Peter Ferber** (AK Janiak, Heinrich-Heine-Universität Düsseldorf) Kläui ligands and their modern applications

15:15	**O8**	**Kim A. Eisenlohr** (AK Holthausen, Goethe-Universität Frankfurt) Triplet Carbenes with Transition-Metal Substituents
15:30	**O9**	**Tim Hieke** (AK Rentschler, Johannes Gutenberg-Universität Mainz) Valence Tautomeric Transitions of Dinuclear Cobalt Complexes with an Innocent Bridging Ligand
15:45	**O10**	**Dominik Moreth** (AK Schatzschneider, Julius-Maximilians-Universität Würzburg) Inorganic click (iClick) reactions: A facile tool for metal complex functionalization
16:00	**O11**	**Meike Merz** (AK Becker, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau) Influence of Bridging Ligands on the Reactivity of Multinuclear Copper Complexes
16:15	**O12**	**Polina Klypina** (AK Burzlaff, Friedrich-Alexander-Universität Erlangen-Nürnberg) Homoleptic Complexes of Bis(4-carboxylpyrazol-1-yl)acetic acid: A new building unit for MOFs
16:30	**O13**	**Sören Jansen** (AK Glaser, Universität Bielefeld) Generation and Reactivity of $Fe^{III}Fe^{III}$ Peroxo Complexes with Dinucleating Ligands
16:45 – 17:15		**Coffee Break**
17:15 – 18:45		**3rd Session “Small Molecule Activation / Photochemistry II”** **Chair: Sandipan Maji** (AK Schneider, Universität Göttingen)
17:15	**O14**	**Katharina Oelschlegel** (AK Schneider, Georg-August-Universität Göttingen) Photochemical Dinitrogen Functionalization
17:30	**O15**	**Jannis Barrera** (AK Limberg, Humboldt-Universität zu Berlin) Insights into the Reactivity of Mononuclear Copper Complexes towards O_2 and H_2O_2: Model Systems inspired on LPMO Active Sites

17:45	**O16**	**Sandra Anila Nair** (AK Rau, Universität Ulm) Tuning the photophysical properties of π-extended Cu-bibenzimidazole complexes
18:00	**O17**	**Sandra Kronenberger** (AK Heinze, Johannes Gutenberg-Universität Mainz) Novel Manganese(I) Complex with a 190 ns metal-to-ligand Charge Transfer Lifetime and Luminescence
18:15	**O18**	**Bruno Lazarevski** (AK Wenger, Universität Basel) Steric Control Over Excited-State Behaviour in Nickel(II) Complexes
18:30	**O19**	**Luise Thomisch** (AK Schulz, Friedrich-Schiller-Universität Jena) Photodriven charge accumulation on Cu(I) 4*H*-imidazolate complexes
18:45 – 20:15		**Poster session (odd numbers) & Get Together**

Tuesday, 25.02.2025

9:00 – 10:30		**4th Session “Coordination Chemistry II”** **Chair: Silene Engbers** (AK Klein, Rijksuniversiteit Groningen)
9:00	**O20**	**Aroua Aouina** (AK Liebing, Friedrich-Schiller-Universität Jena) Chiral heterobimetallic complexes with the $[Ni(SSC\text{-}LPro)_2]_2$– metalloligand (LPro = L-prolinate)
9:15	**O21**	**Julianna S. Doll** (AK Rosca, Ruprecht-Karls-Universität Heidelberg) PNN-based cobalt alkyl complexes: to eliminate, or not to eliminate
9:30	**O22**	**Paula Epure** (AK Werncke, Philipps-Universität Marburg) Dinuclear Imido Complexes of Iron and Cobalt
9:45	**O23**	**Janis Härich**, (AK Ray, Humboldt-Universität zu Berlin) Liquid-Phase Studies of Iron Coordination Complexes supported by Amide based tridentate Ligand Systems

10:00	**O24**	**Maximilian Widmann** (AK Scheer, Universität Regensburg) Nucleophilic Functionalization of a Cationic Pentaphosphole Ligand – A Systematic Study of Reactivity
10:15	**O25**	**Tim Wünscher** (AK Plass, Friedrich-Schiller-Universität Jena) ^{95}Mo-NMR of a molybdenum peroxide complex
10:30 – 11:15		**Coffee Break** **sponsored by:** 
11:15 – 12:45		**5th Session "Catalysis I"** **Chair: Jesvita Cardozo** (AK Braun, Humboldt-Universität zu Berlin)
11:15	**O26**	**Ouchan He** (AK Braun, Humboldt-Universität zu Berlin) Platinum-Catalysed Hydrofluorination of Alkynes Promoted by a Fluoride Shuttle
11:30	**O27**	**Florian R. Neururer** (AK Hohloch, Universität Innsbruck) Mesoionic carbene complexes of group VI metals: Deoxygenation catalysis and further reactivity
11:45	**O28**	**Manh Linh Nguyen** (AK Tuczek, Christian-Albrechts-Universität zu Kiel) Dome-Shaped Complexes: An Approach to Heterogenized Homogeneous Catalysts
12:00	**O29**	**Leon Kambiz Paschai Darian** (AK Gade, Universität Heidelberg) Framing and Taming T-shaped 14 Electron Rh(I) Complexes: C-H Activation or Not?
12:15	**O30**	**Mirko Rippke** (AK Beweries, Leibniz-Institut für Katalyse e. V., Rostock) Late transition metal PN^{H}N complexes for the dehydrocoupling of amine borane adducts

12:30	**O31**	**Matthias Schmitz** (AK Kerzig, Johannes Gutenberg-Universität Mainz) Coulombic dyads as new catalyst class for efficient photocatalysis
12:45 – 14:15		**Lunch Break & PI Meeting**
14:15 – 15:45		**6th Session “Coordination Chemistry III”** **Chair: Maximilian Widmann** (AK Scheer, Universität Regensburg)
14:15	**O32**	**Anja Rehse** (AK Winter, Universität Konstanz) Valence Tautomerism in Half-Sandwich Complex Triarylmethylium Dyads
14:30	**O33**	**Benjamin Rudin** (AK Ballmann, Universität Heidelberg) 2,2’-Diphosphino- and 2,2’-Diarsenotolanes and Their Ruthenium Pincer and Carbene Complexes
14:45	**O34**	**Constantin Schreck** (AK Weber, Universität Bayreuth) Exploring magnetic and electronic coupling in coordination compounds featuring an in-plane bound TTF-moiety
15:00	**O35**	**Maximilian Schulz** (AK Himmel, Universität Heidelberg) Redox isomerism in complexes with redox-active guanidine ligands
15:15	**O36**	**Jo Komeda** (AK Ruben, Karlsruhe Institute of Technology) Switchable Magnetic Properties in a Redox-Active Bis(porphyritnato)(phthalocyaninato)-diterbium(III) Single-Molecule Magnet
15:30	**O37**	**Viktoria Rehbein** (AK Hlina, Technische Universität Graz) Azacryptand-based dinuclear rare-earth and transition metal complexes
15:45 – 16:30		**Coffee Break** **sponsored by:** BRUKER

16:30 – 17:30		**7th Session “Catalysis II”** **Chair: Viola Munzert** (AK Kunz, Eberhard-Karls-Universität Tübingen)
16:30	**O38**	**Dominik Steden** (AK Herres-Pawlis, RWTH Aachen) New Lessons from Tyrosinase Model Systems: How to Balance Conformers and their Influence on Thermal Stability and *ortho*-Hydroxylation Rates
16:45	**O39**	**Miljan Ćorović** (AK Mösch-Zanetti, Universität Graz) Tungsten Complexes for Acetylene Activation
17:00	**O40**	**Philipp D. Engel** (AK Schaub, CaRLa, Universität Heidelberg) Copper(II)-Catalyzed Amination of Aryl Chlorides in Aqueous Ammonia
17:15	**O41**	**Tobias Greven** (AK van der Vlugt, Carl von Ossietzky Universität Oldenburg) Chemical bond activation with mononuclear Rhodium-, Palladium and Platinum complexes
17:30 – 19:00		**Poster Session (even numbers)**
19:15 – 23:00		**Conference Dinner**

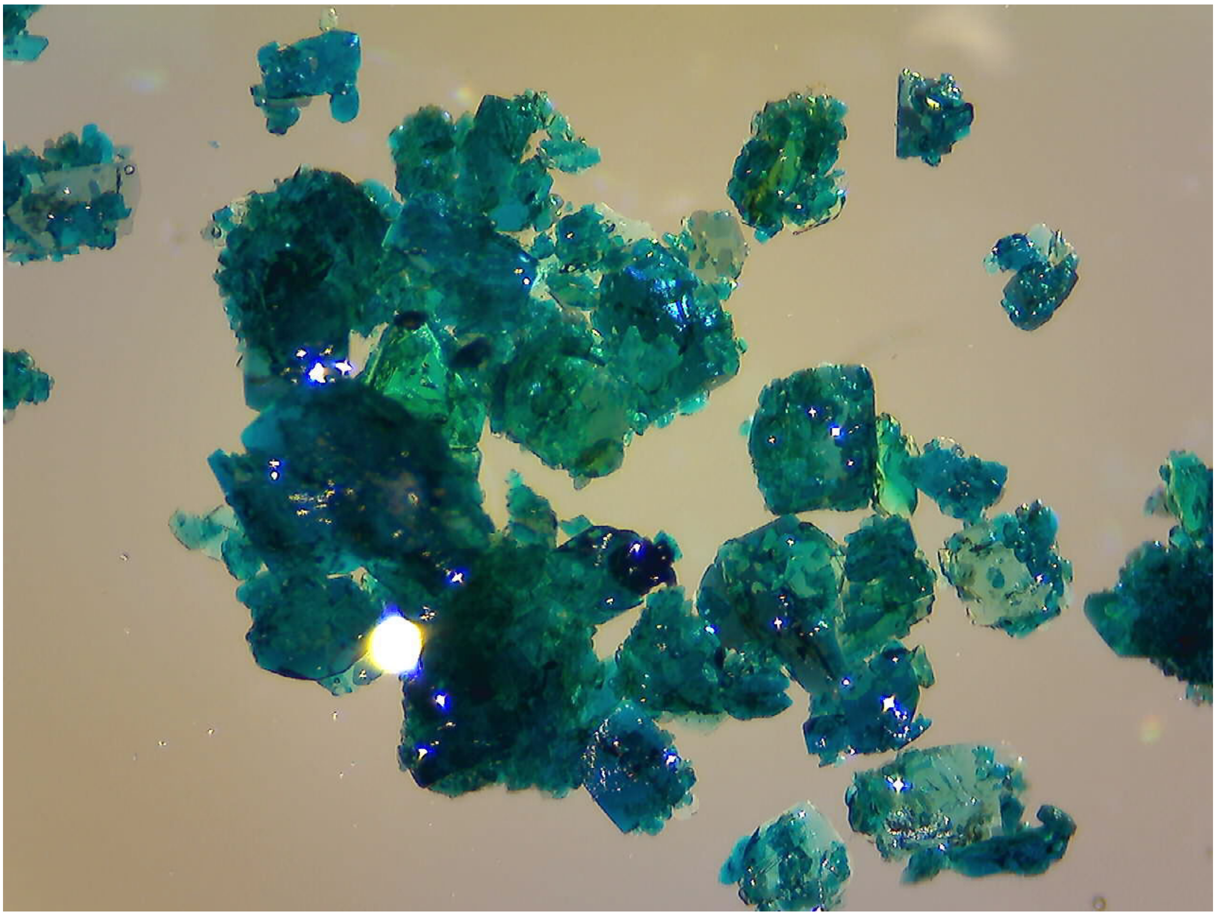
Wednesday, 26.02.2025

9:00 – 10:15		**8th Session “Bioinorganic Chemistry”** **Chair: Florian Altes** (AK Becker, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau)
9:00	**O42**	**Ioana Ciubotaru** (AK Daumann, LMU München) The Elusive Chemistry of Pyrroloquinoline Quinone Dimethyl Ester Lanthanide Complexes in Biomimetic Alcohol Oxidation
9:15	**O43**	**Kevin Keller** (AK Schindler, Justus-Liebig-Universität Gießen) Model Compounds for Cytochrome *c* Oxidase

9:30	**O44**	**Nicolas Montesdeoca** (AK Karges, Ruhr-Universität Bochum) Catalytic Production of Hydroxyl Radicals with a Co(III) Polypyridine Complex for Anticancer Therapy
9:45	**O45**	**Ibrahim Basma** (AK Weigand, Friedrich-Schiller-Universität Jena) Hydrogen Evolution through a photoactive [FeFe]-Hydrogenase Mediator using Visible Light
10:00	**O46**	**Sebastian Günther** (AK Bröring, Technische Universität Braunschweig) Characterising Products of Light-Induced Oxidation of A_2B-Corroles using ^{109}Ag-NMR
10:15 – 10:45		**Coffee Break** **sponsored by:** Carbolution finest chemicals.
10:45 – 12:00		**9th Session "Coordination Chemistry IV"** **Chair: Victoria Müller** (AK Schatzschneider, Julius-Maximilians-Universität Würzburg)
10:45	**O47**	**Sotirios Pavlidis** (AK Abbenseth, Humboldt-Universität zu Berlin) T-Shaped Bismuth Complexes: Transition Metal-like Reactivity and Stabilization of Exotic Radical Species
11:00	**O48**	**Kevin Schwitalla** (AK Beckhaus, Carl von Ossietzky Universität Oldenburg) Tuning Lewis Acidity: Design of FLP-like Titanium Complexes with Pyridine-based Ligands
11:15	**O49**	**Lars Burmeister** (AK Tschierlei, Technische Universität Braunschweig) Three-Coordinate Cu(I) Complexes with an N-Heterocyclic Carbene Carrying a Weakly Coordinating Tris(pentafluorophenyl)borate Anion
11:30	**O50**	**Alok Mahata** (AK Sarkar, Universität Stuttgart) Tuning Spectro-electrochemical Properties of Thiele's Hydrocarbon Derivatives using Acid or Transition Metal Coordination

11:45	**O51**	**Leo Wessel** (AK Tamm, Technische Universität Braunschweig) Is „5” the new „6“? Amino-Imidazolin-2-imine vs. *β*-Diketimine Ligands
12:00 – 12:30		**Organizer´s Farewell, Voting & Awards**

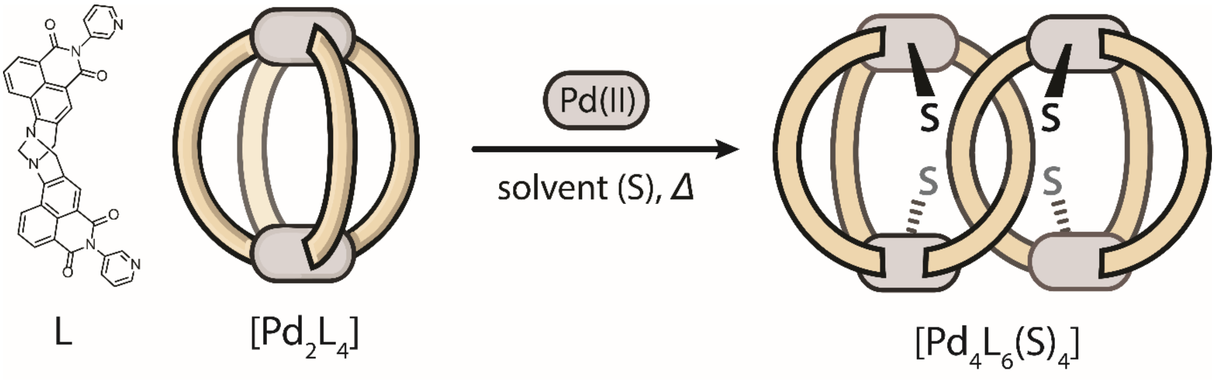
Abstracts
Oral Contributions



Transformation of a Lantern-shaped Tröger’s Base Pd_2L_4 Cage into a Unique Pd_4L_6 Species

B. Schmidt, E. Benchimol, H. M. O’Connor, T. Gunnlaugssonn, and G. H. Clever*
Dept. of Chemistry and Chemical Biology, TU Dortmund, bjoern4.schmidt@tu-dortmund.de

In nature, functionalized binding pockets can be found in receptors and enzymes for specific substrates.[1] In order to improve our understanding of their recognition properties, a broad range of artificial supramolecular systems can be created.[2] Among them, coordination cages are formed by combining organic ligands with metal ions such as Pd(II) suitable to mimic the substrate binding.[3] Recently, our group reported a new chiral Pd_2L_4 lantern-shaped coordination cage based on a Tröger’s base moiety, capable of encapsulating anionic guests and neutral molecules like polyaromatic hydrocarbons or natural products due to the enclosed cavity. Most interestingly, chirality transfer from this host to encapsulated C_{60} and C_{70} fullerenes could be shown.[4] During further investigations of the properties of the Pd_2L_4 cage, we encountered an intriguing phenomenon. In presence of excess Pd(II) and after heating, the transformation of the Pd_2L_4 cage into a new Pd_4L_6 species can be observed and confirmed by ESI-MS. Hereby, four free coordination sites at the palladium are occupied by solvent molecules, which lead to many possible isomers that are difficult to differentiate by NMR spectroscopy. Crystallization finally reveals a new catenane-like structure where two Pd_2L_3 coordination bowls are interlocked.



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[1] C. Koshla, P. B. Harbury, *Nature* **2001**, *409*, 247-252.
[2] M. J. Wiester, P. A. Ulmann, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2011**, 50, 114-137.
[3] S. Pullen, J. Tessarolo, G. H. Clever, *Chem. Sci.* **2021**, *12*, 7269-7293.
[4] E. Benchimol, H. M. O’Connor, B. Schmidt, N. Bogo, J. J. Holstein, J. I. Lovitt, S. Shanmugaraju, C. J. Stein, T. Gunnlaugsson, G. H. Clever, *Angew. Chem. Int. Ed.* **2024**, e202421137.

Anion Recognition and Chiroptical Sensing with Charge-Neutral L_2Zn_2 Helicates

Malavika G. Kalarikkal, David Van Craen*
Department of Chemistry and Chemical Biology, TU Dortmund University, 44227 Dortmund, Germany
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Anion recognition chemistry plays a fundamental role in supramolecular chemistry, with the key objective to develop receptors capable of selectively binding anions, particularly in competitive media. The field of anion recognition has been significantly advanced by the development of our charge-neutral, double-stranded zinc(II) helicates equipped to achieve high-affinity binding of environmentally and biologically relevant dicarboxylates. The hydroxyquinoline-based L_2Zn_2 helicate features exceptional binding constants exceeding 10^8 M^{-1} on selectively binding dicarboxylate anions at nanomolar concentrations. This helicate bridges the gap between traditional organic and metal-assembled receptors, offering a stable, charge-neutral platform free from counteranion interference.[1]
Building on this high-affinity anion recognition, we explored the chiroptical properties of these zinc(II) helicates, incorporating stereodynamic triazole ligands that can rotate and form either meso structures or racemic mixtures of right- and left-handed complexes. Upon recognition of chiral mono- or dicarboxylates, these helicates exhibit distinct circular dichroism responses, enabling accurate chirality analysis and enantiomeric excess determination. Notably, tartrate binding enriches one of the enantiomers of the racemic helicate, leading to clear Cotton effects in the CD spectrum.[2] This receptor-based approach provides high-throughput screening capabilities with minimal waste production, presenting a promising alternative to chromatographic techniques relying on chiral stationary phases.

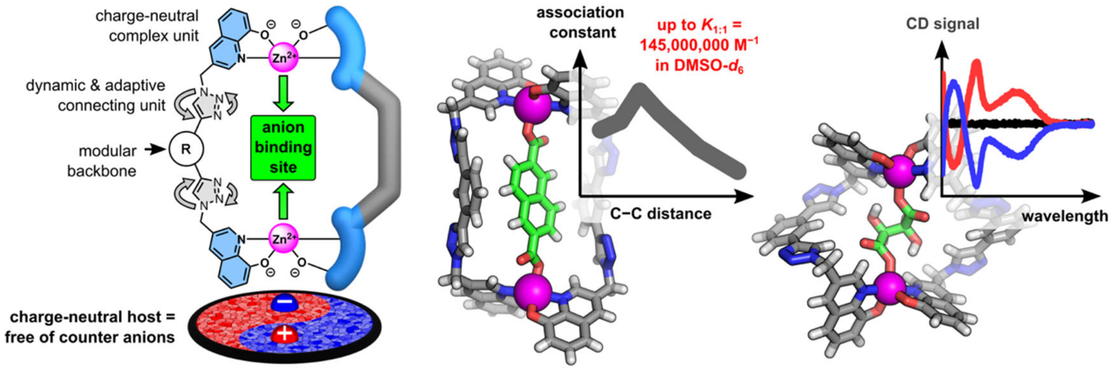

Figure 1. Design principle of the charge-neutral double stranded Zn(II) helicate, size selective binding of dicarboxylates and chiroptical recognition of D-(−)/L-(+) tartrate by CD spectroscopy

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[1] D. Van Craen, M. G. Kalarikkal, and J. J. Holstein, J. Am. Chem.Soc. 2022, 144, 18135-18143.
[2] M. G. Kalarikkal, C. Drechsler, G. Tusha, L.V. Schäfer, D. Van Craen, Chem. Eur. J. 2023, 29, e202301613. 18135-18143.

Photoswitching lanthanoid luminescence with diazocines

N. Winterholler, E. Kreidt*
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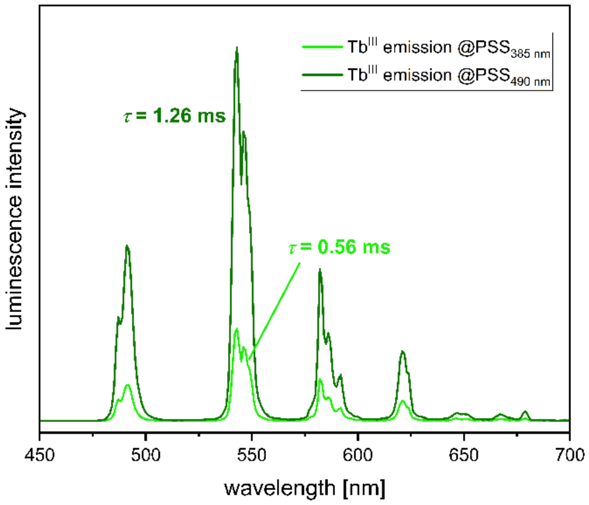
The photophysical properties of the lanthanoids are defined by their narrow and fingerprint like emission bands, which makes them especially suitable for elaborate applications ranging from bioimaging[1] over anti-counterfeiting to information storage[2]. The combination of lanthanoid ions with stimuli responsive molecules like photoswitches has the potential to unlock new layers of complexity to such applications and promises the development of new smart materials. Such materials alter their properties reversibly upon irradiation with light of wavelengths that triggers the switching process of the photoswitch. While some systems with lanthanoids and photoswitches were already described, there are no examples with more than two lanthanoids which are being photoswitchable with the same system.[3] As we were recently able to show, diazocines[5] are an alternative photoswitch scaffold with high potential for this purpose. Diazocines can be switched within the visible range of the electromagnetic spectrum and with high switching efficiency. In simple systems containing unfunctionalised diazocine and dipicolinic acid anions as antenna for indirect sensitisation, we could photoswitch the luminescence intensities of Eu^{III}, Tb^{III}, Dy^{III} as well as Yb^{III} by up to 87%. Eu^{III} and Tb^{III} luminescence lifetimes of the more luminescent states remained in the millisecond range, with a switching effect of up to 1 ms (79%). Furthermore, the combination of the lanthanoids Eu^{III}, Tb^{III} and Dy^{III} has the potential for visible light luminescence and lifetime multiplexing.



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Conformation Dependent Emission and Circularly Polarized TADF in Linear CDP Copper(I) Complexes

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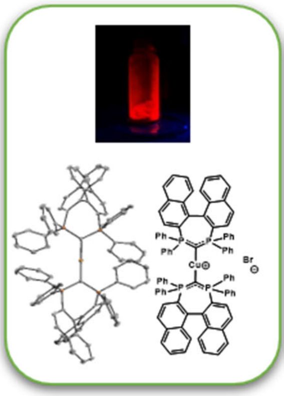
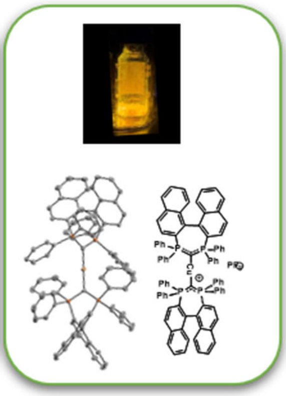
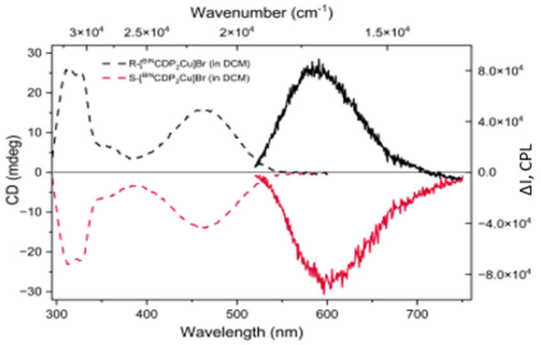
Chiral organometallic charge transfer complexes have great potential nowadays and practical applications of circularly polarized organic light emitting diodes (CP-OLEDs).[1] For this reason, the synthesis of racemic and chiral homoleptic copper (I) complexes supported by racemic and chiral ^{BIN}CDP (Carbodiphosphorane) ligand with binaphthyl ring in the backbone is described.[2] Depending on the conformation, which determines the MLCT emission energies and thermally activated delayed fluorescence (TADF) efficiencies as well as the energy gap between singlet and triplet (ΔE_{ST}), $[Cu(^{BIN}CDP)_2]X$ {X – Br and PF_6} are showing orange to deep red emission ranging from 605 to 715 nm in solution, powders, and rigid polystyrene film. In comparison with $[Cu(^{Me}cAAC_2)]PF_6$, which exhibits blue phosphorescence (λ_{em} = 398 nm), the homoleptic ^{BIN}CDP copper(I) complexes clearly show TADF behavior.[3] The design motif leads to the first homoleptic linear MLCT complex with conformation dependent emission with a radiative rate constant of 7×10^4 s^{-1} in solution state and remarkable dissymmetry factor $g_{lum} = \pm1.5 \times 10^{-2}$ in polystyrene film.







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Low-Temperature Emission of Cyclometalated Cobalt(III) Complexes Linked to Organic Chromophores

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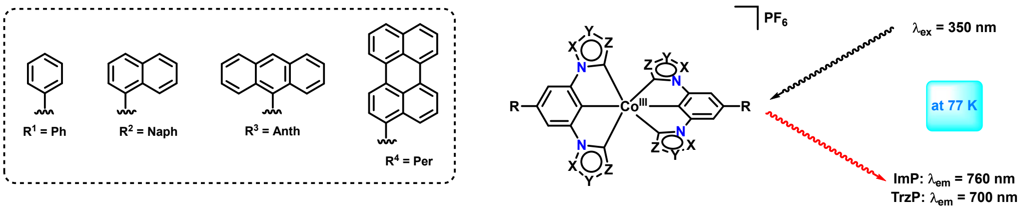
With the aim of developing new sustainable strategies that reduce the use of fossil fuels, one approach uses photosensitisers which are excited by light absorption and subsequently trigger chemical reactions.[1] These photosensitisers are predominantly based on ruthenium, osmium and iridium. However, owing to their rarity in earth's crust, high costs are associated with them. Thus, this work focuses on synthesising photoactive complexes based on cobalt, which is more common and hence less expensive.[2] Due to the weak ligand field splitting of 3d metal-based complexes, the excited-state lifetimes are intrinsically short because metal-centred (MC) states allow for rapid deactivation. This is why i) the bichromophoric approach is introduced to prolong lifetimes of excited states by establishing an equilibrium between the triplet state of the chromophore and an emissive triplet metal-to-ligand charge transfer (MLCT) state, and ii) strong σ donor ligands coordinate the metal centre to increase the ligand field splitting which destabilises MC states.[3,4] Accordingly, two series of cyclometalated cobalt complexes with imidazole- and triazole-based carbenes were synthesised (Fig. 1). These complexes exhibit low-temperature emission originating from a ^{3}MC state. Depending on the type of carbene, the emission is observed in a range of 700 – 760 nm. While these results are already promising, further spectroscopic characterisation is required to fully understand the excited state dynamics.



$[Co(ImP^R)_2]PF_6$: X, Y = CH; Z = NCH_3
$[Co(TrzP^R)_2]PF_6$: X = N; Y = NCH_3; Z = $C(CH_2)_2CH_3$

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Light-driven oxidation of weak X-H bonds by a dinuclear Au(II) carboxylate complex

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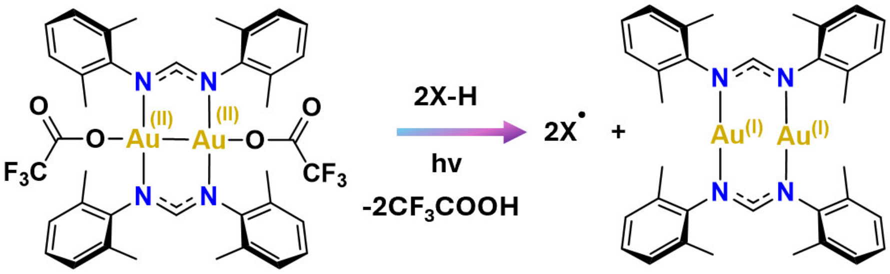
Complexes of the coinage metals featuring the [M-O] core have shown promising behavior as oxidants of weak X-H bonds (X = O, C(sp^3)) via proton-coupled electron transfer mechanisms (PCET).[1]-[3] For instance, mononuclear Cu(III) species supporting this core, were found to exhibit divergent reactivity in the activation of the X-H bonds in phenolic derivatives and hydrocarbons depending on the nature of the *O*-ligand bound to the metal center.[4]-[6] For its heavier congener, gold, similar reactivity with the same substrates has been reported when hydroxy ligands are employed as *O*-donors.[7]-[8] We recently studied the influence of the metal-metal covalent interactions in these oxidations when a bimetallic Au(II)-hydroxo complex featuring a formamidinate ligand is used as the oxidant and found that via metal-metal valence tautomerism, PCET reactivity is triggered.[9] In our quest for understanding the factors that govern PCET-type reactions for gold complexes, we prepared the corresponding dinuclear Au(II) carboxylate analogs and explored their photoreactivity towards the oxidation of phenols and hydrocarbons.



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Kläui ligands and their modern applications

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Cerium(IV) complexes with the Kläui tripod ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OR)_2\}_3]^-$ (L_{OR}^-) are of interest for their electro- [1] and cluster- [2] chemistry as well as their catalytic properties [3]. Here we focus on the less-developed R = Me derivative L_{OMe}^-. Reaction of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$ with NaL_{OMe} resulted in the complex $[Ce^{IV}(L_{OMe})_2(NO_3)_2]$. From $H_2CeCl_6(EGDME)_3$ (ethylene glycol dimethylether) and NaL_{OMe} the coordination polymer 1D-$[Ce^{III}Cl_2L_{OMe}(H_2O)_3]$ (Figure 1) and the complex $[Ce^{IV}Cl_2(L_{OMe})_2]\cdot$acetone were obtained. All crystallize in non-centrosymmetric space groups due the inherent distortion in the Kläui ligand. Compounds $[Ce^{IV}(L_{OMe})_2(NO_3)_2]$ and 1D-$[Ce^{III}Cl_2L_{OMe}(H_2O)_3]$ are active catalysts in the aerobic oxidation of the alkylbenzenes cumene, 1,3-diisopropylbenzene and 1,3,5-triisopropylbenze at temperatures up to 100 °C. The reduction potential for $[Ce^{IV}(L_{OMe})_2(NO_3)_2]$ in acetonitrile was 0.47 V vs Fc^+/Fc.

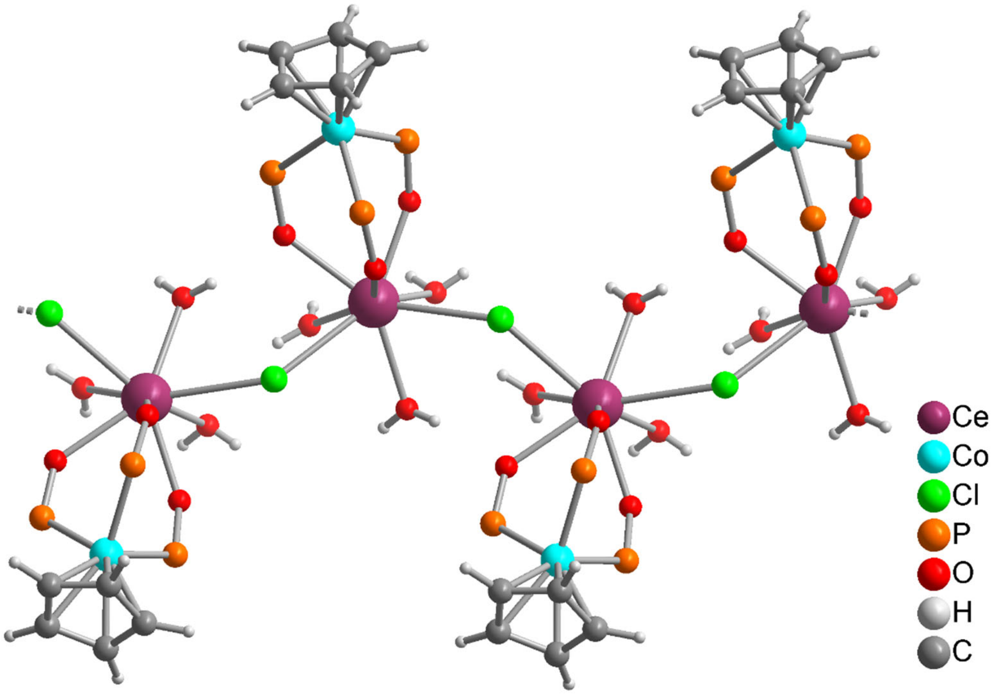

Figure 1. Section of the chain structure of 1D-$[Ce^{III}Cl_2L_{OMe}(H_2O)_3]$. The two OMe groups on each of the phosphorus atoms of the Kläui ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OMe)_2\}_3]^-$ have been omitted for clarity.

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Triplet Carbenes with Transition-Metal Substituents

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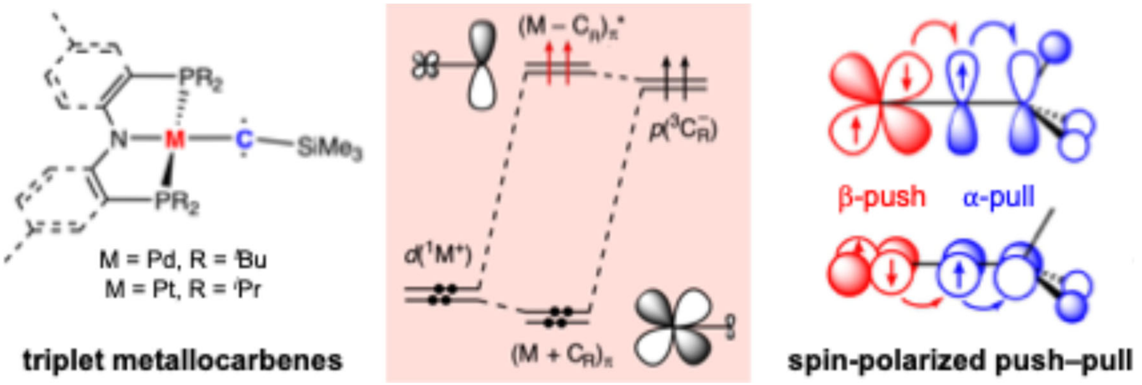

The extraordinary advances in carbene chemistry have been fuelled by strategies to stabilize the electronic singlet state via π interactions.[1,2] In contrast, the lack of similarly efficient approaches to obtain authentic triplet carbenes with appreciable lifetimes beyond cryogenic temperatures hampers their exploitation in synthesis and catalysis. Transition-metal substitution represents a potential strategy, but metallocarbenes (M–C–R) usually represent high-lying excited electronic configurations of the well-established carbyne complexes (M≡C–R). Here we report the synthesis and characterization of triplet metallocarbenes (M–C–$SiMe_3$, M = Pd^{II}, Pt^{II}) that are persistent beyond cryogenic conditions and exhibit selective reactivity towards carbene C–H insertion and carbonylation.[3] Quantum-chemical assessment by means of natural bond orbital (NBO) and natural orbitals for chemical valence (NOCV) analysis reveals significant stabilization by spin-polarized push–pull interactions along both π-bonding planes, which fundamentally differs from bonding in push–pull singlet carbenes. This bonding model, thus, expands key strategies for stabilizing the open-shell carbene electromers and closes a conceptual gap towards carbyne complexes.

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Valence Tautomeric Transitions of Dinuclear Cobalt Complexes with an Innocent Bridging Ligand

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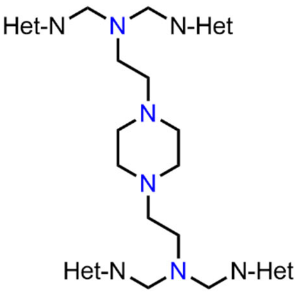
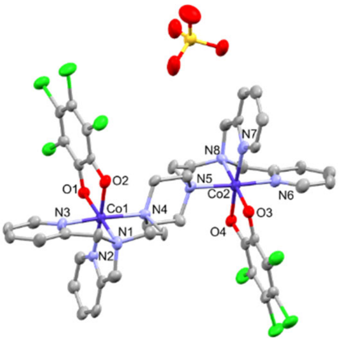
Access to reversible switching between at least two distinguishable electronic states makes multistable electromers ideal candidates for potential application in molecular electronics such as sensors, logic gates and displays.[1] Valence tautomerism (VT) is one of the lesser studied phenomena of switchable molecules. The transition occurs through an intramolecular electron transfer between an electron donating fragment (non-innocent redox-active ligand) and an electron acceptor fragment (metal centre) upon application of an external stimulus such as a change in temperature, light irradiation, or pressure.[1,2] In the case of cobalt ions being the electron acceptors, the switch is accompanied by a spin transition from LS Co(III) to the HS Co(II) state.[3] Compared to the well-studied mononuclear complexes, dinuclear complexes are of great interest because they enable access to more than two states.[4] We investigates as redox active ligands the highly electron withdrawing tetrahalogenated catecholates as well as the ditertbutyl catecholates for their VT behaviour in dinuclear cobalt complexes. The influence on different substituents on the innocent bridging ligands is studied as well.[5]





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Inorganic click (iClick) reactions: A facile tool for metal complex functionalization

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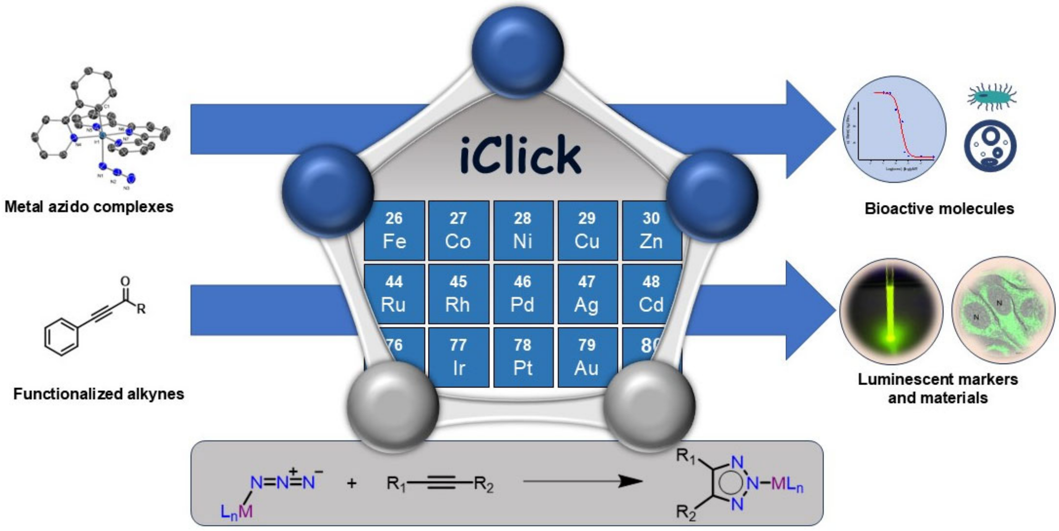
The development of "click" reactions, including the copper-catalyzed azide-alkyne cycloaddition (CuAAC) and its strain promoted variant (SPAAC),[1] has been essentially contributed to the synthesis of small molecules and bio(macro)molecule conjugates. In contrast, the inorganic click reaction ("iClick") occurring within the inner coordination sphere of a metal-azido complex with alkynes leading to stable triazolato products, has received significantly less attention. The following contribution presents a comprehensive overview on steric and electronic factors which govern the kinetics of the iClick reaction and the properties of their triazolato products, which now allow us for a systematic selection of the metal-azido and alkyne building blocks for different applications, from luminescent probes to antibacterial and anticancer drug candidates.[2-6] Highlighted examples span transition metals of the periodic table, showcasing probes synthesized via iClick with novel alkynone precursors. These examples underscore the versatility of iClick as a powerful tool for advancing coordination chemistry across diverse fields.



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Influence of Bridging Ligands on the Reactivity of Multinuclear Copper Complexes

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By combining four copper ions, we seek to prepare multinuclear copper complexes that are inspired by biocatalysts such as laccases or the N_2O reductase. A great advantage of these systems is the ability to accumulate multiple redox equivalents and furthermore, to release those equivalents simultaneously to catalyze multi-electron redox reactions.[1,2] Latest advancements have shown that μ_4-oxido copper clusters of the type $[Cu_4OX_6L_4]$ (X = halide, L = ligand or X, Figure 1, left) activate H_2O_2 to oxygenate aliphatic C-H bonds. In this case, adipic acid can be obtained from cyclohexane under moderate reaction conditions and without harmful by-products.[3,4]

Using monodentate ligands such as 4-phenylpyridine (ppy) yields discrete μ_4-oxido clusters suitable for homogeneous catalysis. For a potential application in heterogeneous catalysis, we seek to connect individual cluster units by bridging ligands to obtain coordination polymers; however, this preparation is challenging as the reaction of such clusters with bridging ligands surprisingly leads to diverse (unexpected) products. E.g., reaction of a template cluster with 4,4'-bipyridine (bipy) leads to the reduction of the copper(II) centers and subsequently, a polymeric copper(I) species (Figure 1, right). To better understand this reactivity, the corresponding reducing agent that is responsible for the formation of the copper(I) species must be found. Also, a systematic variation of the ligand systems allows us to understand the influence of the conjugated π-system of the bidentate ligands.

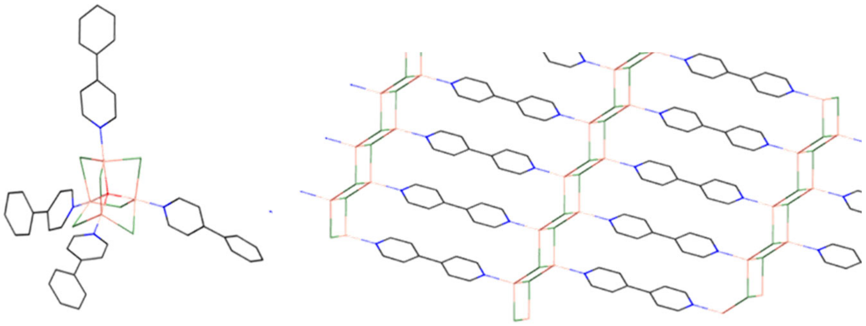

Figure 1: Molecular structure of $[Cu_4OCl_6(ppy)_4]$ (left) and $[Cu_2Cl_2(bipy)]_n$ (right).

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HOMOLEPTIC COMPLEXES OF BIS(4-CARBOXYLPYRAZOL-1-YL)ACETIC ACID: A NEW BUILDING UNIT FOR MOFS

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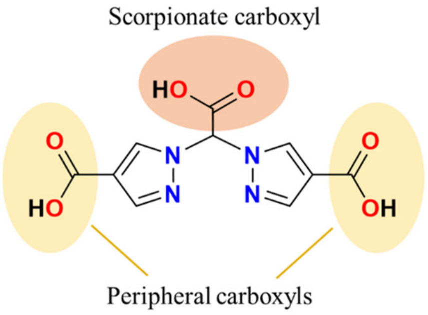
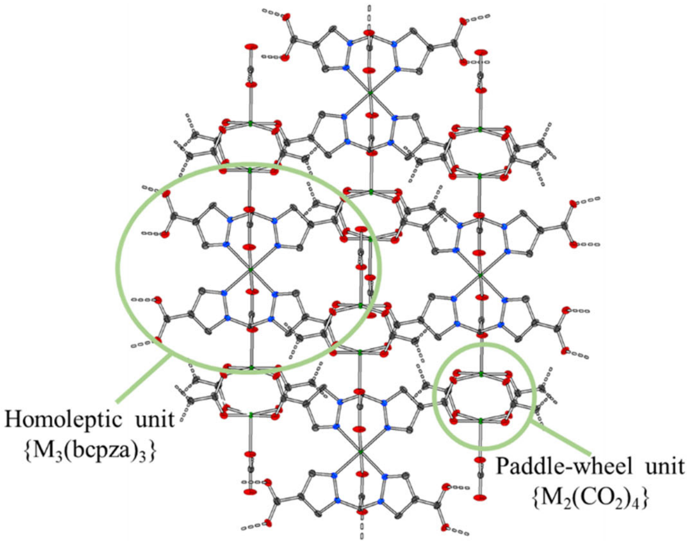
Bis(4-carboxylpyrazol-1-yl)acetic acid (H_3bcpza) ligands show new possibilities in coordination behavior due to the additional peripheral carboxylic acid groups on the pyrazoles.[1] The coordination behavior of H_3bcpza was explored upon synthesis of several homoleptic transition metal complexes of the composition [M(L)$_2$]. These homoleptic complexes [M(L)$_2$] show potential as building units for new metal-organic frameworks (MOFs) due to peripheral carboxylic acid functionalities.[2] The single crystal structure analysis revealed that such microporous materials of the composition $[M_3(bcpza)_2]_n \times 12\ H_2O$ (M = Cu) exhibit a highly regular structure comprised from essentially two building units: the homoleptic units $\{M(bcpza)_2\}$ and paddle-wheel moieties $\{M_2(CO_2)_4\}$. The MOF was studied by powder XRD, TGA and BET analyses which render the MOF suitable for such application as solar driven atmospheric water harvesting (AWH). Current work focuses on a spacer between the pyrazole and carboxylate moieties in order to vary the pore size of the MOFs.



H_3bcpza



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Generation and Reactivity of $Fe^{III}Fe^{III}$ Peroxo Complexes with Dinucleating Ligands

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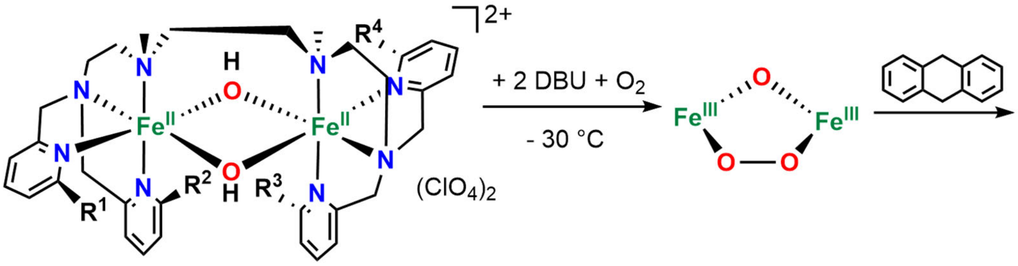
Nature uses non-heme diiron enzymes to activate C-H bonds with O_2. The catalytic cycle of these enzymes contain a $Fe^{III}Fe^{III}$ peroxo intermediate **P**.[1] To obtain more insight into the active sites and the reactivity of these O_2 activating enzymes, we have developed a dinucleating ligand system based on a tetramine backbone with varying terminal donors.[2–5] Here we report a set of ligands with differently substituted pyridine donors for the generation of $Fe^{III}Fe^{III}$ peroxo complexes to investigate the influence of substituents in the 6-position of the pyridine donors towards the stability and the reactivity of the $Fe^{III}Fe^{III}$ peroxo complexes.



$R^1 = R^2 = R^3 = R^4 = H$: susan
$R^1, R^4 = H, R^2 = R^3 = Me$: susan^{HMeHMe}
$R^1, R^2 = H, R^3 = R^4 = Me$: susan^{H_2Me_2}

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Photochemical Dinitrogen Functionalization

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The splitting of multinuclear, N_2-bridged transition metal complexes is a potential entry into synthetic nitrogen fixation that has attracted considerable interest in recent years.[1] Molecular nitrides that result from thermal N_2 splitting often suffer from low reactivity.[1] Thus, photochemical strategies are desirable that are able to drive N_2 activation and functionalization. However, compared with thermal pathways, only a small number of well-defined systems have been re-ported that undergo light-driven N_2-splitting. [1-2]

Our group reported the light-driven N–N bond scission of the N_2 bridged dirhenium complex **2** (Figure 1).[3,4] The resulting Re^V nitride **3** undergoes N-atom transfer in the presence of organic electrophiles (e.g., acid halides) upon chemical or electrochemical reduction at mild potentials.[4] Here, the light-driven use of H_2 as reductant is presented (Figure 1).

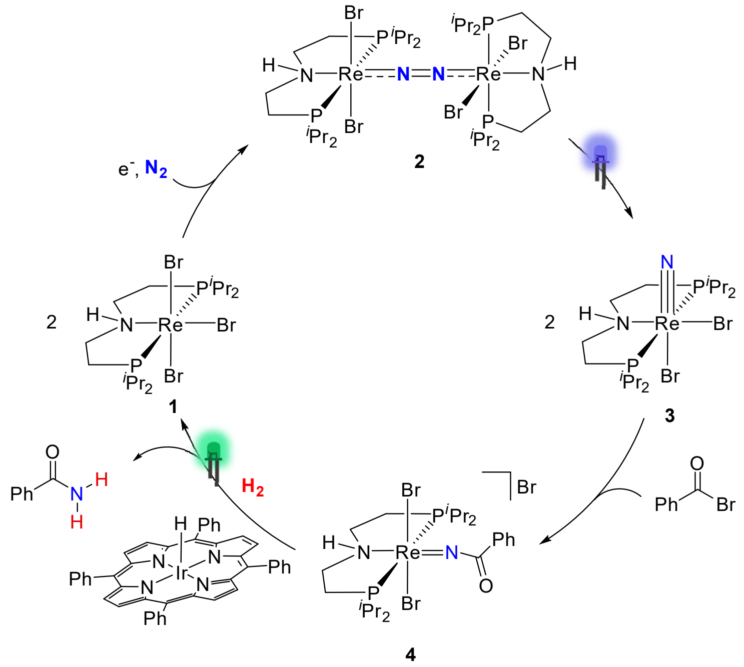

Figure 1: Photochemical N_2 functionalization to benzamide.

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Insights into the Reactivity of Mononuclear Copper Complexes towards O_2 and H_2O_2: Model Systems inspired on LPMO Active Sites

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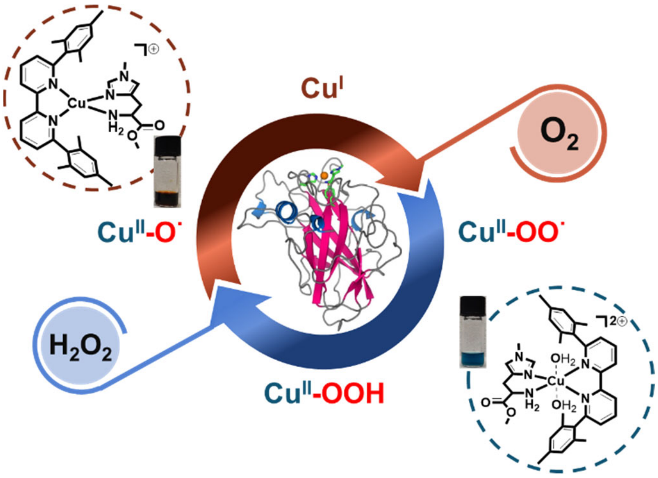
Metalloenzymes incorporating copper ions as cofactors are involved in a range of biological redox processes in which dioxygen activation emerges as a predominant enzymatic function. Within the group of mononuclear copper-containing enzymes, two prominent examples stand out given their ability to effectively oxidize inert C-H bonds at ambient conditions: particulate methane monooxygenases (pMMOs) and lytic polysaccharide monooxygenases (LPMOs). In the case of pMMOs, the active site has been a subject of discussion over the last years in view of the presence of four different copper binding sites.[1,2] In the second case, the oxidative reactivity is known to be promoted by a mononuclear copper center featuring the so-called histidine-brace.[3] The point of debate centers more recently on the capability of LPMOs to exhibit peroxygenase activity, leading attention to the use of hydrogen peroxide as active oxidant instead of dioxygen. However, the mechanisms by which LPMOs perform monooxygenase or peroxygenase activity are still under debate.[4,5]

In an effort to develop new model complexes with potential relevance for biological oxidation processes, we present here our investigations on copper(I) and copper(II) complexes inspired by the active site of LPMOs, including the reactivity of these models towards dioxygen and hydrogen peroxide, which ultimately serve as oxidants for catalytic oxidation reactions.



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Tuning the photophysical properties of π-extended Cu-bibenzimidazole complexes

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In this study, we focus on the synthesis, structural characterization, and photophysical studies of novel heteroleptic Cu(I) complexes containing bibenzimidazole (bbim) and Xantphos ligands, with the aim of advancing sustainable photocatalytic materials. Copper, as an earth-abundant and cost-effective alternative to precious metals, offers tunable redox and luminescence properties, making it an ideal candidate for photochemical applications. Through strategic ligand modifications, including π-system extension in bbim derivatives, significant bathochromic shifts in absorption spectra were achieved, enhancing visible light utilization. The modified bbim ligands were synthesized via Negishi coupling and the Cu complexes were prepared using conventional one-pot-synthesis, with X-ray crystallography confirming their structural integrity and hydrogen-bonding interactions. Photophysical analysis, including UV-Vis absorption and emission spectroscopy, revealed strong correlations between ligand structure and photophysical properties. Modified bbim ligands exhibited extended emission wavelengths compared to standard bbim also translating in the properties of the Cu complexes.

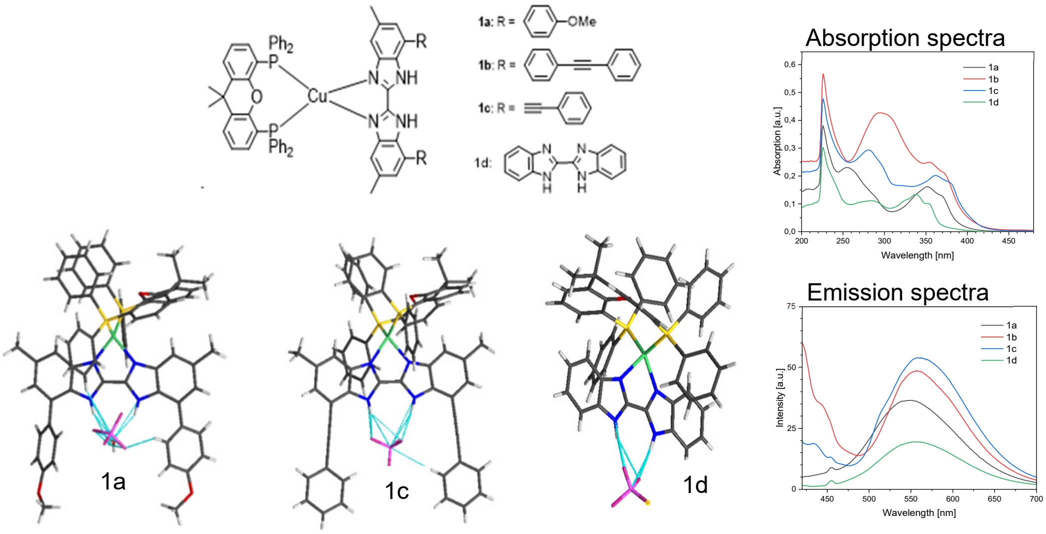

Figure 1: Novel copper-based PS with bibenzimidazole ligands, X-ray structure of different Cu(I) complexes, UV-vis and emission spectroscopic data.

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Novel Manganese(I) Complex with a 190 ns metal-to-ligand Charge Transfer Lifetime and Luminescence

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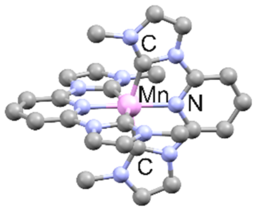
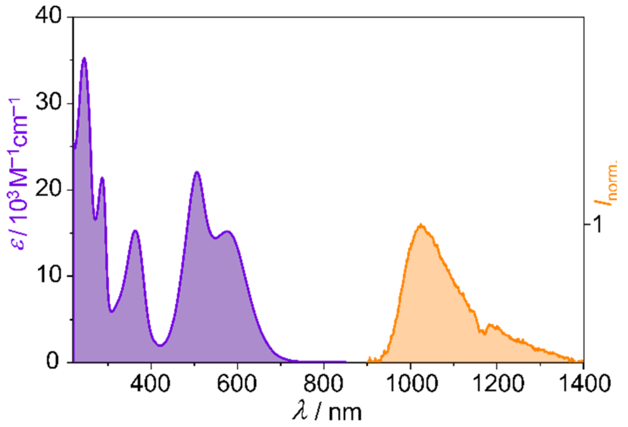
In recent decades high interest for emissive and photoactive transition metal complexes has emerged, due to their attractive properties in lighting[1] and photocatalysis[2]. Whereas precious metal complexes, such as $[Ru(bpy)_3]^{2+}$ or $Ir(ppy)_3$, have dominated this field,[3] the focus of recent investigations has shifted towards earth-abundant first-row metal centres such as manganese. [4] Precious metal complexes with the d^6 valence configuration typically exhibit luminescence from their triplet metal-to-ligand charge transfer (^{3}MLCT) excited states.[5] However, the intrinsically smaller ligand field of first-row metals causes low-lying metal centred excited states that make luminescence from the MLCT states challenging.[6] Recently the first two emissive polyisonitrile manganese(I) complexes with luminescence from the MLCT and lifetimes of 0.7 and 1.7 ns have been reported by the WENGER group.[7]



[1]$^+$



Here, we present a novel manganese(I) carbene complex **[1]$^+$**, which has been characterized via X-ray diffraction, (ns/fs-transient) absorption and emission spectroscopy. The ^{3}MLCT state of **[1]$^+$** is very long-lived and luminescent in dry solution. Experimental data has been underlined with density functional theory (DFT) calculations and time-dependent DFT calculations, allowing the assignment of electronic states and the excited state dynamics.[8]

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Steric Control Over Excited-State Behaviour in Nickel(II) Complexes

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Metal-to-ligand charge transfer (MLCT) excited states and their deactivation pathways through metal-centered (d-d) states play important roles in square planar Ni^{II} complexes.[1][2] The elongation of charge transfer excited state lifetimes could offer a new opportunity to replace the isoelectronic Pd^{II} complexes in cross-coupling catalysis and Pt^{II} compounds in light-emitting devices. Enhancing the cooperative rigidity and preventing the coordination symmetry to undergo molecular distortion is a promising strategy to counteract nonradiative excited-state decays and thus extend the MLCT lifetime.[3] Our approach is to suppress nonradiative deactivation by designing sterically more demanding tridentate scaffolds and introducing very bulky monodentate isocyanide ligands with a *m*-terphenyl backbone. For this, three novel Ni^{II} complexes were synthesized whereby the central cyclometalated phenyl unit is flanked by two coordinating *N*-heterocyclic carbenes. Additionally, different isocyanide ligands were prepared and equipped with *tert*-butyl (L1), phenyl (L2) and mesitylene (L3) moieties. The excited-state behaviour of these Ni^{II} complexes was probed via fs-TA spectroscopy and revealed that combination of a structurally rigid designed tridentate chelate with a bulky mesitylene-substituted monodentate isocyanide ligand resulted in a record-breaking twentyfold increase of the photoactive ^{3}MLCT state lifetime from roughly 50 ps to 910 ps in aerated CH_2Cl_2 at room temperature.[4] The concept of sterically well-designed *N*-heterocyclic carbene units combined with highly bulky monodentate isocyanide ligands could be a guideline for the development of ^{3}MLCT excited states beyond picosecond timescales and potentially emissive square planar Ni^{II} complexes.

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Photodriven charge accumulation on Cu(I) 4*H*-imidazolate complexes

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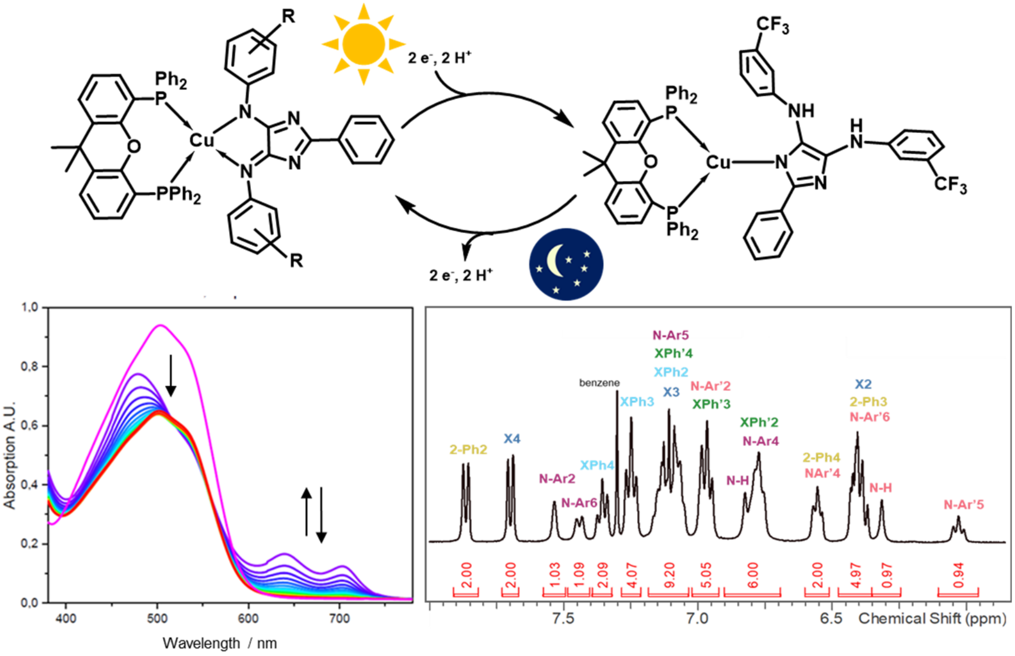
The photoactive Cu(I)4*H*-imidazolate complexes undergo a light-driven two-electron reduction in the presence of an electron and proton donor, such as DMT, BIH or BNAH. The resulting species is stable under inert conditions but releases the stored charges upon addition of an electron acceptor in a light independent process. The system therefore offers a temporal separation of the light and dark reaction. (Spectro)electrochemical investigations indicated a proton-coupled electron transfer pathway.[1]
However, the photoreduction mechanism as well as the structure of the reduced species have so far remained elusive. Systematic investigations with BIH revealed a stepwise single-electron reduction via a radical intermediate. Single crystal X-ray crystallographic studies as well as NMR studies in solution surprisingly revealed a rearrangement of the coordination environment of the metal centre from the initial tetrahedral to a trigonal geometry. The excess charges are compensated via protonation of both exocyclic nitrogen atoms. The presence of protons potentially renders the reduced Cu(I)4*H*-imidazolate complexes hydride/ hydrogen atom donors.



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Chiral heterobimetallic complexes with the $[\mathrm{Ni(SSC\text{-}LPro)_2}]^{2-}$ metalloligand (LPro = L-prolinate)

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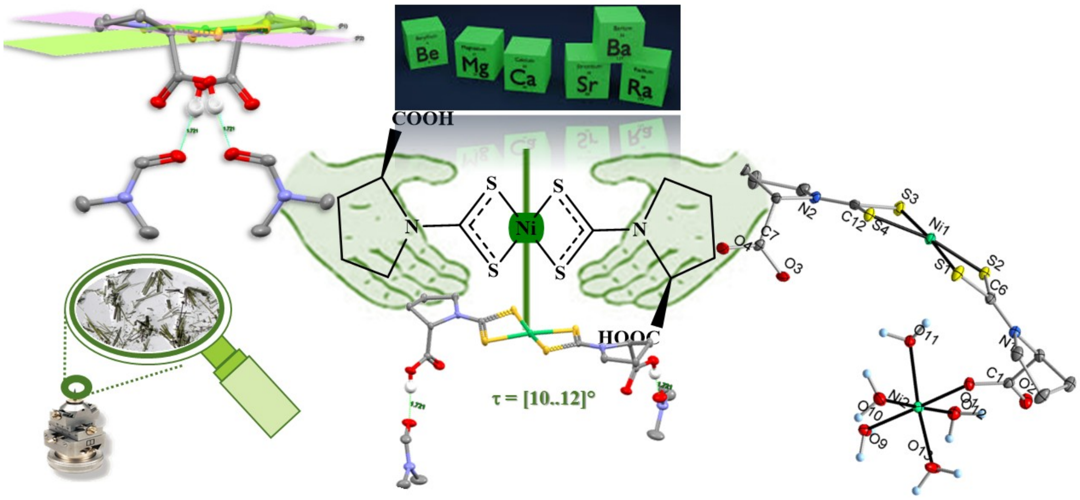
Dithiocarbamates are known for their ability to bind to metal centers through sulfur atoms, offering a wide range of electronic and structural properties that are useful in various applications.[1] Furthermore, the incorporation of carboxylate groups into these ligands enhances their potential by adding another coordination site, which can facilitate the formation of more functional metal-ligand coordination compounds.[2]

In this work, Ni is coordinated to *N*-dithioato-L-prolinate through all-sulfur tetra-coordination. [Ni (SSC-LPro)$_2$]$_2$ metalloligand is used as a building block molecule, characterized using various methods. Crystallization experiments yielded distinct complexes, including the parent carboxylic acid in DMF and coordination compounds with alkaline earth metals (Mg, Ca, Sr, Ba), as well as structurally similar Mn and Ni derivatives, where the oxophilic metal is coordinated to one oxygen atom from the carboxyl group. In all compounds, the coordination of the sulfur-bound Ni center deviates notably from planarity, with a twisting angle ~10° between the two CSS groups in the [Ni(DTC)$_2$] fragment. UV-Vis spectroscopy showed that the sulfur-coordinated Ni center undergoes exchange reactions with metal ions like Co^{2+} and Cd^{2+}.



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PNN-based cobalt alkyl complexes: to eliminate, or not to eliminate

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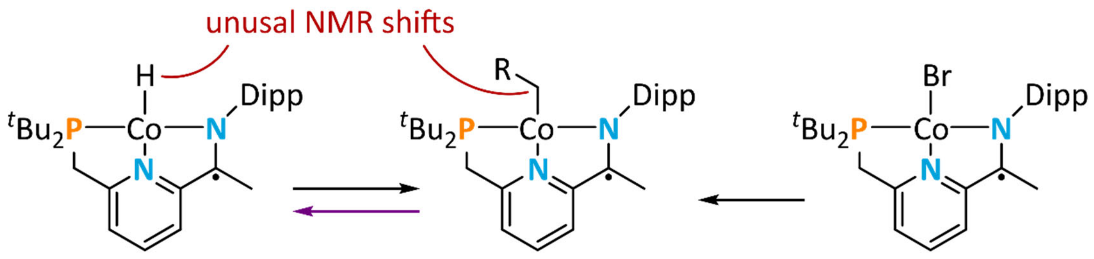
Alkyl metal complexes having a β-hydrogen and a free coordination site, cis to the alkyl fragment are prone to β-elimination, which is one of the key elementary steps in homogeneous catalysis.

When using a redox active PNN pincer ligand,[1-3] the obtained cobalt ethyl complex (**2**, R = CH_3) is however stable in solution at room temperature and under vacuum, despite its singlet ground state and meeting the prerequisites for β-hydride elimination. An elimination of ethene from the ethyl complex could be induced by the presence of carbon dioxide. In comparison, the corresponding complexes with longer alkyl chains undergo β-hydride elimination under vacuum.

Further investigation into the spectroscopic properties using NMR spectroscopy showed that the chemical shifts of the cobalt hydride (**1**) and alkyl complexes (**2**) only display minor deviations from reference diamagnetic values. Important exceptions are the chemical shifts from atoms directly bound to the cobalt center (for example Co*H* and Co*C*H_3). In comparison to the related PNP and NNN complexes these signals show an unusual upfield shift, with record values for singlet transition metal complexes.



1 **2** **3**

R = H, CH_3, C_3H_7, C_4H_{11}

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Dinuclear Imido Complexes of Iron and Cobalt

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Imido complexes of the late 3d-metals (Fe – Cu) play an important role in C–H bond amination reactions. As such the imido-metal bond is under intense scrutiny to delineate the factors that drive its reactivity and electronic structure. In this context the imido-metal bond can be regarded as rather covalent and can share imide ($[NR]^{2-}$), imidyl ($[NR]^{1-}$) as well as nitrene character ($[NR]^{0}$). This has been shown amongst other by our group for mononuclear neutral and anionic trigonal imido metal complexes in higher spin states.[1–4] Thereby, aromatic imido metal complexes are susceptible to delocalisation of unpaired electron density into the aromatic ring.

We're using this behaviour to construct binuclear complexes in which the metals are linked by the imido substituents. By this we aim at a strong electronic communication between the involved metal ions. Taking the prototypical diazidobenzene, two principal limiting electronic scenarios can be expected: On one hand that of bis(imide) based and on the other hand that it can adopt a quinoidal structure via (reversible) dearomatisation. The extent of the interaction can be potentially influenced by the size and linker type. The isolated bis-imido ligand can formally act as a $4e^-$-electron reservoir – ranging from a bis(imide) to a bis(nitrene) (Figure 1, left).

We present now our first endeavours concerning said dinuclear imido complexes. These can be obtained by reaction of linear iron(I) and cobalt(I) silylamides with different bis(azides) bearing aromatic linkers with varying linker sizes (Figure 1, right). In case of the reaction with iron(I), Mößbauer and SQUID measurements have so far supported the description of a weak antiferromagnetic coupling of the iron(II) ions via a diamagnetic bisketimido ligand while additional DFT calculations imply two iron(II) ions linked by a bis(imidyl) ligand.

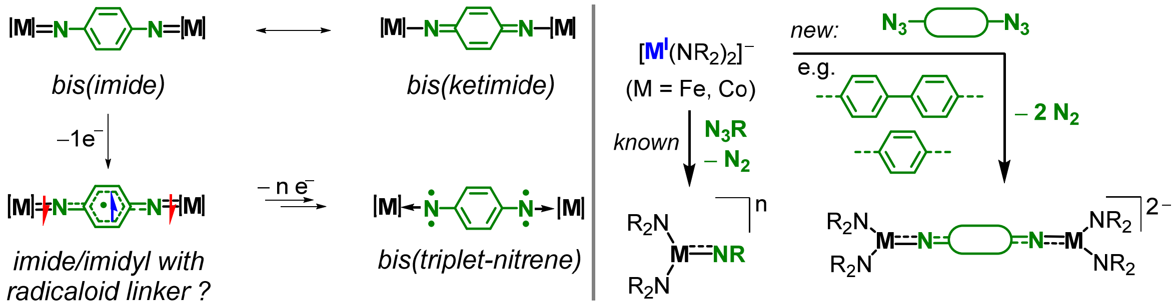

Figure 1. Possible electronic structures of bisimido linked dinuclear complex and effect of oxidation (left). Synthetic approach to dinuclear imido metal complexes (right).

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Liquid-Phase Studies of Iron Coordination Complexes supported by Amide based tridentate Ligand Systems

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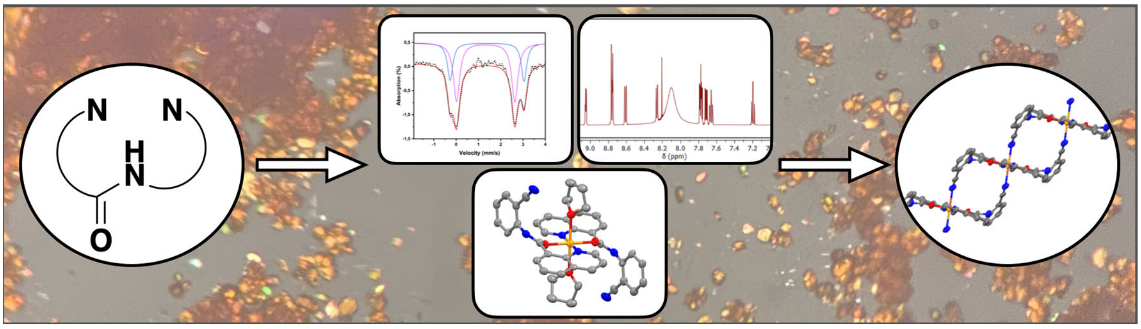
A series of tridentate amide based ligand systems were investigated with regards to their coordination behaviour in the liquid phase. Subsequent Iron Coordination complexes were studied with regards to structure, spin state and reactivity in pursuit of the first tetrahedral Iron(IV)-Oxo complex, presenting a singlet ground state in liquid phase. To our surprise, structural elucidation via SC-XRD revealed the formation of a series of octahedral Iron complexes in octahedral geometry. Further in depth spectroscopic studies in order to explore electronic structure indicated redox non-innocent ligand behaviour, resulting in a formal Iron(0) coordination polymer.



Nucleophilic Functionalization of a Cationic Pentaphosphole Ligand – A Systematic Study of Reactivity

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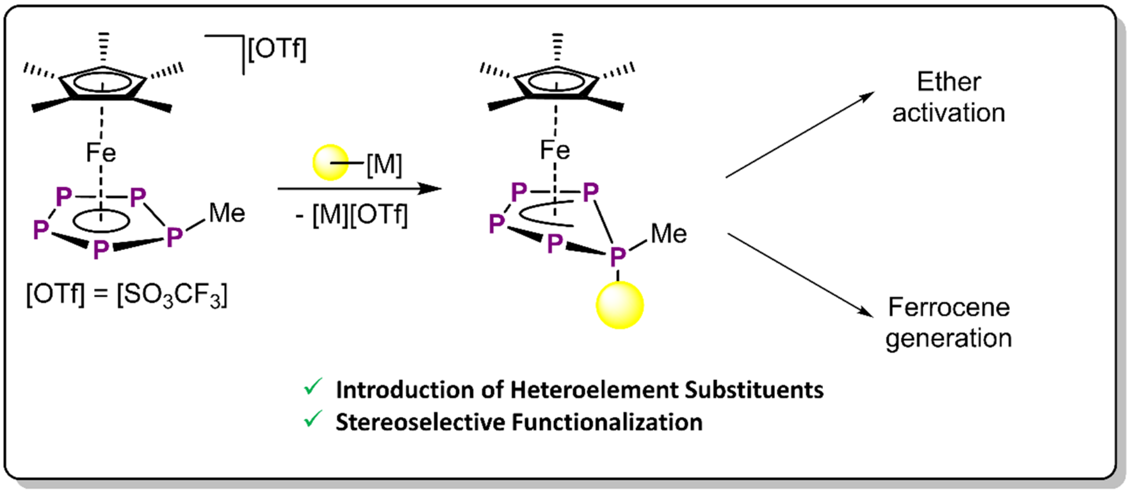
Ferrocene has merged into an essential part of modern scientific world. Valued for its exceptional properties (air stability, high temperature tolerance, soluble in nearly all common organic solvents) it has gained numerous applications within the last decades.[1] Due to its electron-rich character, several mono- or multiple-functionalized ferrocenes could be described.[1] In contrast, functionalizations of the isolobal pentamethylpentaphosphorferrocene [Cp*Fe(η^5-P_5)][2] towards diverse electrophiles[3] as well as nucleophiles[4] demonstrated the potential of single- or double functionalization. However, introducing heteroelement-substituents remains a challenging reaction pathway. This contribution examines the reactivity of cationic pentaphosphole complexes towards group 14, 16, and 17 nucleophiles. Ongoing research on such a pentaphosphole complex highlights a selective 1,1´-substitution on the *cyclo*-P_5 complex, which furthermore can be utilized for subsequent reactivity studies.



Scheme 1: Reactivity of a Cationic Pentaphosphole Complex.

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^{95}Mo-NMR of a molybdenum peroxide complex

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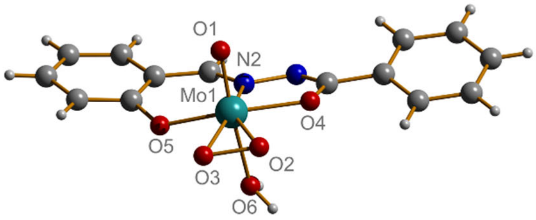
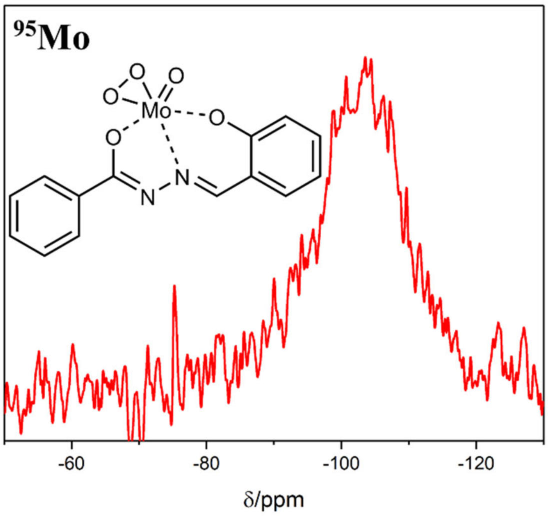
Vanadium and molybdenum are essential elements to numerous marine and terrestrial lifeforms such as algae, fungi, lichens and in case of molybdenum, even humans, where they are found in active centres of enzymes such as haloperoxidases, nitrogenases or sulphite oxidases.[1,2,3] Inspired by nature chemists have developed model complexes to better understand and mimic the reactivity of these natural enzymes. Consequently, a lot of effort has been invested in studying reaction pathways of the various catalytic cycles of both the natural enzymes and their synthetic analogues. In case of catalysts containing vanadium(V)-active sites, often utilizing ^{51}V-NMR studies[4]. The same cannot be said for most molybdenum(VI)-complexes[5] as molybdenum is far less NMR sensitive than vanadium ($R^{\mathrm{H}}(^{95}\mathrm{Mo}) = 0.000521$; $R^{\mathrm{H}}(^{51}\mathrm{V}) = 0.383$[6]) and the most studied isotope ^{95}Mo is with 16% natural abundance much rarer than ^{51}V at 99.8%. These factors combined with ^{95}Mo's quadrupole moment have made the study of molybdenum compounds of low symmetry via NMR difficult. In this presentation we report the observation of multiple C_1-symmetric molybdenum-oxo-monoperoxo complexes featuring complex organic ligands. Similar compounds are commonly proposed intermediates in catalytic cycles, for whose NMR-studies this work might present a starting point.





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Platinum-Catalysed Hydrofluorination of Alkynes Promoted by a Fluoride Shuttle

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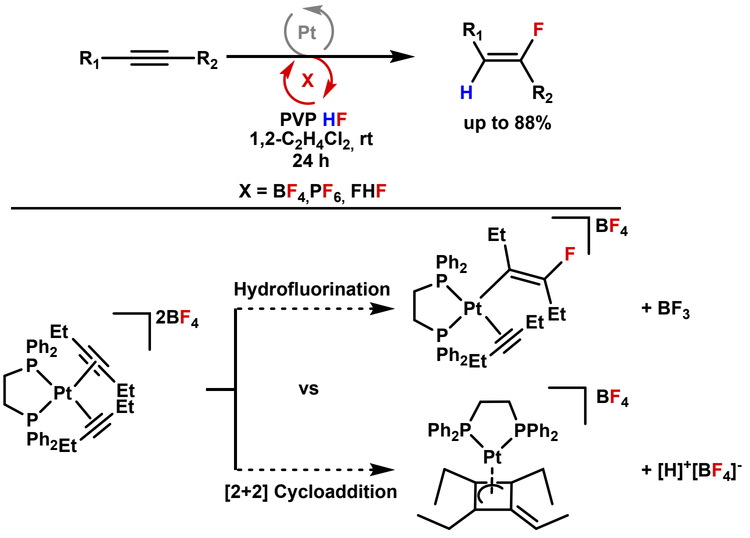
Fluoroalkenes have gained interest as a bioisoster of amide functional groups.[1,2] An efficient synthetic route to incorporate these fluorinated motifs involves the hydrofluorination of alkynes.[3] Previously we reported on the development of a platinum-catalysed process for the hydrofluorination of alkynes.[4] Herewith, we describe a hydrofluorination reaction of internal alkynes catalysed by Pt(II) dichlorido complexes conducted at room temperature. Various Pt(II) dichlorido complexes bearing chelating phosphines were synthesised and studied towards their catalytic behaviour. Mechanistic investigations revealed the involvement of a dicationic Pt(II) bisalkyne as well as a cationic *ß*-fluorovinyl Pt(II) complex in the catalytic cycle. The hydrofluorination is enabled by an outer-sphere nucleophilic attack of a perfluorinated counteranion of the dicationic Pt(II) complex demonstrating the ability of BF_3, HF as well as PF_5 acting as a fluoride shuttle which is also supported by DFT calculations. An off-cycle product was identified as a Pt(II) complex bearing an anionic cycloallyl ligand as a result of a competing [2+2] cycloaddition reaction of the Pt(II) bisalkyne complex. The catalytic hydrofluorination system can be applied to a wide substrate scope to generate fluoroalkenes bearing bulky alkyl, aryl and electron withdrawing groups, such as ester and carbonyl substituents.



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Mesoionic carbene complexes of group VI metals: Deoxygenation catalysis and further reactivity

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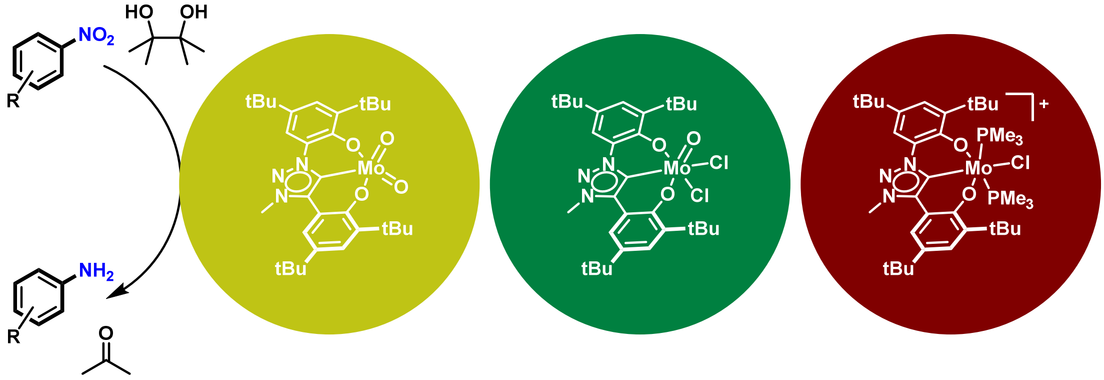
Their unique electronic and structural properties have helped mesoionic carbenes, or *N*-heterocyclic carbenes in general, stabilize high-valent metal centers and facilitate unconventional reactivities.[1,2] Due to their versatility and redox flexibility, group VI metals occupy a central role in numerous catalytic transformations.[3] Catalytic oxygen atom transfer reactions (OATR) are key areas of interest, as these processes are crucial to transforming oxygen-rich substrates into value-added products, often under mild conditions.[4] By combining group VI metals and mesoionic and *N*-heterocyclic carbenes, a series of new bis(phenolate) tethered dioxomolybdenum and -tungsten NHC and MIC complexes was developed.[5-7] These new complexes have been tested in the catalytic reduction of nitroarenes with pinacol as a sacrificial reductant, demonstrating exceptional stability and catalytic activity of the molybdenum MIC complex. Additionally, the dioxomolybdenum and -tungsten MIC complexes can be transformed into corresponding oxodichlorides, enabling access to a wide range of oxidation states in molybdenum and tungsten chemistry. This highlights the potential of molybdenum and tungsten MIC complexes for further catalytic applications or small molecule activation.



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Dome-Shaped Complexes: An Approach to Heterogenized Homogeneous Catalysts

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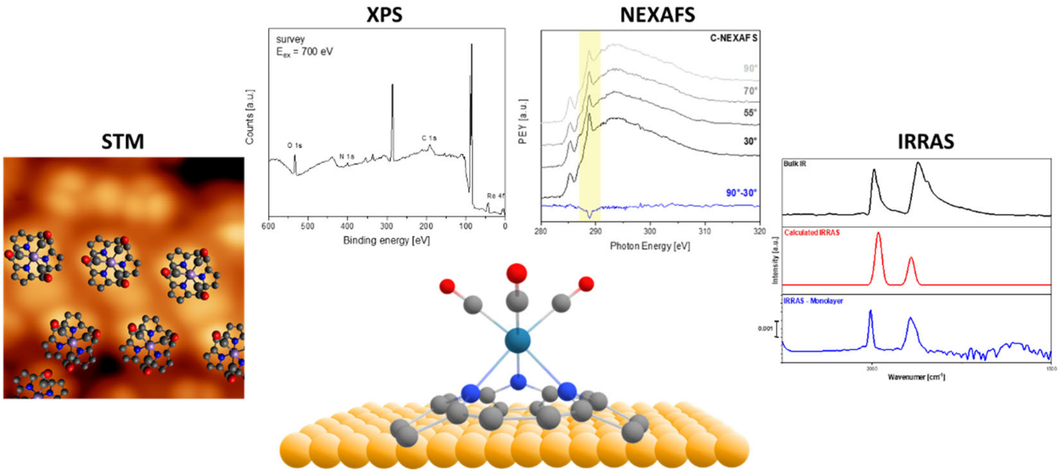
Dome-shaped complexes offer a novel approach in heterogenized catalyst research, focusing on the fundamental understanding of the electronic interactions between the catalytic centre and the metal surface, and providing insight into their potential applications in catalytic processes. Several complexes were synthesized to investigate their stability and reactivity on surfaces. Surface-sensitive spectroscopic techniques (IRRAS, XPS, NEXAFS, and STM) were employed to characterize these complexes.[1] The results confirm the successful deposition of the systems in a perpendicular orientation under ultra-high vacuum (UHV) conditions, as well as a tilted orientation during wet chemical preparation. A key focus of this work was the activation of molecular oxygen (O_2) and its subsequent reactions with small molecules in the gas phase. In this context, a promising system was identified, consisting of a dioxomolybdenum(VI) core (MoO_2Cl) capable of epoxidizing small alkenes. This reaction is facilitated both by peroxo acid in solution and by molecular O_2 upon exposure to light.[2] Preliminary results are presented regarding the reactivity of this complex on surfaces.



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Framing and Taming T-shaped 14 Electron Rh(I) Complexes: C-H Activation or Not?

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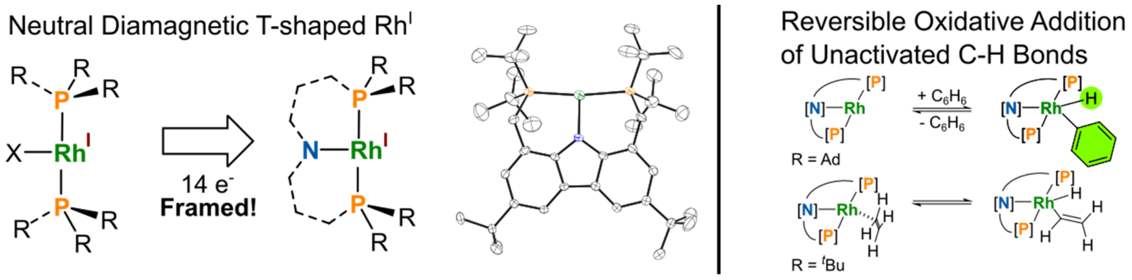
Low coordinate rhodium(I) complexes are proposed as the active species in several catalytic reactions relevant to industrial applications. These include hydrogenations with Wilkinson's Rh catalysts but equally catalytic transformations involving aryl/alkynyl-H or aryl/silyl-X additions, carbonylations as well as alkane dehydrogenations. The investigation of low coordinate rhodium(I) species has led to the isolation of a handful of such complexes. However the isolated complexes do not display C-H activations prominent in the catalytically active species. Previous work on T-shaped cobalt,[1], iron[2] and recently palladium[3] and chromium[4] complexes with the cbzdiphos PNP ligand, as well as work on T-shaped transition metal complexes with related ligand frameworks,[5] led us to investigate the heavier group nine element rhodium.[6]

Two T-shaped 14-electron rhodium complexes, "framed" and thus stabilized by PNP pincer ligands have been synthesized. The bis(t-butyl)phosphine derived PNP$^{t\mathrm{Bu}}$-rhodium complex was isolated from pentane as the more stable cyclometalated Rh(III) hydrido complex and found to be in equilibrium with the T-shaped 14e$^-$Rh(I) complex, which itself could be directly crystallized upon change of the solvent. The cyclometallation is suppressed using an adamantyl substituted PNP$^{\mathrm{Ad}}$ ligand to give the analogous T-shaped Rh(I) species, stabilized through an agostic interaction with one of the adamantyl C-Hs. Depending on the solvent, the PNP$^{t\mathrm{Bu}}$ complex reacted with ethylene either by π-coordination or C-H activation giving a hydrido-vinyl Rh(III) species, both isomers being in equilibrium in solution. The PNP$^{\mathrm{Ad}}$ complex was found to reversibly C-H activate arenes to form the hydrido-aryl Rh(III) complexes.



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Late transition metal PN^{H}N complexes for the dehydrocoupling of amine borane adducts

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Amine borane adducts ($H_3B·NMe_nH_{3-n}$, n = 1, 2) are valence isoelectronic to alkanes and can undergo a dehydrocoupling reaction to form poly- or oligomers which are discussed as precursors for B-N-based ceramics and single-layer hexagonal BN thin films.[1] Transition metal complexes with cooperative PNP ligands with an NH-functionality are among the most active catalysts for these reactions, showing excellent selectivities for linear poly(aminboranes).[2] We were interested whether this behaviour is exclusive to PNP ligands or can be transferred to other cooperative PNN systems. In a previous study, we investigated the coordination chemistry of pyrazole-based Rh(I) PNN^H complexes and the catalytic dehydrocoupling of $H_3B·NMeH_2$.[3] We found an increased activity upon addition of base, likely forming a Rh hydride complex as the active catalyst.

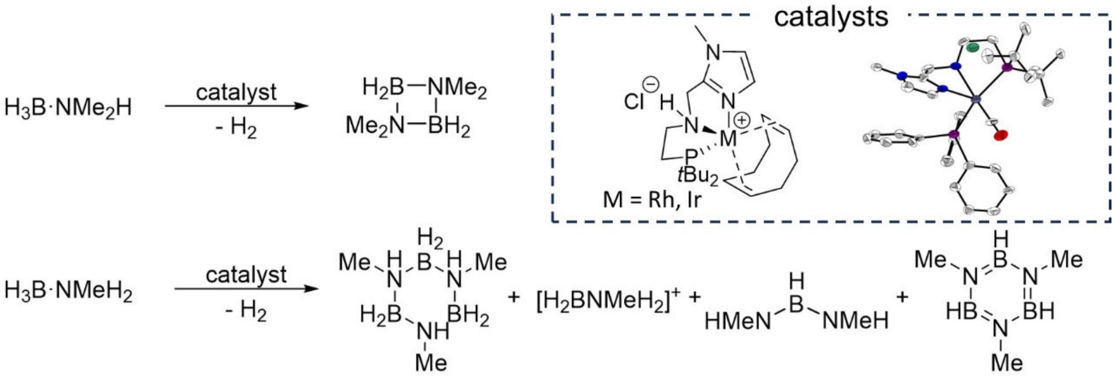

Figure 1: Dehydrocoupling of $H_3B·NMe_2H$ and $H_3B·NMeH_2$ and structures of some of the studied late transition metal complexes with imidazole-based PN^{H}N ligands.

To further understand the activity of cooperative ligands we extended our studies to systems with imidazole-based PN^{H}N ligands which resemble the above-mentioned PN^{H}P systems more closely. We synthesised complexes with the late transition metals rhodium, iridium and ruthenium. These new complexes showed a similar coordination chemistry, were fully characterised and tested for the dehydrocoupling of $H_3B·NMe_2H$ and $H_3B·NMeH_2$. We compared the hydrogen evolution of the different complexes and found unexpected results for the different substrates.

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Coulombic dyads as new catalyst class for efficient photocatalysis

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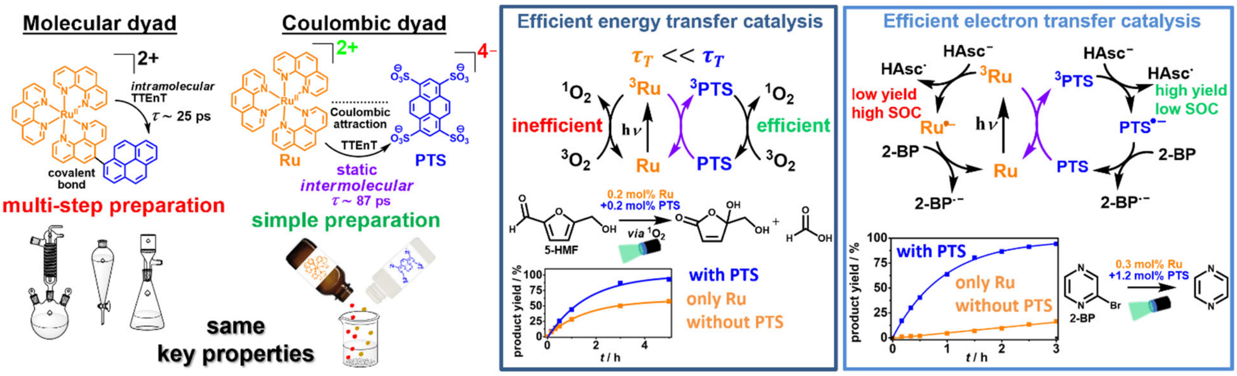
Molecular dyads can be designed such that unique properties for photochemical energy and electron transfer reactions result.[1-3] These properties are based on the interplay of an inorganic chromophore (quantitative intersystem crossing and visible light absorptivity) with a covalently linked organic moiety (long-lived triplet).[2] The major disadvantage of molecular dyads is their multi-step and resource-consuming synthesis hampering large-scale applications.

We have developed a straightforward and more practical alternative to molecular dyads simply by mixing a cationic ruthenium complex with a tetra-anionic pyrene derivative in solution.[4] In this Coulombic dyad based on commercially available “ingredients”, the chromophores form an ion-pair in solution. The long-lived organic triplet state is obtained by practically quantitative static quenching of the excited ruthenium complex, which is almost as fast ($\tau \sim 87$ ps) as intramolecular energy transfer in traditional molecular dyads. The Coulombic dyad has been successfully employed in energy transfer catalysis with similar reactivity and even higher photostability compared to a molecular dyad. In addition, it was shown that this system can also be used to maximize the quantum yield of a photoredox test reaction. This is due to an intrinsically higher cage escape quantum yield after photoinduced electron transfer for purely organic compounds compared to heavy atom-containing systems.[2] The combination of laboratory-scale as well as mechanistic irradiation experiments, detailed spectroscopic investigations and molecular dynamics simulations provided deep mechanistic insights into this easy-to-use dyad class.[4]



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Valence Tautomerism in Half-Sandwich Complex Triarylmethylium Dyads

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Valence tautomerism (VT) is characterized by the co-existence of at least two electronic isomers, which differ in their charge and spin density distribution, i. e. the assignments of oxidation states to the individual redox centers, and therefore also in their optic and, in some cases, also in their magnetic properties.[1] Interconversion between valence tautomers occurs via an intramolecular electron transfer (IET), which can be triggered by external stimuli (e.g. temperature change, irradiation with light).[2,3] The observation of this phenomenon rests on the presence of two (or more) chemically different, electronically decoupled redox-active entities, which are oxidized or reduced at similar potentials.[4]

Herein, we present dyads comprising of a triarylmethylium unit and a transition metal half-sandwich complex unit containing different ligands L at the metal atom. The choice of the ligand L enables the precise tailoring of the oxidation potential of the metal unit and therefore also of the redox potential difference toward the reduction of the triarylmethylium unit. Furthermore, the potential of the latter redox couple can be tuned *via* variation of the substituents R at the phenyl rings between electron-donating and electron-withdrawing, based on electrochemical data from the literature. By this means, VT was purposefully implemented and the valence tautomeric equilibria between the diamagnetic forms (Figure 1, left) and their diradical valence isomers (Figure 1, right) were analyzed by *T*-dependent IR and EPR spectroscopy.[5]

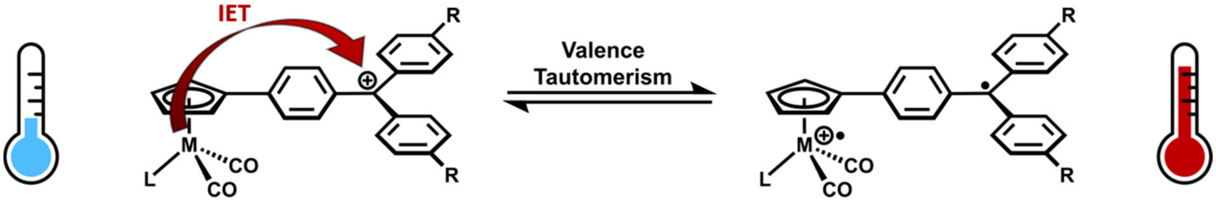

Figure 1. *T*-Dependent valence tautomeric equilibrium between a diamagnetic triarylmethylium transition metal half-sandwich complex (left) and its paramagnetic electronic isomer (right).

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2,2'-Diphosphino- and 2,2'-Diarsenotolanes and Their Ruthenium Pincer and Carbene Complexes

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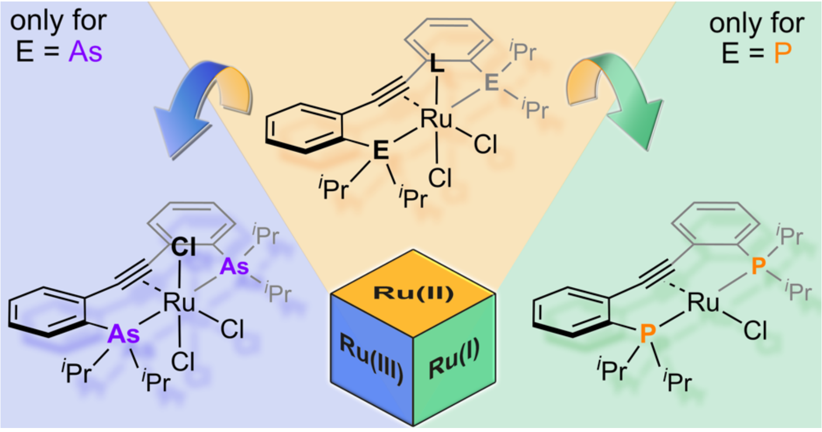
In recent years, our group has been working intensively on the coordination chemistry of 2,2'-diphosphino- and 2,2'-diarsenotolanes.[1] Depending on the choice of metal precursor, two significantly different classes of compounds were observed and isolated: CArY-MICs complexes (cyclic aryl ylidic mesoionic carbenes) and rigid pincer complexes.[1c, 2] By employing the [AsCCAs] ligand scaffold, the formation of cyclized (ylidic) reaction products could be largely suppressed due to the reduced stability of *As*-ylides compared to *P*-ylides.[3]

Here, the chemistry of ruthenium was investigated, which led to both known structural platforms, i.e. with the [PCCP] and with the [AsCCAs] ligand. A variety of different ruthenium complexes could be prepared, not only in the +II oxidation state, but also in the less common +III and +I oxidation states. Furthermore, an unexpected reactivity of the Ru(I) species with TIPF$_6$ was found.



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Exploring magnetic and electronic coupling in coordination compounds featuring an in-plane bound TTF-moiety

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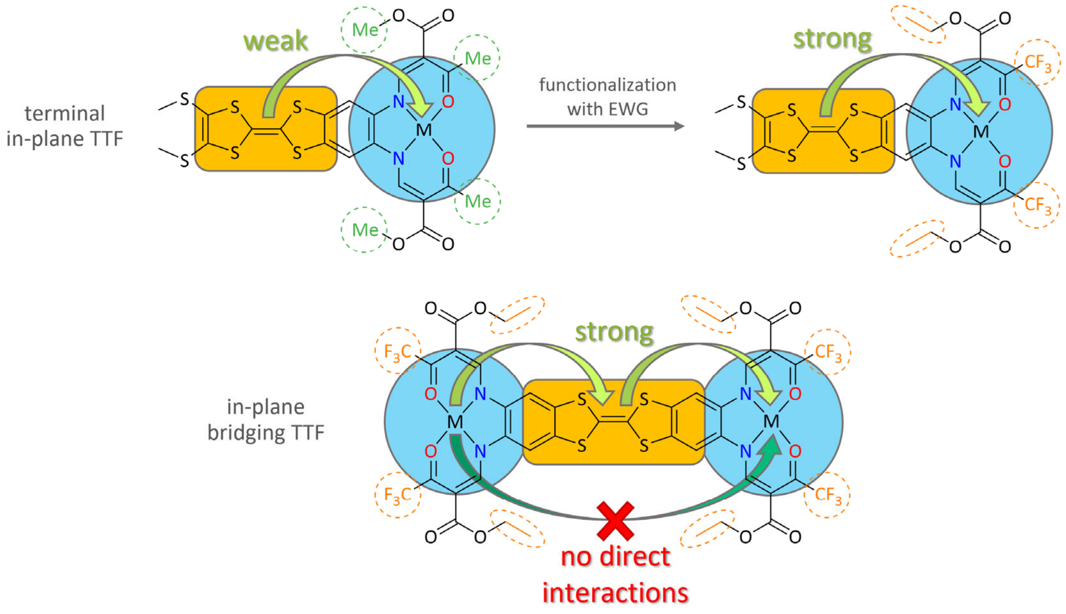
The last two decades have witnessed the synthesis and utilization of an increasing number of multifunctional coordination compounds with metal-borne and ligand-borne redox active sites. Herin, we present the incorporation of twice-reversibly oxidizable tetrathiafulvalene (TTF) into mono- and binuclear coordination compounds.[1] The integration through a fully conjugated plane allows for interactions between the redox active site and the metal centers, which were further adjustable through ligand functionalization. The oxidation behavior of the compounds was investigated through cyclic voltammetry, and electronic states were assigned through UV-vis experiments as well as DFT calculations. Furthermore the obtained iron(II) compounds show spin crossover behavior, combining the switchable electronic states of the iron(II) centers with redox properties of the TTF unit. In the case of the binuclear coordination compounds, the bridging TTF unit leads to magnetically independent metal centers for the reduced ligand, while allowing for electronic metal-metal interactions after oxidation.[2]



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Redox isomerism in complexes with redox-active guanidine ligands

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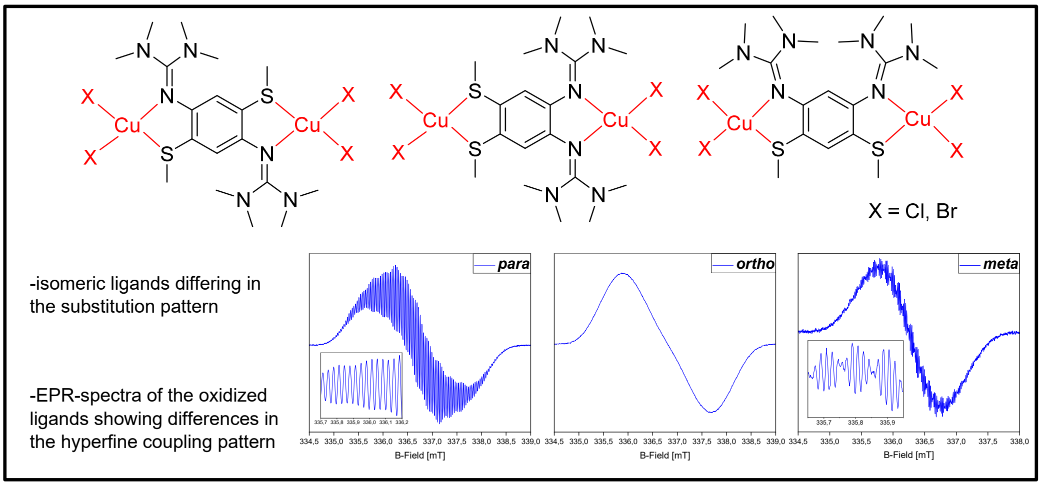
Redox-active ligands have been applied for the design of coordination compounds with switchable optical and magnetic properties[1,2] and of catalysts showing cooperative ligand-metal substrate activation.[3,4] In our group, the multiple redox states arising from the integration of guanidino-functionalized aromatics (GFA) in coordination compounds are studied.[5,6,7,8] For mono- and binuclear complexes with GFA ligands, temperature- and solvent-dependent equilibria between two valence tautomers have been found.[5,6] Here, we report the synthesis of novel redox-active guanidine ligands, consisting of benzene cores with two guanidino and two alkylthio substituents. These ligands can be oxidized in two steps to their respective dicationic redox state. Changing the substitution pattern affects the redox potential of the ligands and the hyperfine coupling pattern of their respective radical cations.

Our results indicate that the substitution pattern also determines the electronic structures and redox isomerisms of binuclear metal complexes, as evidenced by the solid-state structures and spectroscopic and magnetometric measurements.



-isomeric ligands differing in the substitution pattern

-EPR-spectra of the oxidized ligands showing differences in the hyperfine coupling pattern

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Switchable Magnetic Properties in a Redox-Active Bis(porphyrinato)(phthalocyaninato)-diterbium(III) Single-Molecule Magnet

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Spin transport measurements on tris(phthalocyaninato)-dinuclear rare-earth(III) molecules represent a promising platform for nuclear spin qudits with increased multiplicity.[1–3] However, the absence of radicals in these molecules has hindered studies on the coupling between lanthanide ions and conduction electrons. In this study, bis(porphyrinato)(phthalocyaninato)-dinuclear rare-earth(III) molecules with thiomethyl groups were synthesized. The designed molecules were then oxidized to obtain a ligand-based radical, which was achieved by adjusting the HOMO-LUMO gap of the neutral complexes. A combination of CASSCF calculations and static magnetic measurements revealed the nature of their coupling. Dynamic magnetic measurements showed that the magnetic properties change upon oxidation, specifically from field-induced single-molecule magnets (SMM) to zero-field SMM. The findings of this study, along with the strong bond between the thiomethyl group and the gold electrode, could pave the way for new materials in quantum information processing.

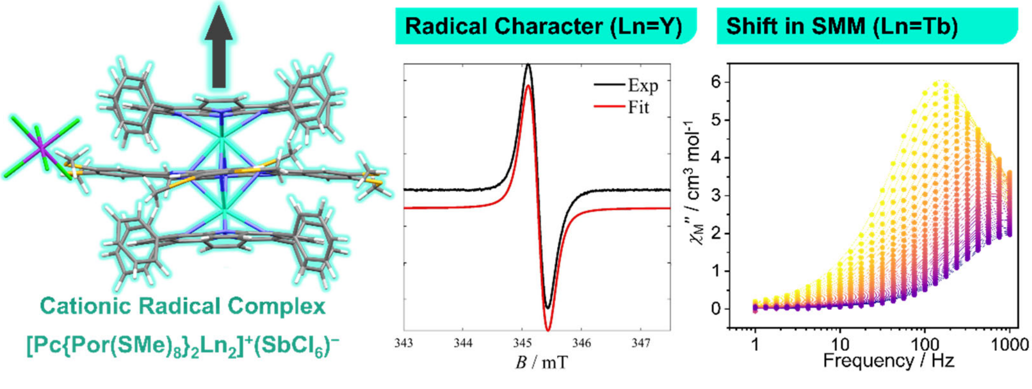

Figure 1. Structure of the target complexes and spectroscopic data.

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Azacryptand-based dinuclear rare-earth and transition metal complexes

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There is an increasing interest to utilize dinuclear complexes towards small molecule activation as they exhibit a high potential to face current challenges.[1-3] We recently presented our first results on our research into azacryptand-based rare-earth metal complexes.[4] Here, we would like to present our recent work on dinuclear azacryptand compounds. These rare-earth metal complexes are able to coordinate cyanide, which is isoelectronic to carbon monoxide and dinitrogen, as well as borohydride that acts as a hydrogen source.[4] With the acquired knowledge, we want to understand azacryptand complexes of early transition metals, e.g. group 6 metals, towards application in small molecule activation.

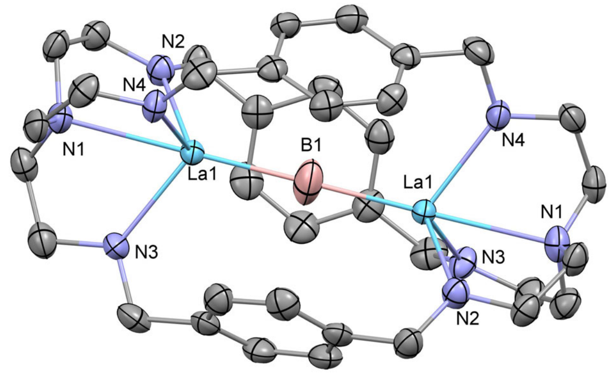

Figure 1: Borohydride adduct of a dilanthanum azacryptand complex.

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New Lessons from Tyrosinase Model Systems: How to Balance Conformers and their Influence on Thermal Stability and *ortho*-Hydroxylation Rates

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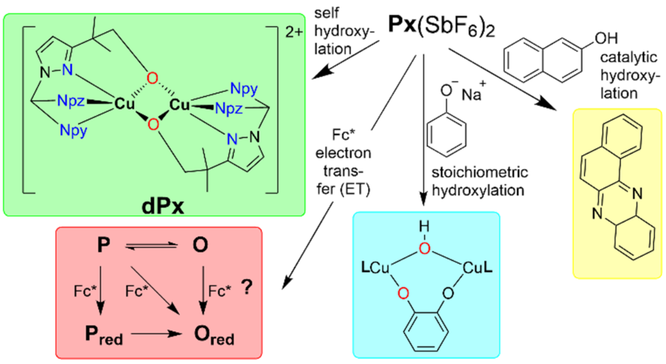
Tyrosinase is an enzyme that catalyzes the *ortho*-hydroxylation of L-tyrosine, a phenolic substrate, to form dopaquinone. This reactivity has been subject to numerous studies,[1] both with the real enzyme and a few catalytically active model systems, however only recently could the reaction mechanism of the real enzyme be deciphered.[2]



Using a bis(pyrazolyl)methane based model system, which has previously shown to be highly versatile in the *ortho*-hydroxylation, even of non-natural substrates,[3] the reactivity was studied in detail with respect to phenolate activation, electron transfer chemistry, catalytic activity and thermal stability. Therefore, the electronic donor properties of the ligands were systematically varied, showing dramatic effect on the resulting Cu_2O_2 chemistry. To further understand these effects, computational chemistry was employed in order to gain insight into equilibria between **P** and **O** (μ-η^2:η^2-peroxidodicopper(II) and bis-μ-oxido-dicopper(III)) isomers,[4] conformers[5] and transition states, which are difficult to differentiate experimentally. Marcus reorganization energies were used to determine the mechanism of electron transfer to the Cu_2O_2 species,[6] as this step was shown to play an important role in the catalytic cycle of the real enzyme. Michaelis-Menten kinetics were employed to gain insight into substrate activation. The systems were also shown to be catalytically active in the ortho-hydroxylation of 2-naphthol, which, after a condensation reaction, allows for the isolation of benzo[a]phenazine, an antimicrobial agent.[7] Overall, this study expands the knowledge about one of the most versatile tyrosinase model systems to date.

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Tungsten Complexes for Acetylene Activation

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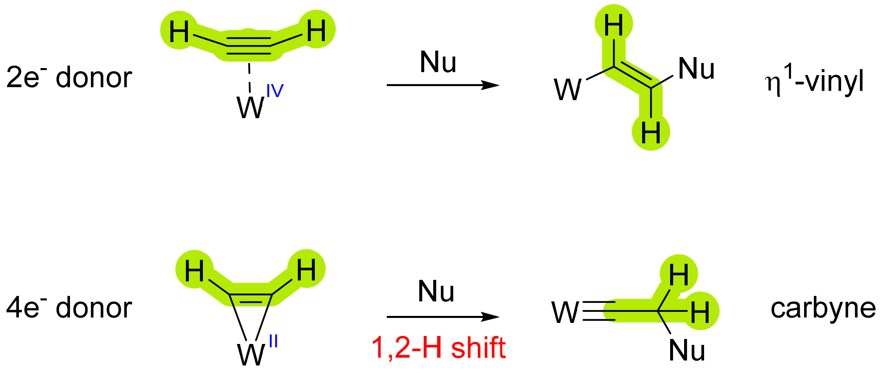
The mechanism of acetylene hydration catalyzed by the tungstoenzyme acetylene hydratase remains elusive. This transformation likely involves acetylene coordination followed by a nucleophilic attack by water – a reactivity that has not yet been reported with model complexes.[1] Importantly, understanding the enzyme's mechanism depends on a deeper understanding of the reactivity of tungsten-acetylene adducts. Despite their diversity, not all their reactivity patterns have been fully understood or systematically classified. This gap highlights the need for further exploration in this area.

To address this gap and better understand the conditions under which acetylene is activated for nucleophilic attack, we have investigated the reactivity of differently bound acetylene ligands in bioinspired tungsten complexes bearing pyridine- and pyrimidine-2-thiolate ligands. Our studies reveal that tungsten(IV)-acetylene adducts readily react with nucleophiles to yield η^1-vinyl complexes, consistent with the expected behavior of two-electron donor alkyne ligands. By contrast, tungsten(II)-acetylene adducts exhibit unexpected reactivity, leading to the formation of stable carbyne complexes. This surprising outcome, which arises from a challenging 1,2-H shift, required detailed spectroscopic and computational studies.[2]

In this work, we discuss a mechanistic explanation for carbyne formation and propose an extension to the established classification of alkyne complex reactivity. These findings provide a foundation for further development of tungsten complexes, with the potential to enable more sustainable approaches to acetylene activation.



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Copper(II)-Catalyzed Amination of Aryl Chlorides in Aqueous Ammonia

P. D. Engel,[1,2] L. S. Mello, P. Orecchia, K. Bleher, F. Rominger, K. Borate, R. Goetz, P. Deglmann, A. Schäfer, C. Winter, M. Rack, P. Comba, A. S. K. Hashmi, T. Schaub*
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Anilines are motifs frequently present in compounds of industrial and medicinal interest, such as agrochemicals and pharmaceuticals.[1] Their classic synthesis is done by nitration of aromatic compounds followed by reduction to aniline.[2] Alternatively, anilines can be produced by cross-coupling of aryl halides and amino sources. However, most approaches in the literature are directed to aryl bromides and iodides, palladium-catalyzed or done in harmful organic solvents. [1-4] Hence, the development of new routes is necessary.

We developed a Cu(II)-catalyzed system for the amination of aryl chlorides in aqueous ammonia with low catalyst loading under non-inert conditions. A combination of simple copper(II)salts and *N*-donor ligands enables the amination of several aryl chlorides containing electron-neutral, -donating and -withdrawing groups to the corresponding anilines with good to excellent yields. DFT investigations reveal a radical mediated S_NAr pathway with a three-coordinate copper-amido intermediate as active species.[5]

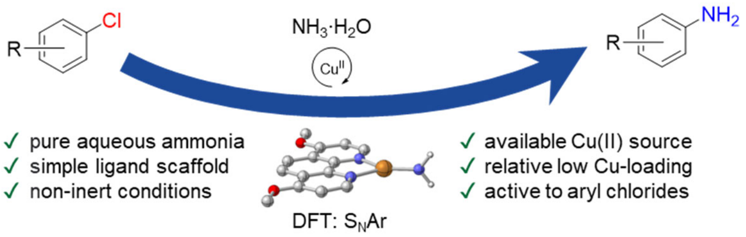

Figure 1: TOC graphic for the Cu(II)-catalyzed aniline synthesis in aqueous ammonia.

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Chemical bond activation with mononuclear Rhodium-, Palladium and Platinum complexes

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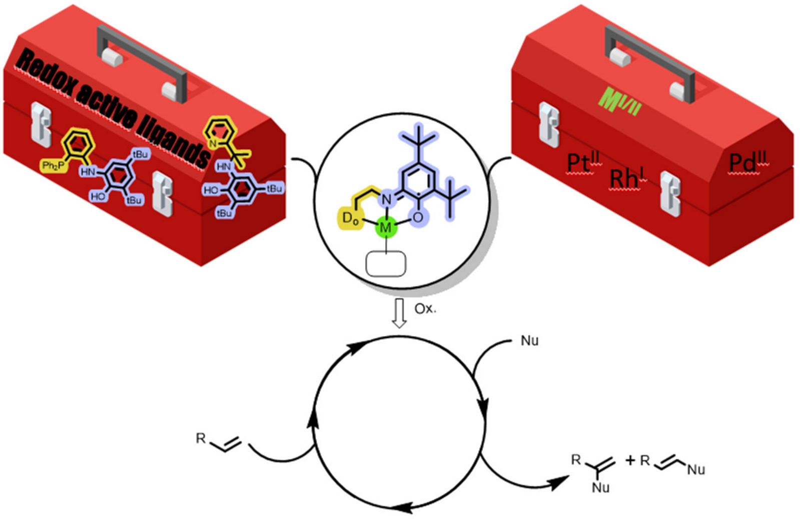
Redox-active, non-innocent ligands in mononuclear transition metal complexes often result in novel unique properties. Of particular note is the access to new reaction pathways for the selective preparation of a broad spectrum of synthetically useful compounds.[1] Our group published a tridentate PNO^{H2} and NNO^{H2} ligand on a Pd$^{\mathbf{II}}$ platform for homolytic bond activation of disulfides and the generation of reactive sulfide radicals or the aminocyclization starting from organic azides, catalyzed by Pd^{II} or Fe^{III}, respectively.[2,3,4] Inspired by these results we currently focus on the synthesis of suitable Rh^{I} and Pt^{II}/Pd^{II} complexes for C-H$_{\text{alkene}}$ functionalizations, including model complexes for evaluation of their intrinsic redox chemistry. We will report on their synthesis, characterization using multinuclear NMR spectroscopy, UV-Vis absorption spectroscopy, cyclovoltammetry, EPR and XRD analysis supported by DFT calculations.



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The Elusive Chemistry of Pyrroloquinoline Quinone Dimethyl Ester Lanthanide Complexes in Biomimetic Alcohol Oxidation

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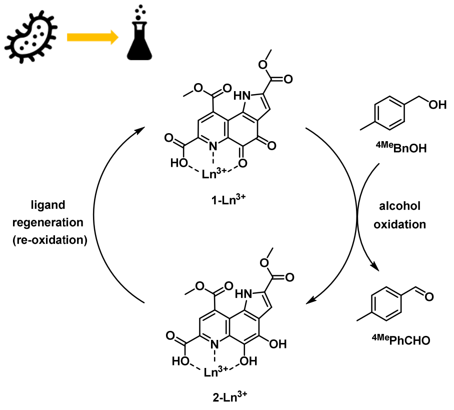
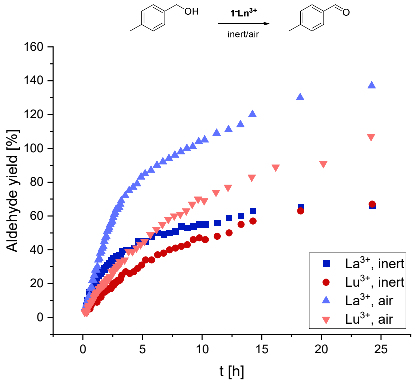
Since its discovery, pyrroloquinoline quinone (PQQ) has been under constant investigation regarding its efficiency in biomimetic complexes for alcohol dehydrogenation. Since the discovery of lanthanide (Ln) dependent methanol dehydrogenases, lanthanide complexes bearing PQQ derivatives have been used to stoichiometrically and catalytically oxidize alcohols.[1] However, the mechanism of these oxidations is still a subject of debate. Herein, we report La^{3+} and Lu^{3+} complexes of PQQ dimethyl ester (PQQDME, **1**) that are able to stoichiometrically oxidize an alcohol substrate. In the presence of air, we observe some catalytic turnover, but less than with other modified PQQ biomimetics known in the literature.[2] We set out to find the reason for this low turnover and hereby synthesize the reduced counterpart, $PQQDMEH_2$ (**2**). We show that in the presence of atmospheric oxygen, the complexes of the reduced counterpart undergo autoxidation and can also convert alcohol to aldehyde. We further investigate the involvement of radicals in the alcohol oxidation reaction and look for the origin and nature of these radicals.





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Model Compounds for Cytochrome c Oxidase

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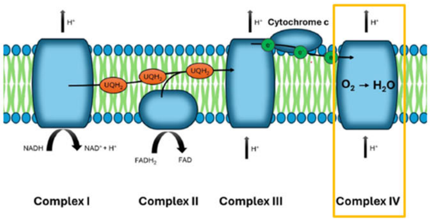
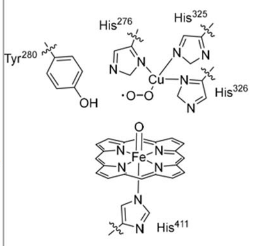
Oxygen is essential for generating metabolic energy and has been an important factor in the development of animal life.[1,2] The key energy production mechanism in eukaryotic cells is the so-called mitochondrial oxidative phosphorylation, which forms adenosine-5´- triphosphate (ATP), the universal energy currency in biological systems.[3,4] Cytochrome c oxidase, complex IV of the respiratory chain, maintains the proton gradient.1 This gradient is then utilized by ATP synthase to produce adenosine-5′-triphosphate from adenosine-5′-diphosphate. The energy for this process is provided by the simultaneous reduction of elemental oxygen to water, which takes place in the active center of cytochrome c Oxidase. In this four-electron reduction of dioxygen four molecules of reduced cytochrome c are consumed, as well as four protons from the matrix space.[5,6] Even though cytochrome c oxidase is one of the most fundamental enzymes of life, not all intermediates formed during its process are yet known. These intermediates are usually generated through oxygen adduct formation and undergo a specific catalytic cycle at the active center. Fully elucidating this process could provide new insights into potential applications in enzymatic biofuel cells. The bond cleavage of activated dioxygen is already used in industrial organic oxidations or energy production in fuel cells. It shows the great benefits of understanding the elementary kinetic steps of cytochrome c oxidase.[7] The research also holds medical relevance, as certain diseases are linked to malfunctions of cytochrome c oxidase. My research focuses on modeling the active center to isolate potential oxygen adducts formed after complexation. This could provide insights into the processes occurring within the enzyme. One can use "untethered complexes[8]" or "tethered complexes" to build such model complexes. The difference lies in whether the two involved metal centers are connected via linkers or not.



Scheme of the respiratory chain.



Sketch of Cytochrome c Oxidases (Complex IV) active side in the F-state[9]

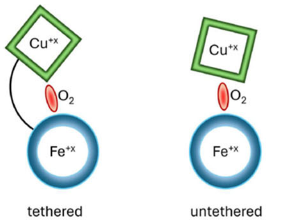


Illustration of a tethered complex (linker between the two metal complexes) and an untethered complex.

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Catalytic Production of Hydroxyl Radicals with a Co(III) Polypyridine Complex for Anticancer Therapy

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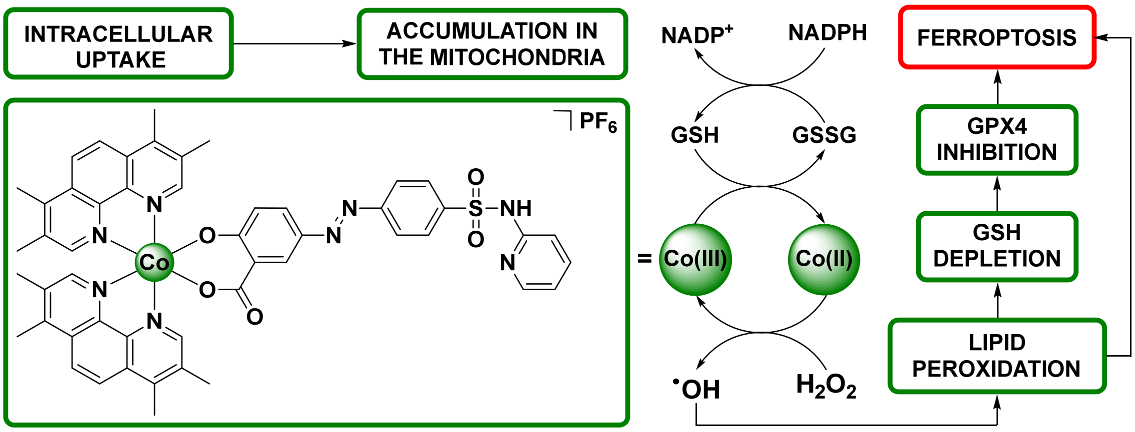
Chemotherapy often faces challenges such as severe side effects, low specificity, and the risk of cancer cells developing resistance. To address these limitations, researchers are exploring new therapies with innovative mechanisms. One promising approach involves generating hydroxyl radicals ($^{\cdot}OH$) within cancer cells to induce ferroptosis, a form of cell death distinct from traditional methods. However, only a few compounds can catalytically produce $^{\cdot}OH$ in cancer cells, and these often lack efficiency and pharmacological effectiveness. One of these compounds is the organic drug sulfasalazine. To enhance the therapeutic properties, we have sought to incorporate this compound in a redox-active metal complex, enabling efficient electron transfer and therefore higher catalytic conversion. Indeed, the complex was found to selectively and highly efficiently generate $^{\cdot}OH$ inside a cuvette as well as a cancer cell. Further analysis has shown that the catalytic mechanism follows a Fenton-type reaction, where hydrogen peroxide is broken down into highly reactive $^{\cdot}OH$ species upon reduction of the metal complex. The metal center is then re-oxidized by glutathione, a cellular antioxidant, which simultaneously drives the oxidation of NADPH. This cycle of reactions not only generates $^{\cdot}OH$ radicals but also promotes the accumulation of lipid peroxides, ultimately leading to oxidative damage within the cell and ultimately cell death of the cancer cell. Combined these findings demonstrate the potential of metal complexes to act as specific catalysts inside of cancerous cells.



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Hydrogen Evolution through a photoactive [FeFe]-Hydrogenase Mediator using Visible Light

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[2,9]Chemistry Department and State Research Center OPTIMAS, RPTU Kaiserslautern-Landau, 67663 Kaiserslautern, Germany.
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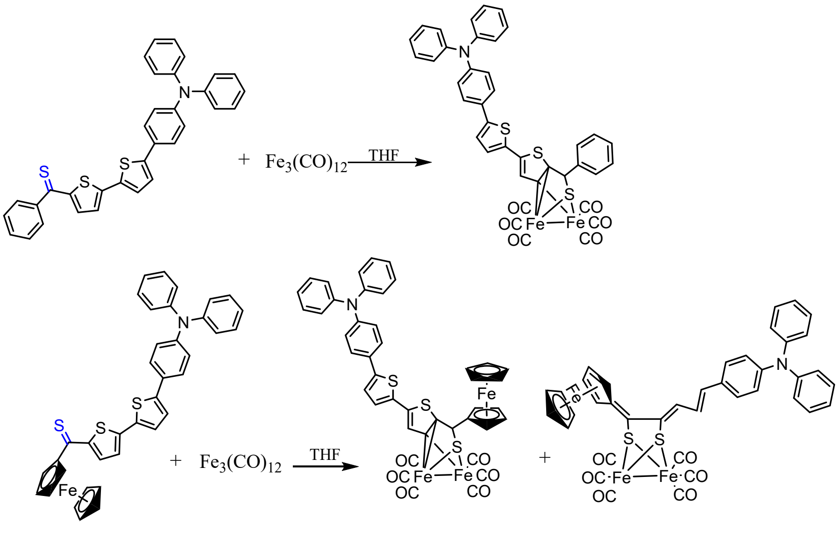
Nowadays the concerns about global warming and increasing demands of energy consumption has spurred much interest in developing eco-friendly and renewable energy technologies[3,4]. Molecular hydrogen (H_2) is considered as an energy carrier, and presently getting more popularity as an alternative fuel[3-5]. Natural [FeFe]- and [NiFe]-hydrogenases enzymes convert protons and electrons into H_2 with remarkably high rates at low overpotential. Photocatalytic H_2 generation through photoactive [FeFe]- hydrogenase mimic using visible light irradiation could make H_2 a real competitor to fossil fuels[1-5]. Thus, a series of novel photoactive hydrogenase mimics using triphenylamine (TPA) as electron donor, thiophene derivatives as π-conjugated molecules, phenyl and ferrocene moiety was designed for photocatalytic hydrogen evolution under visible light irradiation (Scheme 1).



Scheme 1. Synthetic pathways of the complexes.

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Characterising Products of Light-Induced Oxidation of A_2B-Corroles using ^{109}Ag-NMR

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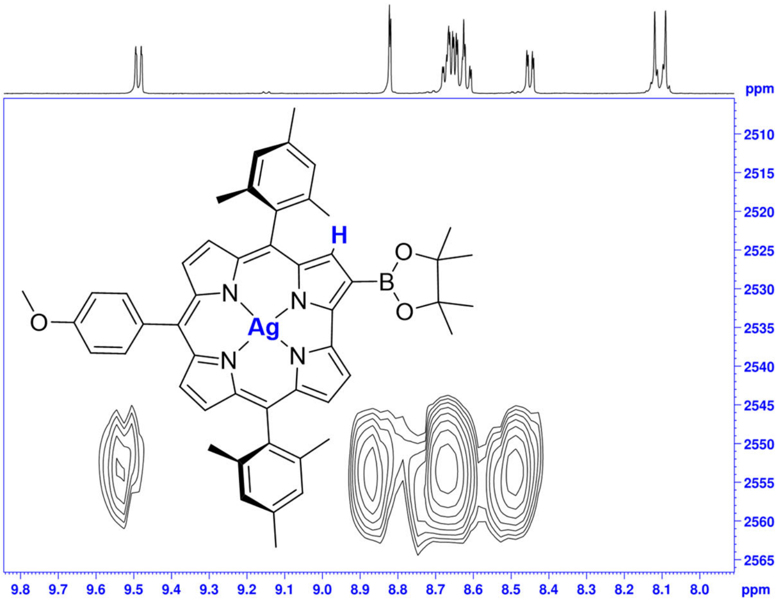
Technische Universität Braunschweig, Institut für Anorganische und Analytische Chemie

This presentation will highlight the use of ^{109}Ag as an underutilised NMR probe for the structural determination of products from photooxidative coupling reactions of different triarylcorroles.[1,2] ^{109}Ag-^{1}H HMBC NMR spectroscopy on silver metalated products and reference systems was introduced to characterise the outcome of these reactions. Different symmetrical and asymmetrical ß,ß'-coupled dicorroles are readily distinguished upon their respective spectral pattern (see figure). The obtained findings help to further understand product formation under photooxidative conditions.



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T-Shaped Bismuth Complexes: Transition Metal-like Reactivity and Stabilization of Exotic Radical Species

S. Pavlidis, E. Fischer, A. Guilherme Buzanich, A. Opis-Basilio, K. Krause, F. Emmerling, M. Römelt and J. Abbenseth*
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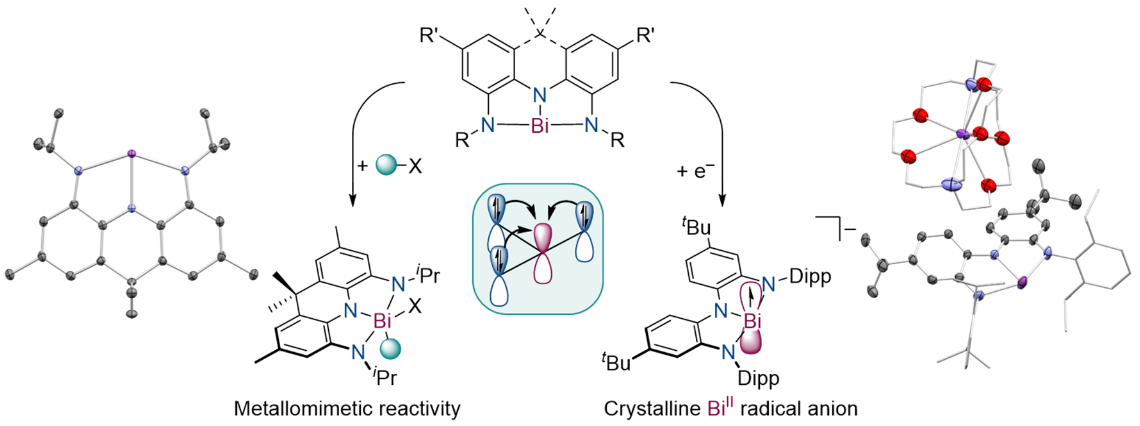
Valence Shell Electron Pair Repulsion (VSEPR) theory predicts the geometries of main-group compounds based on the number of electron pairs surrounding the central atom. Deviations from these preferred geometries can unlock novel reaction pathways and significantly influence selectivity in small molecule activation.[1] Among such systems, geometrically constrained pnictogens demonstrate unusual ambiphilic reactivity due to perturbation of the frontier molecular orbitals upon planarization. While geometrically constrained phosphines have been extensively studied for their roles in diverse (catalytic) small molecule activation reactions, analogous bismuth(III) compounds remain largely unexplored.[1,2]



Our research focuses on designing rigid NNN pincer ligands that constrain pnictogens in the +III oxidation state into a T-shaped geometry while also imparting significant redox activity.[2a,3] This presentation will highlight our recent discoveries in the chemistry of T-shaped bismuth complexes. Full planarization and conjugation with redox-active ligands enable unique reactivity patterns typically associated with transition metals. Furthermore, this unconventional orbital arrangement allows stabilization of unprecedented Bi radical complexes.

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Tuning Lewis Acidity: Design of FLP-like Titanium Complexes with Pyridine-based Ligands

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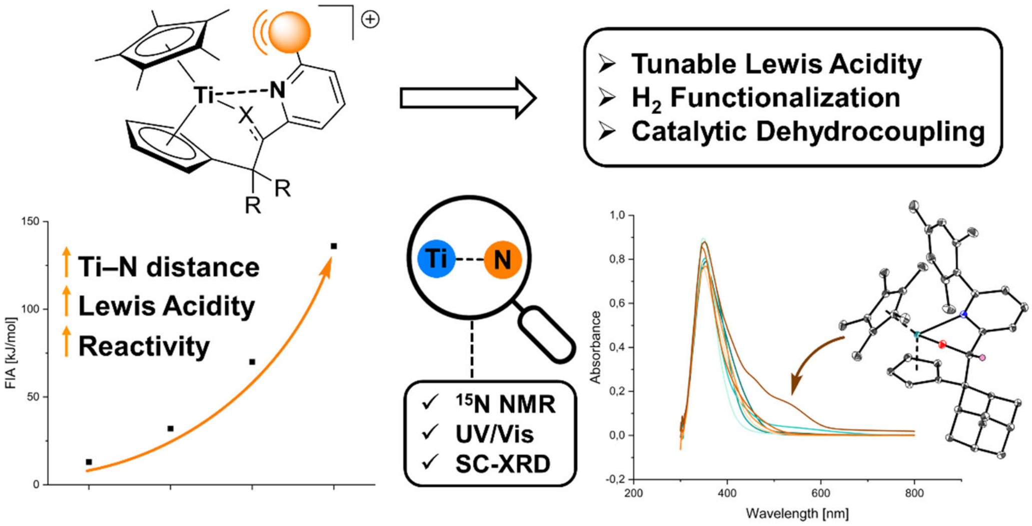
Carl von Ossietzky Universität Oldenburg, D-26111 Oldenburg, Germany, kevin.schwitalla@uol.de

The creation of molecular architectures for homogenous catalysis and bond activation is of fundamental interest. By combining metal-ligand cooperativity[1] with the concept of Frustrated Lewis Pairs,[2] highly active catalysts can be developed. While many transition metal-based FLPs (tm-FLPs) are based on phosphine ligand systems, nitrogen-based tm-FLPs are less common. In particular, pyridine-based FLP-type complexes are underdeveloped despite the effectiveness of the main group FLP analogues like the standout Lutidine/$B(C_6F_5)_3$ pair,[3] other *N*-heterocyclic pairs and intramolecular systems.[4] One major challenge in the development of pyridine-based systems is to overcome the strong interaction between the pyridine derivative and the Lewis acid, which results in a low reactivity.[4] Herein, we employed pyridine-containing ligand systems to create FLP-like titanium(IV) complexes with *Cp*,*N*,*N* and *Cp*,*O*,*N* tridentate ligands. Based on the ligand design and Lewis acidity, the complexes exhibit different reactivities, such as hydrogen functionalization, Lewis pair formation and catalytic dehydrocoupling of amine boranes. The introduction of moderately strong coordinating triflato ligands provides insight into the nucleophilicity of the respective pyridinyl ligands and, in turn, into the Lewis acidity of the complexes, whereas well-established protocols for the determination of Lewis acidity quantify our findings. The ^{15}N NMR chemical shift values of the pyridine-based ligands and UV/Vis spectra further support the determination of the coordination modes and reactivities, while the determination of fluoride ion affinities quantifies the Lewis acidities of the complexes.



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Three-Coordinate Cu(I) Complexes with an N-Heterocyclic Carbene Carrying a Weakly Coordinating Tris(pentafluorophenyl)borate Anion

L. E. Burmeister[1], L. J. Groth[2], P. R. Meinhold[2], J. P. Zurwellen[1], D. Bockfeld[2], R. Frank[2], M. Karnahl[1], M. Tamm[2,*], and S. Tschierlei[1,*]
[1] Department of Energy Conversion, Institute of Physical and Theoretical Chemistry, Technische Universität Braunschweig, Rebenring 31, 38106 Braunschweig, Germany; lars.burmeister@tu-bs.de
[2] Institute of Inorganic and Analytical Chemistry, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany.

Beginning with the pioneering work of McMillin in the 1970s, who demonstrated the ability of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) to participate in photochemical reactions[1], Cu(I) based complexes have attracted significant interest as sensitizers in various photoinduced reactions.[2,3] Since then, a wide variety of Cu(I) complexes has been explored, with the majority being four-coordinate and containing diimine and/or diphosphine ligands. In contrast, only a limited number of three-coordinate complexes are reported.[4] Therefore, we present the synthesis, structural characterization as well as the electrochemical and photophysical properties of four novel three-coordinate Cu(I) complexes. These compounds are composed of different symmetrical methyl-substituted dipyridylamine-based ligands (DPA) and *N*-heterocyclic carbene ligands with a weakly coordinating tris(pentafluorophenyl)borate anion (NHC-WCA, see Figure 1).

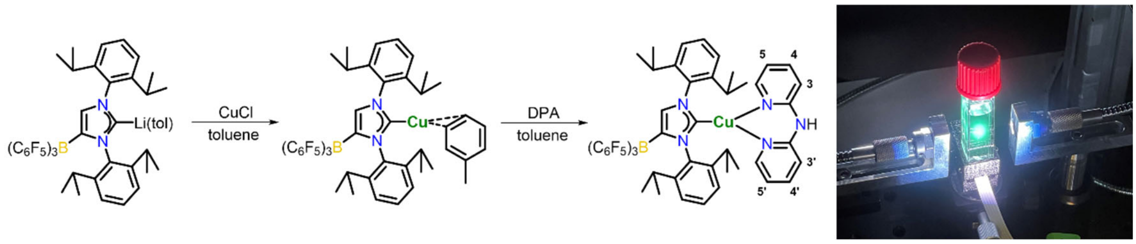

Figure 1. Synthetic route for the synthesis of the three-coordinate Cu(I) complexes investigated (left)[5], yielding green luminescent dyes in solution (right).

Interestingly, the introduction of the NHC-WCA ligand yields neutral complexes that exhibit deep green luminescence in solution with relatively high quantum yields and long luminescence lifetimes. This is not the case for previously reported structurally related, but cationic complexes.[6] Finally, the beneficial photophysical properties enable these complexes to sensitize the interconversion of norbornadiene to quadricyclane as a molecular solar thermal energy storage system.

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Tuning Spectro-electrochemical Properties of Thiele's Hydrocarbon Derivatives using Acid or Transition Metal Co-ordination

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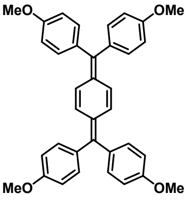
Thiele's hydrocarbon (TH) derivatives play a central role in the field of organic diradicaloids[1] due to their unique photo-physical properties[2] and applications in organic electronics.[3] Several strategies, such as varying spacer lengths,[4] heteroatom doping,[5] and exploring syn-anti isomerism,[6] have been employed to modulate their diradical character.

In this study, we synthesized a library of TH derivatives based on phenyl, pyridine, and pyrazine spacers (**I–III**) and investigated their spectro-electrochemical properties. A clear trend emerges in their properties as the degree of nitrogen doping in the spacer increases. Their properties can be further reversibly tuned through coordination with Lewis or Brønsted acids (**IV–V**). The presence of nitrogen atoms also enables these compounds to act as ligands for transition metal complexes (**VI–IX**).

In this talk, I will present the synthesis of these diradicaloids and demonstrate how their spectro-electrochemical properties can be tailored using a combination of experimental and theoretical approaches.



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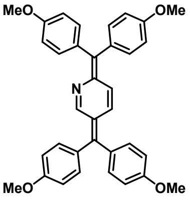

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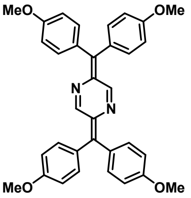

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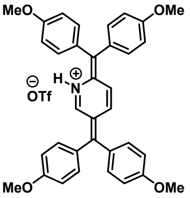

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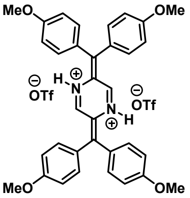

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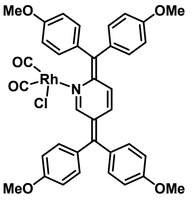

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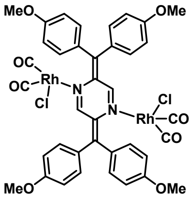

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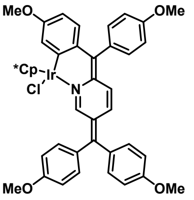

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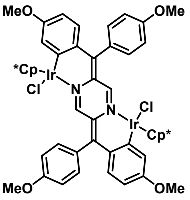

IX

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Is „5” the new „6“ ? Amino-Imidazolin-2-imine vs. *β*-Diketimine Ligands

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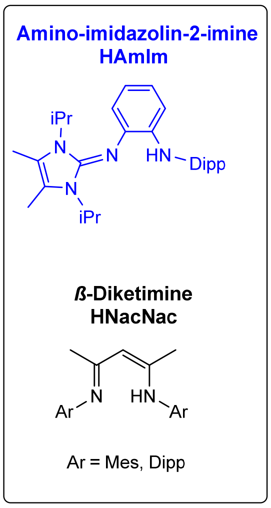
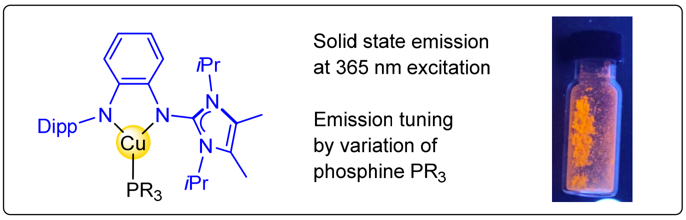
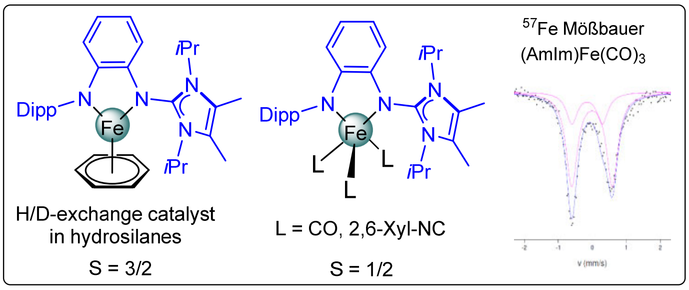
β-Diketimines (HNacNac) are widely recognized as monoanionic *N,N´*-chelate ligands to stabilize six-membered metallacycles. In contrast, powerful analogues to afford more stable five-membered chelates were not available until we recently introduced the new class of amino-imidazolin-2-imine ligands (HAmIm).[1] Since then, the advantages of HAmIm ligands have been demonstrated, and examples include the series of group 13 carbenoids E(AmIm) for E = Ga(I), In(I) and Tl(I)[2] but also cobalt(I) complexes of type [(AmIm)Co(η^6-C_6H_6)], which were shown to be highly efficient catalysts in silane activation and hydrosilylation of terminal olefines.[3] Stimulated by these promising findings, the HAmIm ligand class was studied in a series copper(I) complexes of type [(AmIm)Cu(PR_3)]. The latter were found to be emissive in the solid state upon excitation at 365 nm and allowed for a systematic fine tuning of the emission upon variation of the phosphine ligand PR_3. In further studies the iron(I) complex [(AmIm)Fe(η^6-C_6H_6)] (S = 3/2) was obtained. Besides the highly efficient activity in catalytic H/D exchange reactions of hydrosilanes,[4] the labile benzene entity in this complex gave rise to substitution with neutral ligands (CO, isonitriles) with alteration of the spin state to S = 1/2.







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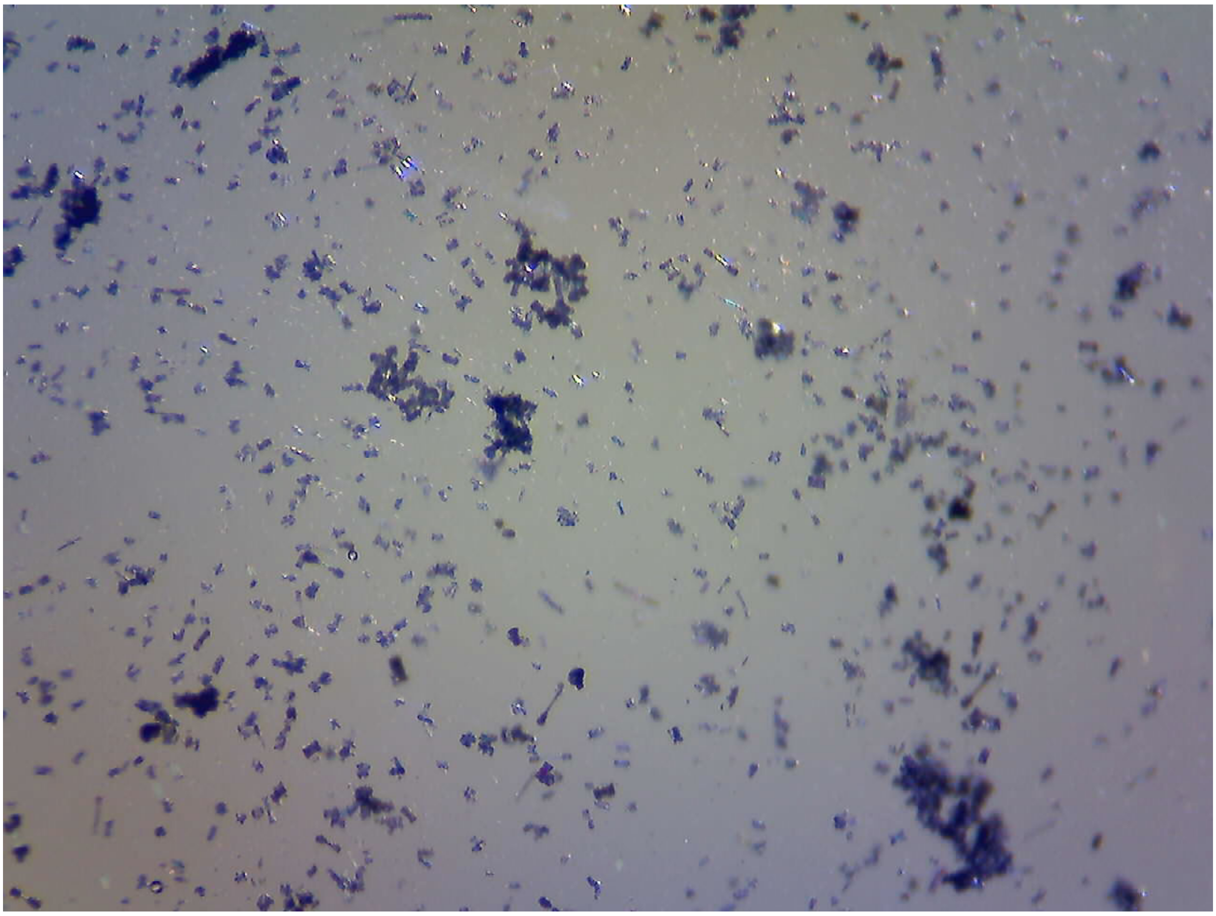
Poster List & Abstracts



Poster #	Presenting Author	Abstract Title
P1	**Srijita Bar** (AK Apfel, Ruhr-Universität Bochum)	Design and Synthesis of Cyclam Based Complexes for Oxygen Evolution Reactions
P2	**Lukas Eberle** (AK Ballmann, Universität Heidelberg)	(Hetero)anilines from Dinitrogen via Tungsten Nitrides
P3	**Franziska Lux** (AK Bauer, Universität Paderborn)	Photocatalytical Reactions using CCC-Cobalt(III)- and CCC-Iron(II)-Complexes
P4	**Anabel Miletic** (AK Bauer, Universität Paderborn)	Investigating the influence of functional groups on bidentate Co(III)-species
P5	**Florian Altes** (AK Becker, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau)	Development of a reaction-based zinc sensor
P6	**Nesrin I. Dilmen** (AK Becker, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau)	Encapsulating ligands for the stabilization of μ_4-oxido copper clusters
P7	**Kushik Kushik** (AK Beweries, Leibniz-Institut für Katalyse e. V., Rostock)	Exploring the Coordination Chemistry of a Phosphaalkene-based Monoanionic P,N,P-type Ligand
P8	**Shubham Goel** (AK Beweries, Leibniz-Institut für Katalyse e. V., Rostock)	Development of cooperative late transition metal complexes for Dehydrocoupling of amine boranes
P9	**Jesvita Cardozo** (AK Braun, Humboldt-Universität zu Berlin)	Iridium Triazolophosphinite Pincer Complexes: Structure, Reactivity and Catalysis
P10	**Simon Hansen** (AK Bröring, Technische Universität Braunschweig)	Alkali corroles – Synthesis of new alkali corals and highlighting the influence of chosen substitution patterns
P11	**Bastian Kraul** (AK Bröring, Technische Universität Braunschweig)	Tin Corroles: Redox-active Photosensitisers
P12	**Marie Kaiser** (AK Burzlaff, Friedrich-Alexander-Universität Erlangen-Nürnberg)	2-(1*H*-Pyrazol-3-yl)phenol: A nice toy for coordination chemistry
P13	**Seunghyeon Nam** (AK Burzlaff, Friedrich-Alexander-Universität Erlangen-Nürnberg)	Metal complexes with Bis(4-carboxylpyrazol-1-yl)acetic Acids
P14	**Aiswarya Roby** (AK Clever, Technische Universität Dortmund)	Self-Assembly of Functional Cages based on Co(III) Salphen Complexes
P15	**Lars Hebenbrock** (AK Clever, Technische Universität Dortmund)	Photoredox-active Coordination Cages
P16	**Agi Kishore** (AK Comba, Universität Heidelberg)	Development of a Differential Sensing Platform from Metallo-Miniproteins
P17	**Rejith Raj Radhamani** (AK Comba, Universität Heidelberg)	A μ-oxo bispidine diiron(III) mediated selective halogenation of alkanes

Poster #	Presenting Author	Abstract Title
P18	**Philippe de Bary** (AK Daumann, Heinrich-Heine-Universität Düsseldorf)	Promethium-147: Supporting Growth and Enzymatic Function in Lanthanide-Dependent Bacteria
P19	**Sarah Luciana Hügel** (AK Daumann, Heinrich-Heine-Universität Düsseldorf)	Synthesis and Affinity Studies of the structurally–modified Lanthanophore Methylolanthanin
P20	**Tim Diedrich** (AK Enders, Universität Heidelberg)	Electronic and Magnetic Properties of a true Square-Planar Ferrous Phthalocyanine and its Reactivity
P21	**Felix Braun** (AK Gade, Universität Heidelberg)	Carbon-Carbon Bond Activation at Chromium(I): An 11-Electron Complex Cleaving Dialkynes
P22	**Tim Bruckhoff** (AK Gade, Universität Heidelberg)	(PNP)-stabilized Mononuclear, Homo- and Heterodinuclear Group 10 M(I) Complexes
P23	**Maximilian Böhm** (AK Glaser, Universität Bielefeld)	The Methyl Effect: The Influence of Methyl Groups in Complexes with 2,7-Disubstituted 1,8-Naphthalenediol Ligands
P24	**Christoph Bendel** (AK Greb, Ruprecht-Karls-Universität Heidelberg)	Isolation of an Aluminum-Stabilized Aminonitrene
P25	**Senta Judith Kohl** (AK Greb, Universität Heidelberg)	Nitrogen Monoxide and Calix[4]pyrrolato Aluminate: Structural Constraint Enabled NO Dimerization
P26	**Alexandra König** (AK Heinze, Johannes Gutenberg-Universität Mainz)	The First NIR-II Luminescent Vanadium(II) Complex with a 0.59 µs Lifetime in D_2O
P27	**Julian Neuner** (AK Heinze, Johannes Gutenberg-Universität Mainz)	$[Cr(tpPO)]^{3+}$ – a highly photooxidizing and photostable photoredox catalyst
P28	**Fangfang Nie** (AK Herres-Pawlis, RWTH Aachen)	New (chiral) heteroscorpionate copper-nitrene complexes for the aziridination of styrene
P29	**Martin Schäfer** (AK Herres-Pawlis, RWTH Aachen)	DFT- and ML-Supported Catalyst Design for the Ring-Opening Polymerization of Lactide
P30	**Maxi Liesa Heldner** (AK Hierlmeier, Julius-Maximilians-Universität Würzburg)	Cyclodimerization of Internal Alkynes via Photoinduced Titanium Catalysis
P31	**Carmen Luisa Maria Henel** (AK Himmel, Ruprecht-Karls-Universität Heidelberg)	New guanidino-functionalized aromatics (GFAs) with secondary amines as coordination spheres
P32	**Franka Kreis** (AK Himmel, Ruprecht-Karls-Universität Heidelberg)	Heteroleptic complexes with two different types of redox-active ligands
P33	**Johannes A. Hlina** (AK Hlina, Technische Universität Graz)	Catalytic Application of Rare-Earth/Group 10 and 11 Metal Complexes
P34	**Arnd Fitterer** (AK Holthausen, Goethe Universität Frankfurt)	Electronic Structure of a Singlet Platinacarbene as Intermediate in an *in-Crystallo* Wolff Rearrangement

Poster #	Presenting Author	Abstract Title
P35	**Zisis Papadopoulos** (AK Karges, Ruhr-Universität Bochum)	Excitation of a Ru(II) Polypyridine Complex with Red Light as a Photocatalyst in Cancer Cells
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P40	**Robin Riskes** (AK Kreidt, Technische Universität Dortmund)	DOTA-based photoswitchable ligands for lanthanoids
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P44	**Sebastian Schicktanz** (AK Kunz, Eberhard Karls Universität Tübingen)	Intramolecular oxidative addition of halide-functionalized bimca-ligands
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Poster #	Presenting Author	Abstract Title
P52	**Simon P. Muhm** (AK Munz, Universität des Saarlandes)	The Hexaphenyl-1,2-diphosphoniumdication $[Ph_3P–PPh_3]^{2+}$
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P58	**Marius Müßler** (AK Rau, Universität Ulm)	Cucurbituril-based light switch assemblies with Ruthenium Complexes
P59	**Evgenia Ryndin** (AK Rau, Universität Ulm)	Synthesis and DNA intercalation of novel iron complexes
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P64	**Viktoria Puea Bothe** (AK Roşca, Universität Heidelberg)	Improving Selectivity in Iron Promoted Catalysis of Azides *via* a Hemilabile σ-Donor in the Second Coordination Sphere
P65	**Johannes Zeh** (AK Roşca, Rennes Institute of Chemical Sciences)	Synthesis and characterization of low-valent phosphino-α-iminopyridine iron imido complexes
P66	**Pratibha Jakhar** (AK Sarkar, Freie Universität Berlin)	Cyclopentadienyl Cobalt Diamidobenzene Complex for Catalytic Ammonia Oxidation to Dinitrogen
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Poster #	Presenting Author	Abstract Title
P68	**Victoria V. L. Müller** (AK Schatzschneider, Julius-Maximilians-Universität Würzburg)	The Role of Ancillary Ligands in Cyclometalated Iridium(III) Complexes with a [3+2+1] Coordination Sphere
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P79	**David Ocklenburg** (AK Van Craen, Technische Universität Dortmund)	Tailored charge-neutral self-assembled L_2Zn_2 container for taming oxalate
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P83	**Florian Walter** (AK Weber, Friedrich-Schiller-Universität Jena)	Preparation of nanoparticles by incorporation of spin crossover coordination polymers in a block-copolymer matrix
P84	**Andres Gonzales** (AK Werncke, Universität Marburg)	Low-coordinate iron organoazide complexes

Poster #	Presenting Author	Abstract Title
P85	**Lea Bauer** (AK Winter, Universität Konstanz)	Luminescent BOPHY platinum complexes
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Design and Synthesis of Cyclam Based Complexes for Oxygen Evolution Reactions

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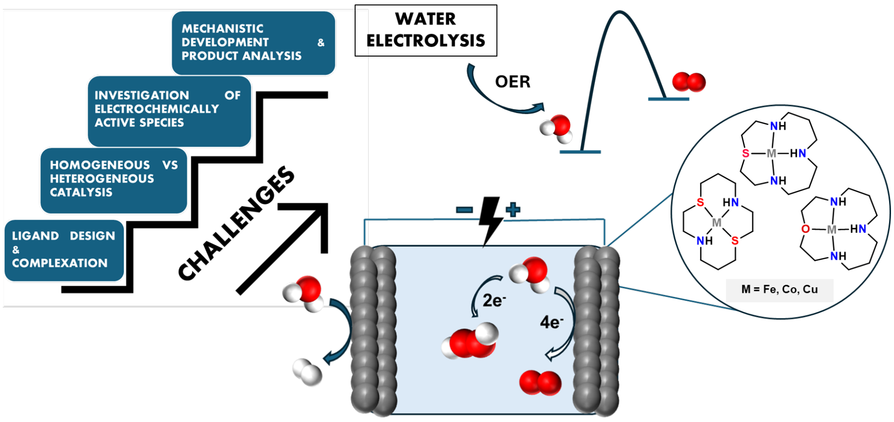
Global warming continues to drive natural disasters, with CO_2 emissions reaching 37.4 gigatons in 2023, a 1.1% rise primarily fuelled by coal and gas use in developing nations. To counteract this the IEA projects that renewable energy will supply over 60% of global energy by 2050, with solar power contributing about one-fifth.[1] Among renewable energy strategies, water splitting in fuel cells using sustainably generated electricity emerges as a promising approach for clean energy production. This method relies on efficient design and the use of earth-abundant electrocatalysts. The production of hydrogen (H_2) and oxygen (O_2) is hindered by a high energy requirement (237.2 kcal mol^{-1} at 298K). The oxygen evolution reaction, which involves complex multi-electron transfer during water oxidation, poses significant kinetic challenges and demands additional energy (E_0 = 1.23V vs RHE). To address these obstacles, advancing low-cost catalysts and integrating renewable electricity are essential.[2]

Here, we present the design, synthesis, and catalytic evaluation of cyclam (1,4,8,11-tetraazacyclotetradecane)-based metal complexes for OER. Cyclam, with its tetradentate coordination environment and tuneable electronic properties, offers a robust platform for stabilizing transition-metal centres essential for catalytic activity under oxidative conditions.

Using established procedures [3] different cyclam-based ligands with heteroatom substitution (N, S, O) and altered geometry (isocyclam) are synthesised and the electrochemical behaviour of different metals (Fe, Co, Cu) with these macrocyclic ligands are examined. Water oxidation ability is investigated in different aqueous buffer systems to gain insights into the interactions between ions and the electrode surface, the formation of metal oxides, and the influence of pH. These parameters were optimized to develop an effective molecular, homogeneous catalyst with efficient activity.



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(Hetero)anilines from Dinitrogen via Tungsten Nitrides

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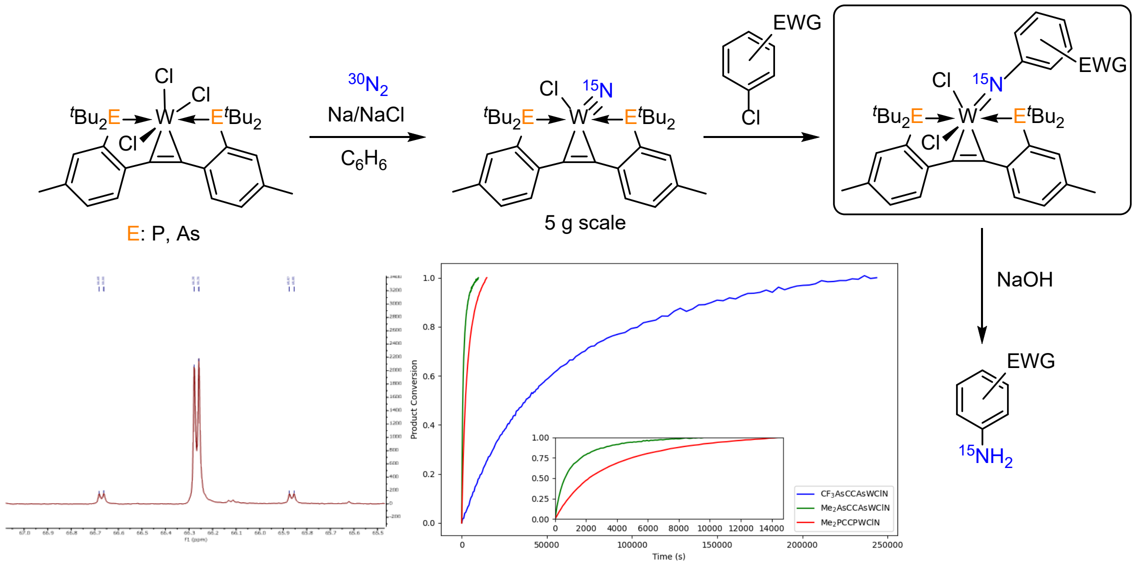
Activating dinitrogen by means of binding and splitting has been an ongoing point of interest in coordination chemistry for decades.[1] By the growing number of examples and the better understanding of the nature of these compounds, the focus is nowadays set on stochiometric functionalization reactions for the preparation of (isotopically labeled) *N*-containing fine-chemicals.[2]

In our group, we recently reported that an [AsCCAs]-coordinated tungsten complex effectively splits N_2. The resulting tungsten nitride may be converted to collidine by an “O-for-N swap”.[3] To further investigate the nucleophilic nature of this tungsten nitride, the reaction with electrophilic aromatic substrates was probed. These reactions furnished imido complexes of the type [AsCCAs]$WCl_2{}^{15}NAr$, which could be reacted with sodium hydroxide to release ^{15}N-labeled anilines and heteroanilines. To monitor these reactions by NMR spectroscopy and to avoid the use of toxic arsenic, a protocol to synthesize the *phospha*-analog [PCCP]$WCl^{15}N$ from dinitrogen was developed.[4] Differences and similarities between the [AsCCAs]- and [PCCP]-coordinated complexes are presented here.



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Photocatalytical Reactions using CCC-Cobalt(III)-and CCC-Iron(II)-Complexes

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The use of photoredox catalysis is critical as it can enable previously elusive transformations to access value-added products for pharmaceuticals, etc. [1,2] The use of second- and third-row transition metal complexes such as Ru^{II}- or Ir^{III}-polypyridyl species as photoredox catalysts is already established for various reactions given their visible light excitation and long-lived excited states.[1] However, for continued and sustainable application, first-row metals like iron or cobalt are preferred, but the challenge with these metals lies in their lower ligand-field splitting, leading to shorter excited-state lifetimes due to decay processes. To lengthen the lifetimes, the MC-states can be destabilized by using strong σ- donor ligands and supporting octahedral geometry while MLCT-states can be stabilized with π- acceptor ligands or by electronic delocalization. Additionally, the Marcus theory, specifically the Marcus-inverted region can be leveraged for longer lifetimes of the cobalt complexes as an increase in the excited-state energy correlates with a rise of the activation energy barrier for the decay.[1]

Here, we report testing the EvoluChem PhotoRedOx Box TC™ photoreactor and the first experiments on boronic acid hydroxylation with CCC-Co(III)- and Fe(II)-complexes (Fig. 1). Future work will explore the effect of different metal centers and ligands on the photoredox properties.

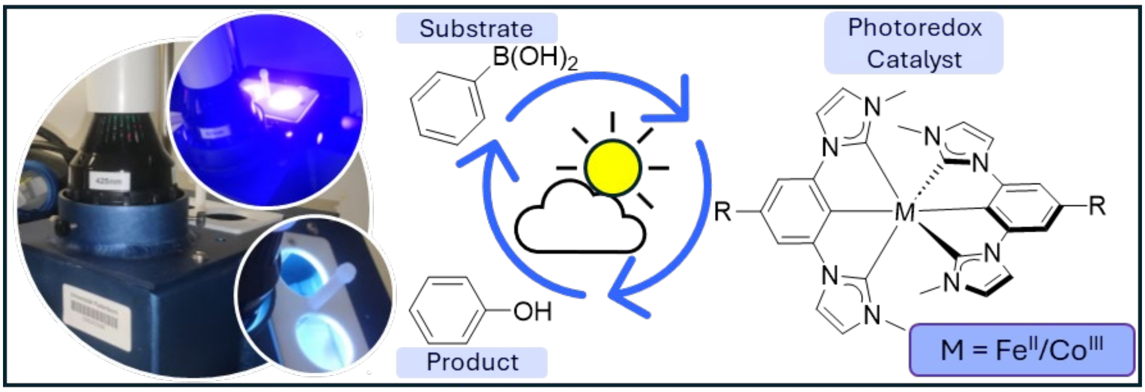

Figure 1: Schematic representation of the investigated photoredox catalytic reaction utilizing Fe(II) and Co(III) complexes as catalysts

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Investigating the influence of functional groups on bidentate Co(III)-species

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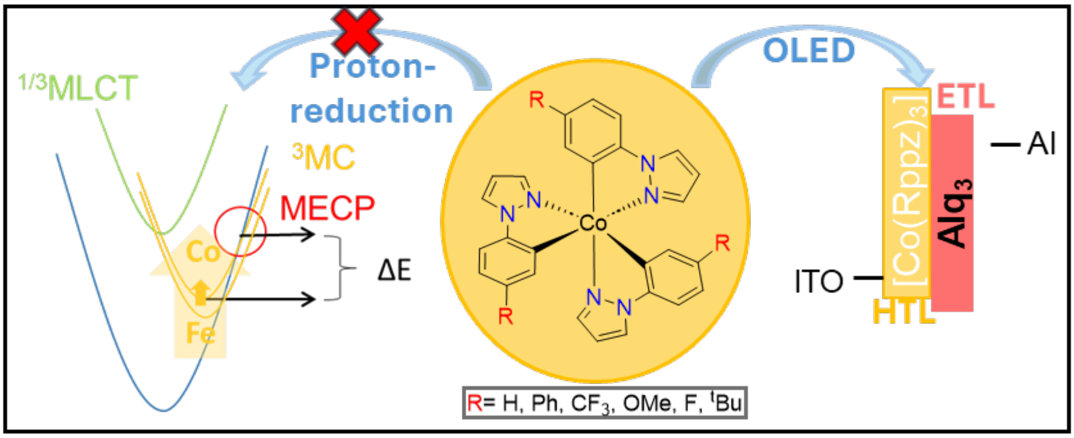
The growing need for renewable resources highlights the environmental impact of fossil fuel use. Interest in energy sources like molecular hydrogen (H_2) has risen due to its production via water splitting powered by solar energy. A key challenge is identifying a suitable photosensitizer (PS). While traditional options include Ru^{II}, Os^{II}, and Ir^{II} transition metal complexes, focus is shifting to inexpensive, earth-abundant first-row transition metals, such as cobalt.[2,3]

A suitable PS requires a long-lived metal-to-ligand charge transfer (MLCT) state for water splitting, but cobalt's small ligand field splitting causes rapid deactivation to the metal-centered (MC) state. In this work Co^{III}-bidentate species with enhanced ligand field splitting were synthesised, where pyrazole (π-acceptor) stabilises the MLCT state, and a phenyl group (σ-donor) destabilises the MC state.[1,2,3]

Herein, we report the synthesis of Co(III)-cyclometalated complexes (Fig. 1) linked to phenyl-pyrazole ligands with various electron-donating and electron-withdrawing groups. The complexes exhibit ligand-centered (LC) absorption below 300 nm and mixed MLCT and MC absorption, as confirmed by TD-DFT calculations. Despite a lack of emission, attributed to a small calculated ^{3}MC-MECP energy gap, the complexes showed promising results as HTL layers in OLED systems, particularly with π-extended moieties. Future work will focus on tuning these systems for OLED applications.



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Development of a reaction-based zinc sensor

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Zinc is the second most abundant trace element in the human body and performs a variety of different tasks, including signal transduction in the central nervous system. Studies show links between disordered zinc homeostasis and neurodegenerative diseases like Alzheimer disease. However, these processes are only poorly understood on a molecular level, which is an urging problem in an aging society.[1]

To enhance our understanding of the molecular processes, fluorescent zinc sensors are valuable tools. While most sensor design primarily rely on the HSAB concept for zinc detection[2]; cross-sensitivities with other metal ions can occur. To address this limitation, we seek to establish a new zinc detection principle that not only incorporates the HSAB concept, but furthermore, exploits the Lewis acidity of Zn^{2+} as selectivity criteria and thus, excludes common cross-sensitivities.

This new approach (Figure 1) involves connecting a fluorophore to a receptor unit via a relatively weak bond. The binding of Zn^{2+} to the receptor weakens this bond due to its Lewis acidity, triggering its cleavage. As a result, the fluorophore is released, and, in contrast to its bound state, fluoresces, enabling the detection of zinc.

To allow the fine-tuning of the sensor properties, e.g. the emitted color or the affinity towards zinc, the design is based on a modular construction kit. On this poster, several variations of this new prototype are presented.

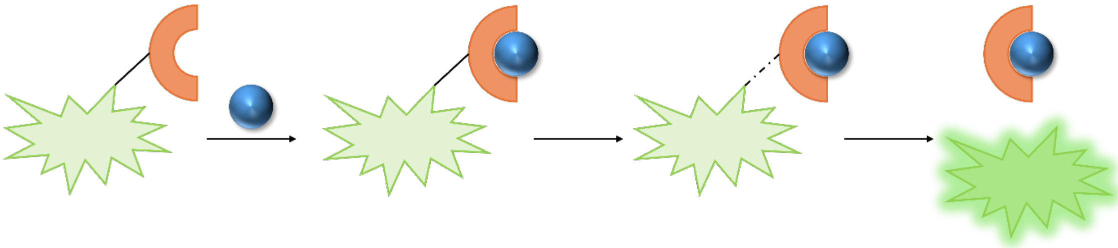

***Figure 1**: Sensor principle of the new reaction-based sensor class. The pale green piece represents the fluorophore, the orange semicircle the receptor unit. Both are linked through a relatively weak bond. Among coordination of Zn^{2+}(blue sphere), the bond is further weakened and consequently cleaved, which allows fluorophore to fluoresce.*

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Encapsulating ligands for the stabilization of μ_4-oxido copper clusters

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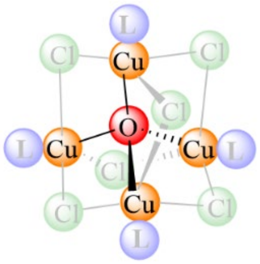
Multinuclear copper complexes are able to release more than one redox equivalent at once and therefore, are of special interest for catalysis of multi-electron reactions. In nature, such multinuclear copper catalysts perform electronically challenging reactions under mild conditions. Such an example is the N_2O reductase, which couples four Cu^{2+} and two S^{2-} ions in its active center. To detail, a μ_4-sulphido unit {**Cu_4S**} is coupled to a μ_2-sulphido ligand.[1] This special structure enables the metalloenzyme to convert nitrous gas, which is known as one of the most harmful greenhouse gases, into nitrogen and water. Inspired by such naturally occurring catalysts, we seek to create similar μ_4-oxido copper clusters [$Cu_4OCl_6L_4$] with the central {**Cu_4O**} motif and to investigate their reactivity in oxidation reactions.



Scheme 1: Schematic representation of a μ_4-oxido copper cluster [$Cu_4OCl_6L_4$] (L = ligand).

Indeed, in recent studies, such μ_4-oxido copper clusters were able to catalyze the formation of adipic acid starting from cyclohexane and H_2O_2.[2] The analogous industrial process needs harsh conditions, whereas the multinuclear copper catalyst performs this reaction under mild conditions. However, a remaining challenge is the stability of the catalyst, which easily decomposes during the catalytic process due to its sensitivity towards water. To enhance its stability, we sought to use encapsulating ligands instead of monodentate ligands. For this, we designed ligands similar to those that have already been used for the preparation of artificial iron sulphur clusters.[3]

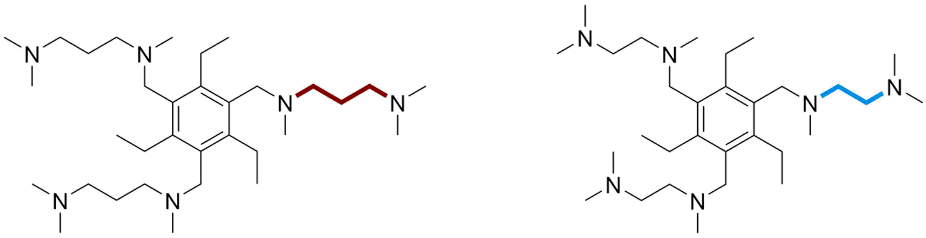


Figure 1: Encapsulating ligands used in this study.

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Exploring the Coordination Chemistry of a Phosphaalkene-based Monoanionic P,N,P-type Ligand

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Phosphinopyridine P,N- and iminopyridine N,N-type ligands have been ubiquitously used in coordination chemistry and their application in catalytic processes has been demonstrated.[1] In contrast, apart from Geoffroy‘s studies of a pyridine-based phosphaalkene (PA) P,N-type Cu complex,[2] only very few examples of Ru P,N-type complexes were reported by Cain and co-workers.[3] Our group has recently demonstrated the synthesis of π-extended P,N-type PA 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 C−H bond activation at the o-*t*Bu group of the Mes*-group. Moreover, the Ir(I) P,N-type PA complex has been shown to be a good pre-catalysts for the Guerbet-type upgrading of EtOH to *iso*-butanol.

To further extend the library of P,N,P-type PAs, we have been interested to use carbazole-based dialdehyde. This afforded after a phospha-Wittig reaction with Mes*P(PMe$_3$) a P,N,P-type ligand (Figure 1a), which could be deprotonated to give its anionic variant (Figure 1b). When this *bis*-PA ligand was treated with one equiv. [Rh(cod)Cl]$_2$, two dinuclear Rh(I) complexes were obtained. One of the complexes showed two CH-activated Mes*-groups in a bisphospholene complex, while the other is a bis-PA complex with the PA-units in three different coordination modes with respect to Rh(I). Furthermore, the reactivity of the P,N,P-type bis-PA platform towards Zr and Hf precursors will be presented.

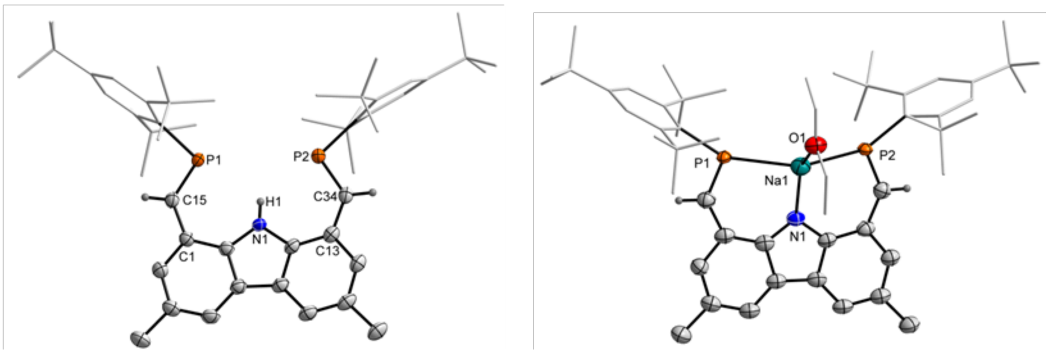

Figure 1: Molecular structure of carbazole-based P,N,P–type bis-PA ligand (left) and its Na salt (right).

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

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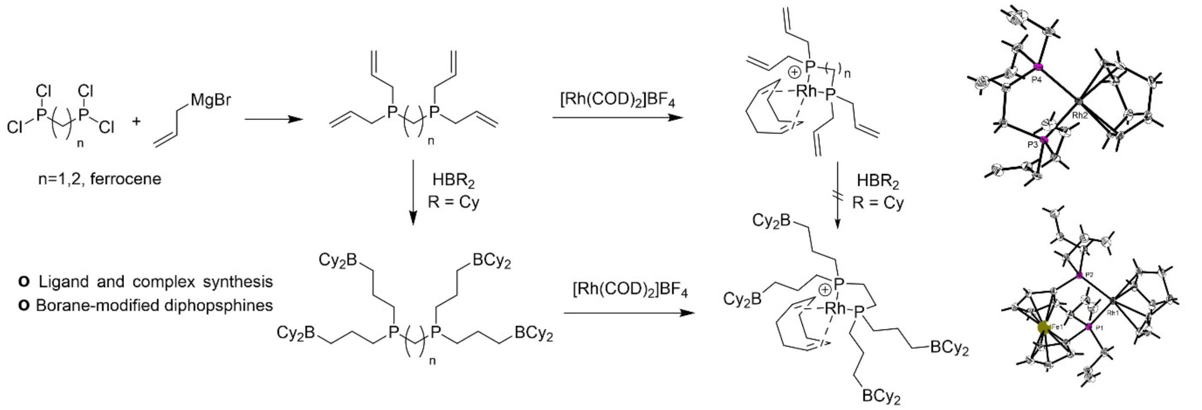
The isovalence electronic analogy between B-N and carbon-based compounds and the expanding interest in polymeric materials based on main-group elements makes boron-nitrogen based polymers interesting targets. B-N polymers are promising compounds for applications as preceramics or as nonlinear optical materials.[1] Catalytic dehydropolymerisation of primary amine boranes provides a promising atom efficient route to access these polymers. Compared to traditional methods such as reductive coupling or high temperature condensation this method allows to adjust polymer properties.[2] Several groups have demonstrated that primary amine-borane adducts can be dehydrocoupled using various transition metal complexes to afford a linear poly(aminoboranes).[3] In recent years, our group focused on group 8/9 complexes bearing phosphorus-based pincer ligands. Recently, we reported the use of Rh(I) PNN pincer complexes for dehydrocoupling of amine boranes.[4] Cationic Rh(I) diphosphine complexes were first studied by the Weller group and showed good activity for the dehydropolymerisation of methylamine borane.[5]



Here, we report the synthesis new phosphine ligands with introduction of Lewis acidic borane units in the secondary coordination sphere [6], as well as their complexation with Rh, producing a set of new Rh(I) complexes that could be used as catalysts for the dehydrocoupling of amine boranes. The role of the borane functionality for the activity and selectivity of the systems is discussed.

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Iridium Triazolophosphinite Pincer Complexes: Structure, Reactivity and Catalysis

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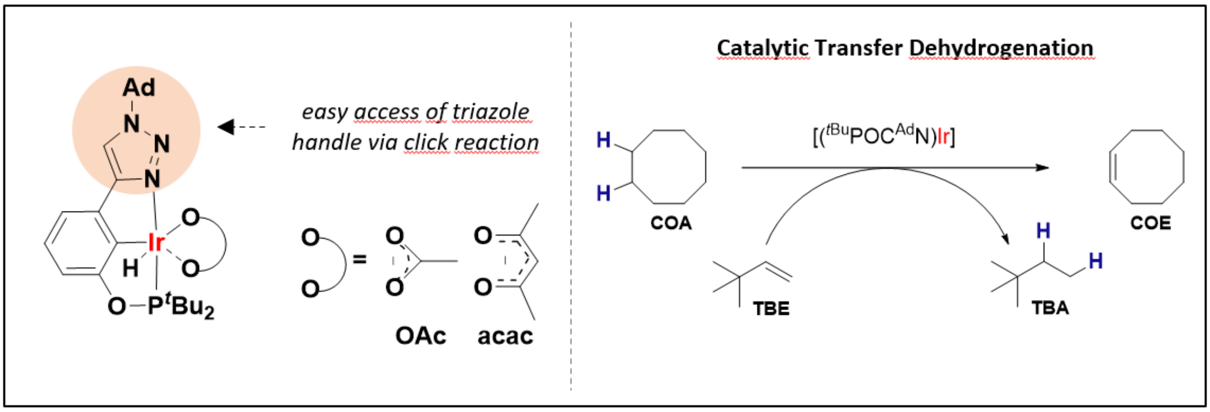

Iridium pincer complexes have been reported as excellent catalysts for transfer dehydrogenation of alkanes to obtain the corresponding alkenes, [1,2] which can be subsequently functionalized to various other derivatives. [3] Herewith, we describe a new iridium pincer catalyst with an unsymmetrical ^{tBu}POC^{Ad}N pincer ligand having an adamantyl (Ad) substituted-triazole arm, that can be accessed via Cu-catalyzed click reaction and a phosphinite handle. The synthesis of Ir-pincer complexes with different oxygen donor ancillary ligands was accomplished by employing the appropriate Iridium metalation precursors. The complexes [(^{tBu}POC^{Ad}N)Ir(H)(OAc)] complex and a [(^{tBu}POC^{Ad}N)Ir(H)(acac)] complex could thus be generated, and were characterized by XRD and NMR. Reactivity of these complexes was also studied, especially with carbon monoxide that gave further insights into the structure of the pincer backbone. These complexes were employed for the catalytic transfer dehydrogenation of alkanes and saturated heterocycles using *tert*-butlylethylene as the hydrogen acceptor.

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Alkali corroles – Synthesis of new alkali corals and highlighting the influence of chosen substitution patterns

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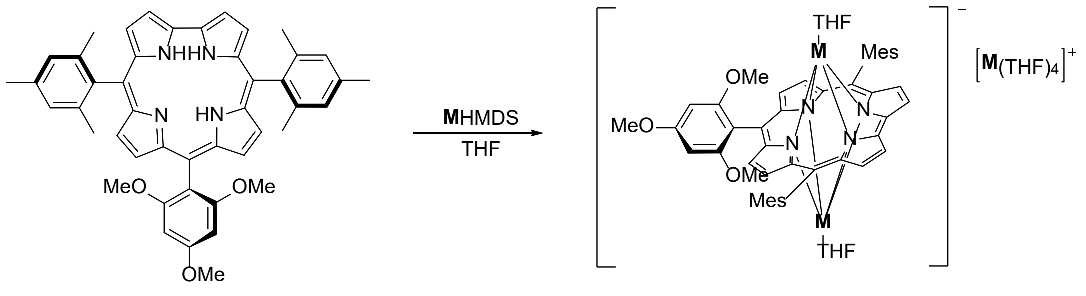
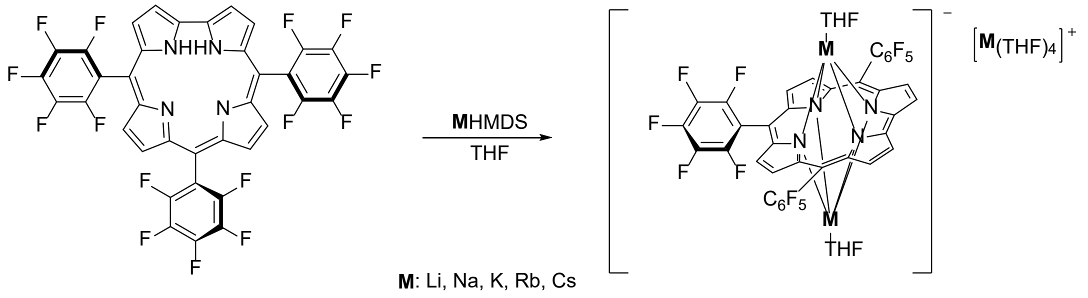
In the porphyrinoid field corrole macrocycles are used to stabilze coordinated metals in high oxidation states due to a 18-π-system and trianionic nature. Structures containing alkali or early transition metals have hitherto remained scarce.[1] Only lithium corroles are known and used for salt metathesis for obtaining early transition metals.[2]

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

The poster will present ongoing research and results on the synthesis of alkali corroles emphasizing on different substitution patterns and their properties.





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Tin Corroles: Redox-active Photosensitisers

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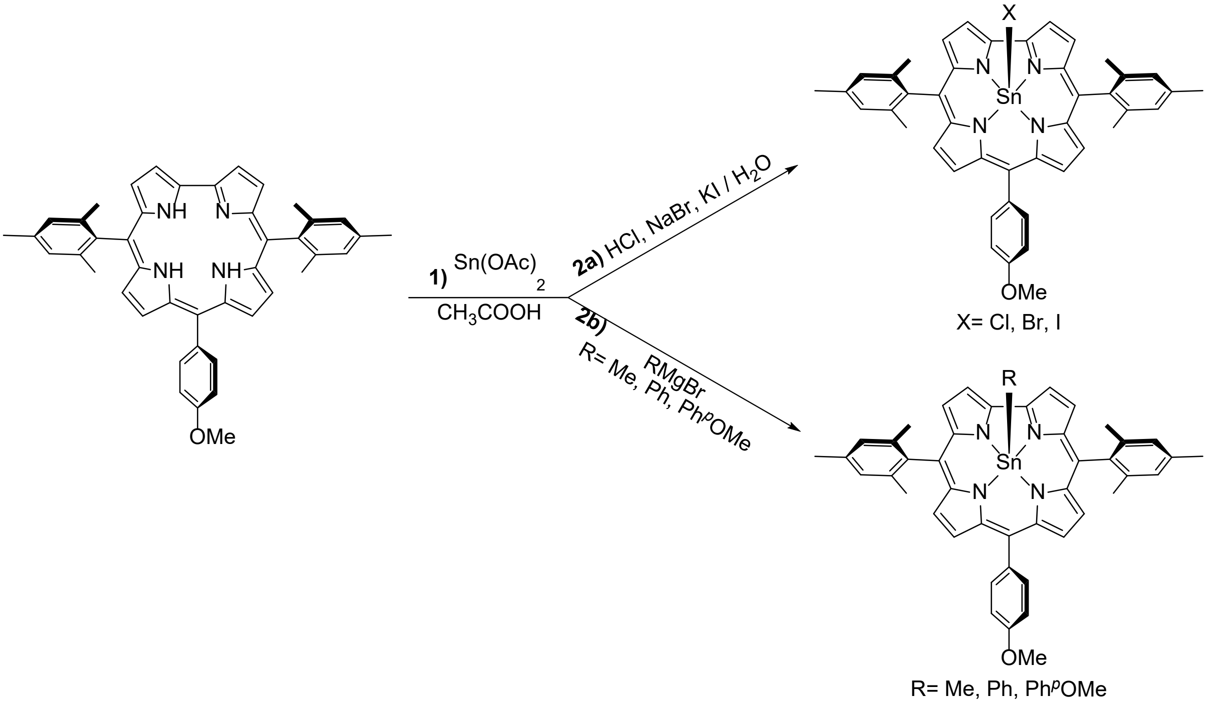
Due to their electron-rich 18π system and their trianionic character, corrole macrocycles are capable of stabilizing metals in high oxidation states from +3 to +6.[1] This feature has successfully been used for numerous 3d and 4d transition metal complexes. On the other side, main group metal corroles[2,3] are not quite as common, and their redox behavior has so far only been investigated in a small number of antimony derivatives.
Tin corroles are potentially redox active and show great potential for catalysis[4] as well as singlet oxygen photosensitisers.[5] Ongoing research and first results on the synthesis and characterisation of tin corroles with different axial ligands will be presented on the poster.



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2-(1*H*-pyrazol-3-yl)phenol: A nice toy for coordination chemistry

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The bidentate ligand 2-(1*H*-pyrazol-3-yl)phenol is easily available starting from chromone.[1] In an attempt to broaden the spectrum of bis(pyrazol-1-yl)acetato ligands, a reaction between two equivalents of this pyrazole and dibromoacetic acid was attempted. However, the insertion happened intramolecularly, giving rise to the novel bidentate *N*,*O*-ligand 5*H*-benzo[*e*]pyrazolo[1,5-*c*][1,3]oxazine-5-carboxylic acid. To investigate the coordinating behavior of both ligands we laid the focus on complexation reactions with divalent transition metal ions, mainly zinc(II) and copper(II).

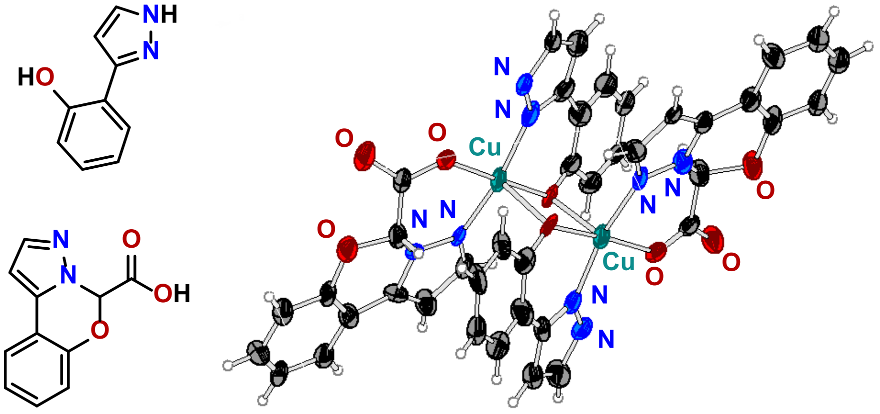

Figure 1 Ligand and copper(II) complex derived from 2-(1*H*-pyrazol-3-yl)phenol.

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Metal complexes with Bis(4-carboxylpyrazol-1-yl)acetic Acids

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The poly(pyrazolyl)borate, commonly referred to as the scorpionate ligand, was firstly synthesized by Trofimenko back in 1967.[1] In 1999, A. Otero and his group expanded this class of scorpionate ligands by the bis(pyrazol-1-yl)acetic acids.[2] More recently, bis(4-carboxylpyrazol-1-yl)acetic acid and bis(3,5-dimethyl-4-carboxylpyrazol-1-yl)acetic acid were successfully synthesized, resulting in improved water solubility.[3,4]

Due to the significant advantage of the ligand, heteroleptic metal complexes bearing these bis(pyrazol-1-yl)acetato ligands were synthesized, such as [Ru(H_2bcpza)Cl$(CO)_2$] and [Re(H_2bcpza)$(CO)_3$].[3] Herein, we report on the synthesis and characterization of additional heteroleptic metal complexes featuring rhenium(VII) and vanadium(IV) coordinated by these ligands. Moreover, the coordination chemistry of the new bis(3,5-dimethyl-4-carboxylpyrazol-1-yl)acetic acid ligand will be discussed.[4]

Figure1. Bis(carboxypyrazol-1-yl)acetic acid and Bis(3,5-dimethyl-4-carboxypyrazol-1-yl)acetic acid: Scorpionate ligands for homoleptic and heteroleptic transition metal complexes.

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Self-Assembly of Functional Cages based on Co(III) Salphen Complexes

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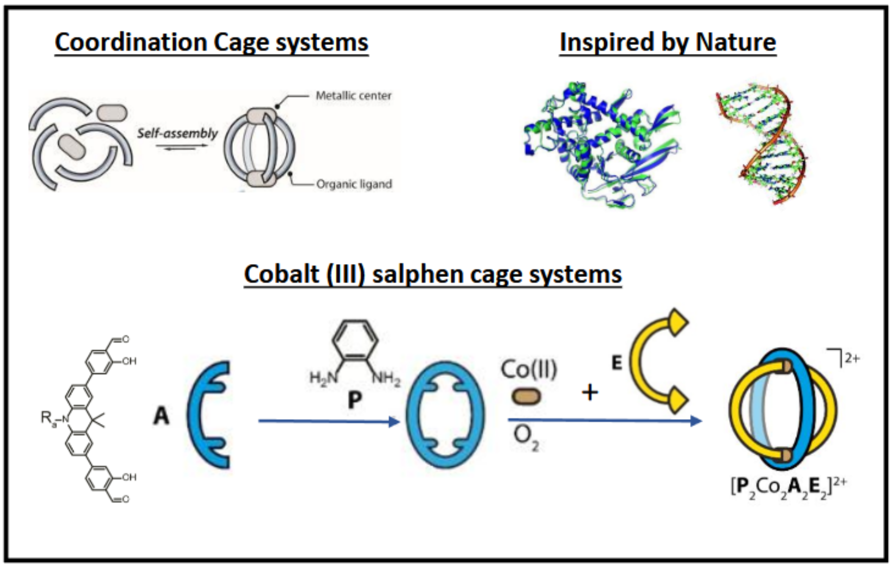
Inspired by nature, where protein folding and DNA formation rely on weak interactions, we aim at forming discrete nanoscale self-assembled systems, based on dynamic interactions such as hydrogen bonding and metal-ligand coordination. Furthermore, functionality can be introduced into these supramolecular systems by either using functionalized ligands or carefully chosen metal centers. Pd(II) cages are well known for their structural dynamicity and kinetic lability making them applicable in stimuli-responsive complex systems and self-sorting cascades. But there are certain other application areas, which require inert coordination environments and Cobalt(III)-based cages are one of the best choices for these. Herein, the assembly is done with labile Cobalt (II) cations, which are subsequently readily oxidized without a change in the coordination geometry preference to give inert Co(III) systems. The first aim of this study was to synthesize Cobalt(III)-based cage systems and then to study their ligand exchange kinetics, thus checking for the structural and chemical stability. Organic ligands were synthesized and then cages were self-assembled by adding Cobalt(II) salts, followed by aerobic oxidation. Formation of cages was followed by NMR spectroscopy in solution, mass spectrometry in the gas phase and by single crystal X-ray studies in the solid state. Further plans include the examination of ligand exchange between Pd(II) and Co(III)-based cages in complex systems and the incorporation of donor/acceptor functionality for studying cage-based charge separation.



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Photoredox-active Coordination Cages

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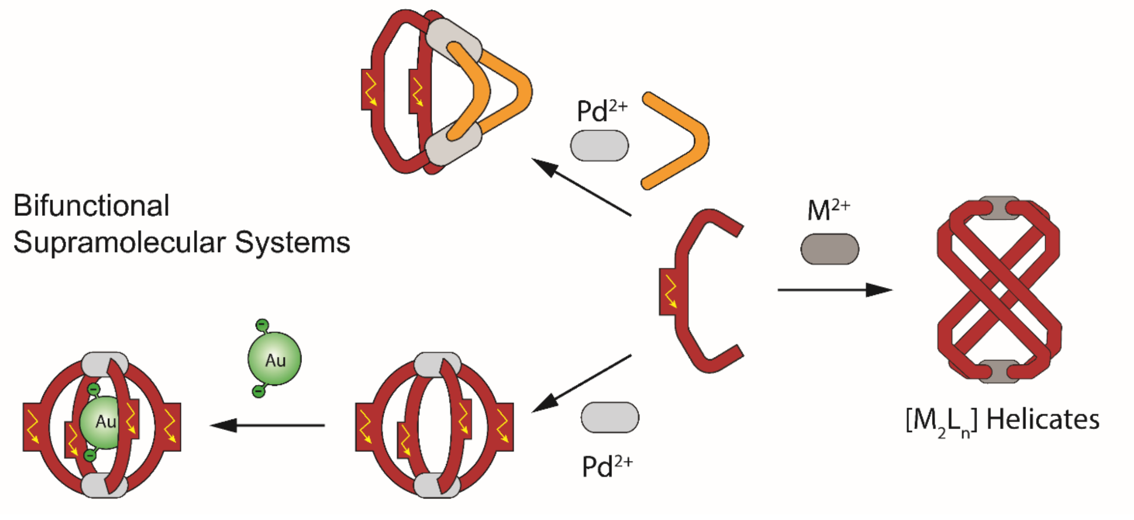
In nature, enzymes use their three-dimensional structure to create a distinct microenvironment equipped with substrate binding sites and reactive functional groups to perform highly selective and efficient catalysis. The self-assembly of organic ligands and metal-ions into supramolecular cages and capsules is an approach to mimic these properties by creating an inner environment that is different from bulk solution.[1] Through the use of shape-complementary ligands we can achieve a non-statistical self-assembly of multiple different ligands into a single coordination cage, which can be used to increase the number of functional moieties.[2] Additionally, further complexity can be achieved by encapsulation of a functionalized guest molecule into the cavity of the cage. In our research we investigate Pd(II)- and Zn(II)-based assemblies of photoredox-active ligands that can be combined with e.g. H-bond donors, chiral moieties or transition-metal catalysts to create multifunctional systems. These systems are studied towards their photophysical and electrochemical properties as well as their performance as catalysts in organic transformations. We could show guest encapsulation of an Au(I) catalyst in a Pd_2L_4 coordination cage based on photoredox-active ligands as well as the non-statistical formation of $Pd_2A_2B_2$ cages. Furthermore, the formation of M_2L_n (n=2-4) helicates with these ligands and M(II) metal-ions is studied.



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Development of a Differential Sensing Platform from Metallo-Miniproteins

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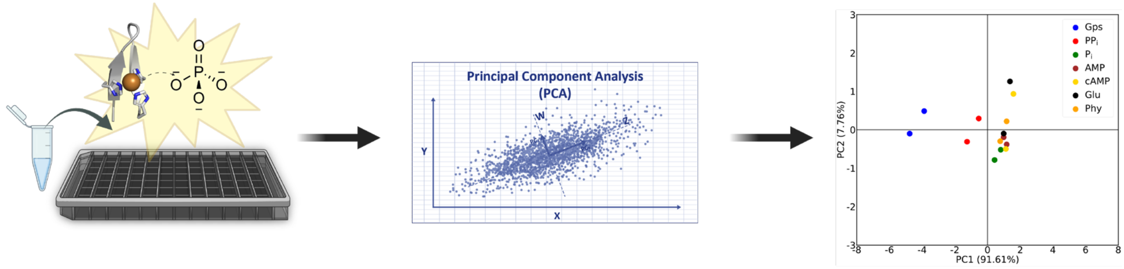
Of the five human senses, taste and smell are designed to detect chemical substances. The individual components of odor and taste interact differently with a myriad of receptors, creating a unique pattern that is stored in the brain and recalled upon subsequent encounter, leading to recognition.[1] Mimicking this molecular recognition of nature through the concept of differential sensing using *de novo* designed synthetic peptides is still unexplored. In this project, we use an array of twelve metal-binding β-hairpin peptides derived from the Trpzip2 peptide, a 12 amino acid β-hairpin peptide with a unique tertiary structure,[2] to differentiate biologically relevant analytes. The metal binding site on the polar surface of Trpzip2 was engineered by replacing the three amino acids with different combinations of histidine, serine and glutamate, which were then equilibrated to bind to three different metal ions; Cu^{2+}, Zn^{2+} and Ni^{2+}. An approach similar to the Indicator Displacement Assay (IDA) was used, but instead of displacing an indicator on a receptor in the presence of an analyte, we relied on the change in tryptophan fluorescence, as these metallopeptides interact differently with the added analytes. The results obtained were then analyzed using Principal Component Analysis (PCA). The simplicity of the system, together with the advantage of being able to tailor the chemistry and structure of the peptides as required, opens up a huge potential for our system, which can then be used in the future to differentiate small inorganic molecules and complex sugar molecules, even cell lines.



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A µ-oxo bispidine diiron(III) mediated selective halogenation of alkanes

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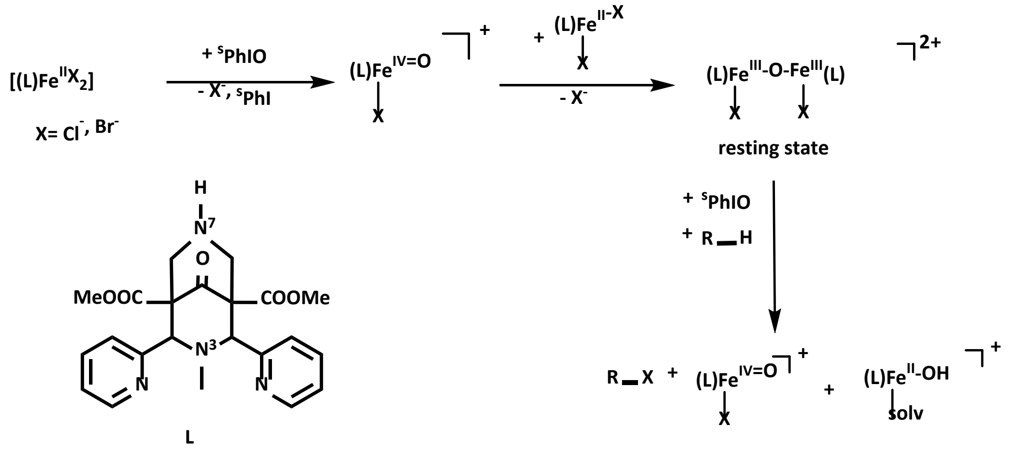
Non-heme iron enzymes are known to oxidize a range of substrates by catalyzing the activation of dioxygen. The iron(IV)-oxido species are generally key reactive intermediates in non-heme iron enzymes for performing different natural transformations like halogenation, hydroxylation or olefin epoxidation. Spectroscopic studies implicate high-valent diiron species as intermediates in the oxidation chemistry of the diiron centers in methane monooxygenase (MMO) and ribonucleotide reductase (RNR), while mononuclear iron(IV)-oxido units have been proposed as the oxidant for several mononuclear nonheme iron enzymes.[1,2] Our synthetic efforts to obtain models for such high-valent intermediates have yielded $[X(L)Fe^{III}\text{-}O\text{-}Fe^{III}(L)X]^{2+}$, ($X=Cl^-$ and Br^-) as a resting state, where L is a bispidine ligand.[3] This resting state complex has been successfully synthesized by the stoichiometric oxidation of $[(L)Fe^{II}X_2]$, ($X=Cl^-$ and Br^-) and is fully characterized. Reactivation of $[X(L)Fe^{III}\text{-}O\text{-}Fe^{III}(L)X]^{2+}$, ($X=Cl^-$ and Br^-) with iodosylbenzene (sPhIO) in the presence of cycloalkanes as substrates resulted selectively in halogenation products. For a detailed understanding of the mechanism of the selective halogenation of alkanes, a thorough computational study was conducted.



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Promethium-147: Supporting Growth and Enzymatic Function in Lanthanide-Dependent Bacteria

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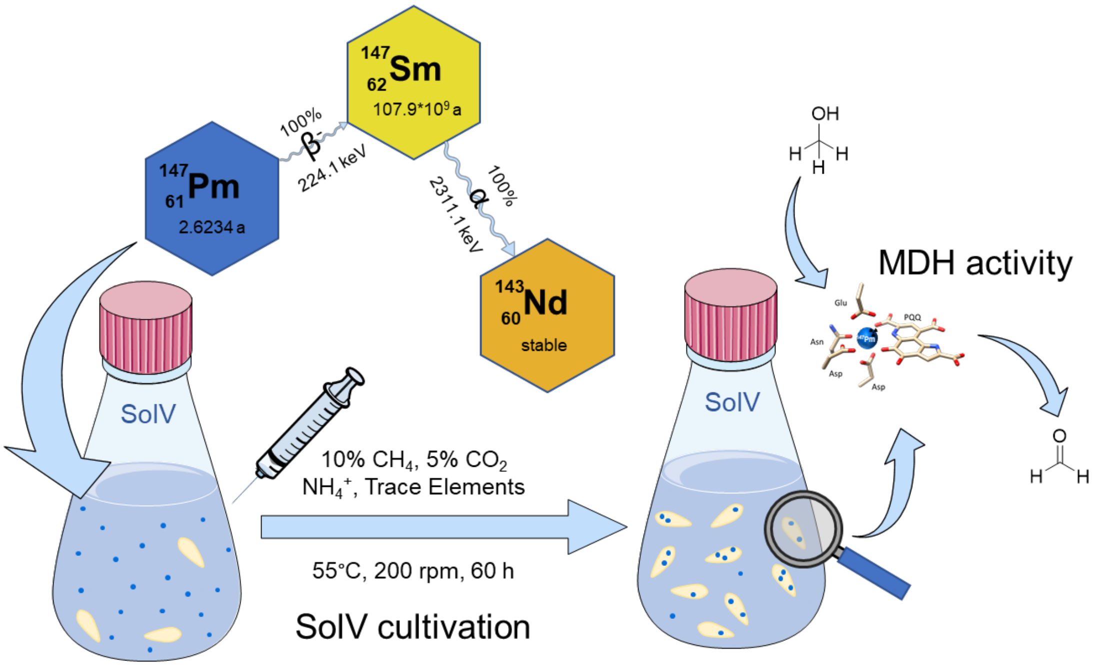
Lanthanides have recently been recognized as essential cofactors in methanotrophic and methylotrophic bacteria, playing key roles in enzymatic processes.[1] These bacteria utilize lanthanides to activate methanol dehydrogenase (MDH), a critical enzyme for their metabolism.[2] However, promethium, the only lanthanide that exists solely as unstable isotopes, has not previously been studied in a biological context due to its radioactivity and scarcity.

Growth studies and enzymatic assays with the acidophilic methanotroph *Methylacidiphilum fumariolicum SolV* (SolV) confirm that promethium acts as a functional cofactor in lanthanide-dependent MDH. Promethium occupies its predicted position within the lanthanide series, enabling enzymatic activity comparable to stable lanthanides. Remarkably, the β^- emissions from promethium-147 do not impair bacterial growth or metabolism.

These findings mark the first demonstration of promethium's biological relevance and highlight the adaptability of methanotrophic bacteria to utilize even radioactive lanthanides. Given strain SolV's ability to accumulate lanthanides, its successful cultivation with promethium-147 suggests potential applications in bioremediation, offering strategies for managing radioactive contamination in metal-rich environments.



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Synthesis and Affinity Studies of the structurally–modified Lanthanophore Methylolanthanin

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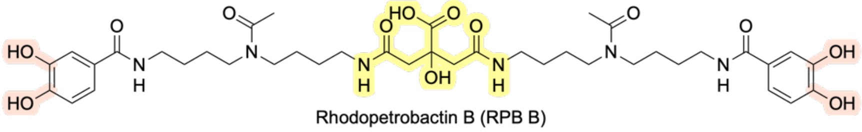
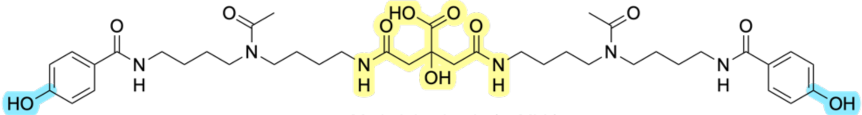
Munich, Germany

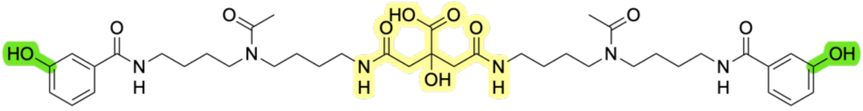
In recent years, lanthanides have gained more attention due to their indispensable role in modern technology and medicine.[1,2] However, their importance in bacterial metabolism has long been overlooked, primarily due to their limited bioavailability under physiological conditions.[3] This has led to increased interest in the hypothesis that bacteria utilize metallophores – known as lanthanophores when associated with lanthanides – to facilitate lanthanide uptake.[4] Recently, we identified and isolated methylolanthanin (MLL) from *Methylobacterium extorquens* AM 1[5] which bears structural resemblance to the siderophore rhodopetrobactin B (RPB B).[6] Surprisingly, MLL features a *para*–substituted hydroxybenzoic acid moiety whereas other phenolate–type siderophores are *ortho*–substituted. Here we present the total synthesis of MLL and its (non–natural) derivatives (e.g. *meta*–MLL) and investigate the effects of the hydroxy–groups of MLL in comparision to RPB B on its binding affinity towards lanthanides using UV–Vis spectroscopy.[7]



Rhodopetrobactin B (RPB B)



para–Methylolanthanin (*p*–MLL)



meta–Methylolanthanin (*m*-MLL)

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Electronic and Magnetic Properties of a true Square-Planar Ferrous Phthalocyanine and its Reactivity

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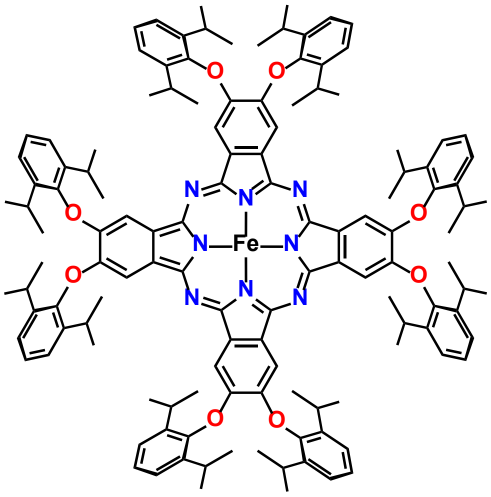
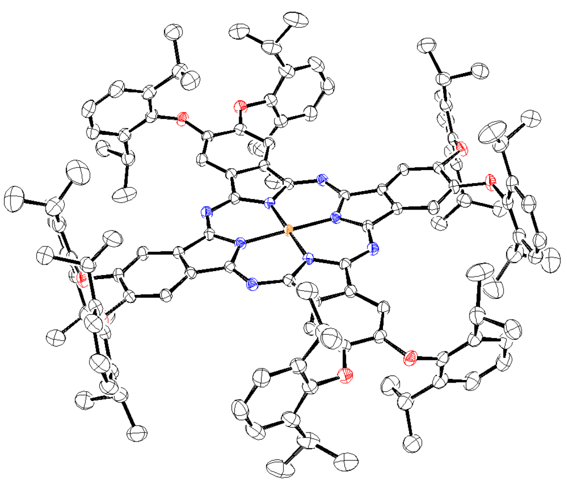
Iron in square-planar coordination can exist in different spin states and shows a wide range of reactivity, making it useful for catalysis.[1] Iron(II) phthalocyanines ($FePc^R$) are examples of such complexes with $S = 1$ spin state and large zero field splitting (*zfs*). However, most derivatives are prone to aggregation, which hinders the identification of true intramolecular electronic and magnetic properties. In addition, their low solubility makes them unsuitable for NMR studies. This can be overcome by incorporating bulky substituents that prevent stacking of the planar phthalocyanine core.[2] This allows to study the true molecular properties by various techniques like paramagnetic NMR (*pNMR*), EPR or Mößbauer spectroscopy. The use of high-field, high-frequency EPR is necessary for the determination of g-anisotropy and *zfs*. The same parameters were extracted from temperature dependent *pNMR* measurements. Furthermore, we obtained a deeper insight into the reactivity of our bulky $FePc^{OAr}$ system by employing *pNMR.*



$FePc^{OAr}$



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Carbon-Carbon Bond Activation at Chromium(I): An 11-Electron Complex Cleaving Dialkynes

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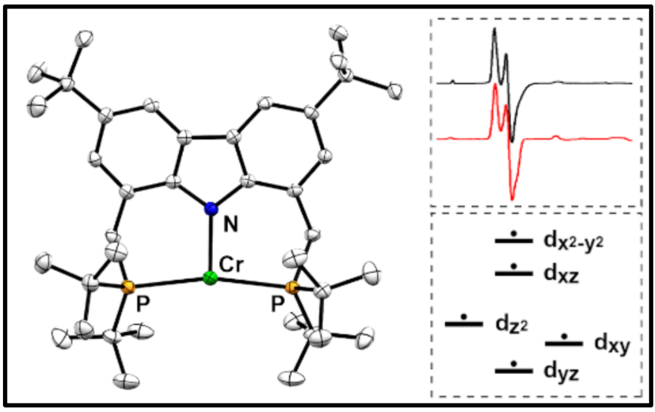
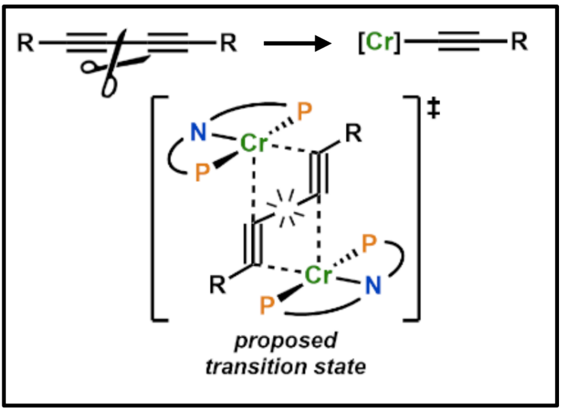
Low coordinate high spin complexes of Cr(I) are still rare. Most examples are either two-coordinate linear species [1] or Y-shaped three-coordinate species that require dissociation of one ligand to activate substrates.[2] We were able to synthesize a novel PNP-supported chromium(I)-complex by reduction of a chromium(II) halide precursor. The T-shaped geometry of the complex results in one free coordination site, giving access for substrates to interact with the d^5 high-spin chromium center. Paramagnetic NMR, EPR and magnetic measurements support this assignment.

While investigating the reactivity of this complex towards π-acceptor-ligands, we found that it readily reacts with dialkynes under cleavage of the internal C-C bond, forming the respective acetylide complexes. Isolation and characterization of dinuclear dialkynedichromium intermediates was possible by varying the alkyne substituents, thus providing insight in the mechanistic steps of the cleavage reaction.[3]





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(PNP)-stabilized Mononuclear, Homo- and Heterodinuclear Group 10 M(I) Complexes

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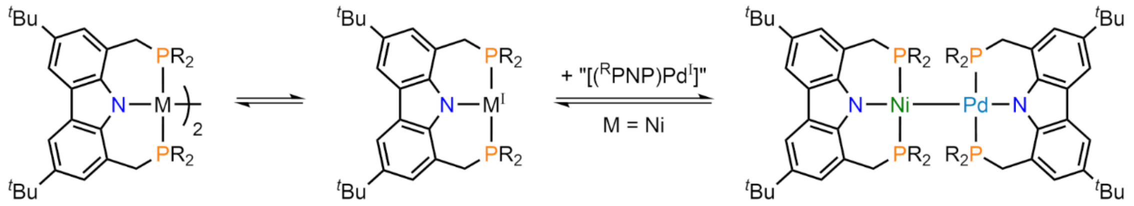
Mononuclear nickel(I) complexes are well-established, with their chemical properties being progressively clarified through detailed characterization of a growing variety of examples.[1] In addition, the corresponding palladium(I) compounds have been successfully synthesized over the course of the past decade, and now their respective reactivities are increasingly investigated.[2] Yet, the prevalence of isolable and characterizable mononuclear Pd(I) complexes is scarce owing to their strong propensity towards dimerization. Consequently, homodinuclear closed-shell dimers with supported and unsupported Pd-Pd bonds have been obtained primarily, which may be utilized as reservoirs for the *in-situ* generation of mononuclear intermediates.[3, 4] In contrast, for nickel, unbridged dimers are generally unusual.[1] Moreover, unsupported heterodinuclear Ni-Pd complexes remain scarcely examined. Herein, we describe the systematic investigation of the influence of the phosphine substitution in (PNP)-stabilized Ni(I) and Pd(I) complexes on their structures, stabilities and reactivities. Furthermore, the first unsupported heterobimetallic Ni-Pd complex and its redistribution reactivity is presented.



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The Methyl Effect: The Influence of Methyl Groups in Complexes with 2,7-Disubstituted 1,8-Naphthalenediol Ligands

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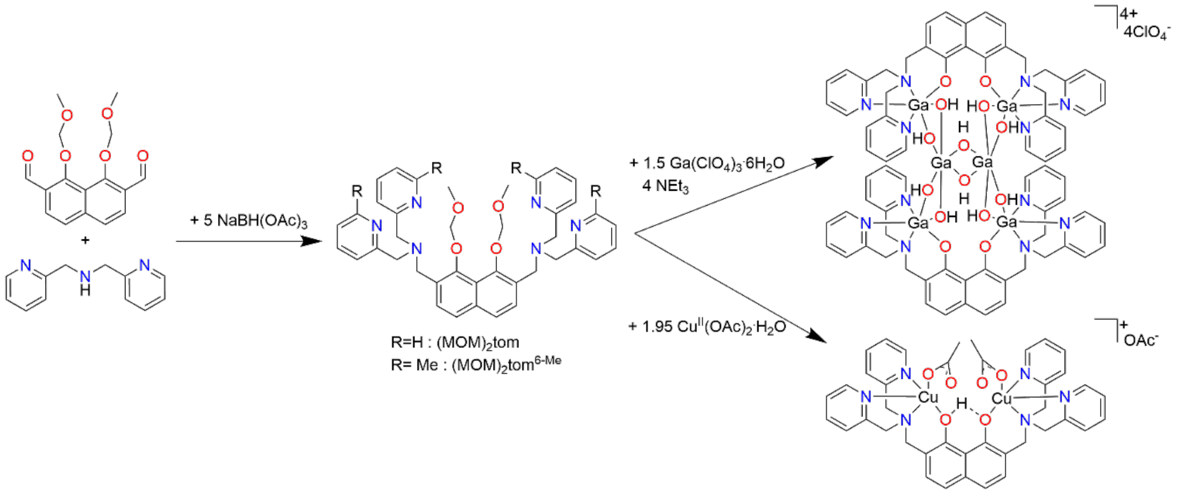
Based on the established anti-cancer drug cisplatin binding to the nucleobases of DNA, we have developed a family of ligands based on 2,7-disubstituted 1,8-naphthalenediol based ligands to bind to the negatively charged phosphate diester backbone of DNA.[1] So far, cytotoxic dinuclear complexes have been prepared using the pre-ligand $(MOM)_2tom^{6\text{-}Me}$ due to the better crystallization behavior. Here, we report for the first time the synthesis of two complexes with the pre-ligand $(MOM)_2tom$ using Cu^{II} and Ga^{III}. The Cu^{II}-complex inhibits DNA synthesis in PCR experiments at lower concentrations than the Cu^{II}-complex with 6-methyl pyridins.[2] The absence of the 6-methyl group also allows for the first time a synthesis of a complex with trivalent ions, here with Ga^{III} leading to a hexanuclear Ga^{III} complex with a central $\{Ga^{III}_6(\mu\text{-}OH)_{10}\}$ core.[3]



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Isolation of an Aluminum-Stabilized Aminonitrene

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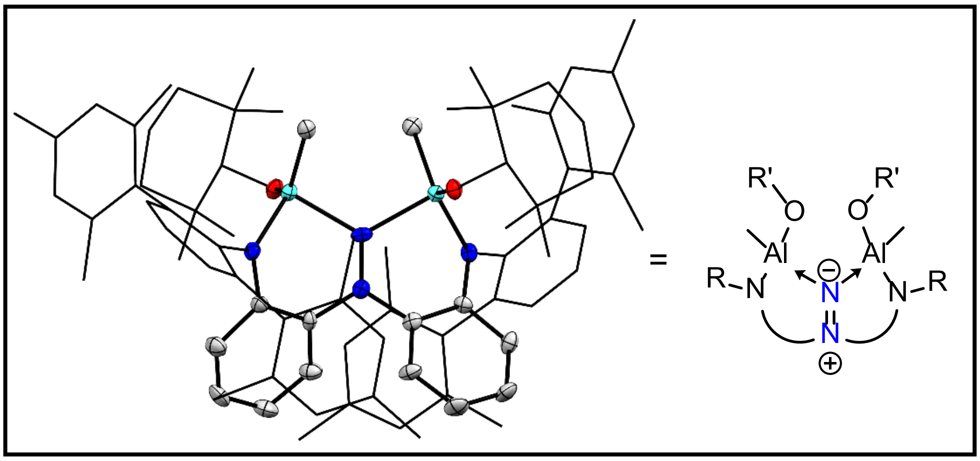
1,1-Diazenes (aminonitrenes) are compounds that are highly reactive and usually challenging to isolate. After initial computational studies by *Goddard* in 1977[1], the *Dervan* group managed to corroborate the theoretical findings by characterizing cyclic aminonitrenes *via* UV-Vis-, NMR-, and IR-spectroscopy at low temperatures, yet the isolation of these compounds remained elusive.[2] This feat was later achieved by coordination of the aminonitrene to transition metals utilizing either an iron porphyrin scaffold[3] or a PCP iridium complex[4].

Taking advantage of the steric shielding of a newly developed NNN pincer ligand, we present the isolation of an aminonitrene which is stabilized by two aluminum centers that act as (σ)-acceptors. The reactivity of this compound is investigated and the bonding analyzed by quantum-chemical methods. Comparison to a less steric aluminum NNN complex and *in-crystallo* irradiation of the respective azide precursors sheds light on the intermediates that are formed upon light-induced extrusion of dinitrogen and the influence of the steric bulk of the ligand.



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Nitrogen Monoxide and Calix[4]pyrrolato Aluminate: Structural Constraint Enabled NO Dimerization

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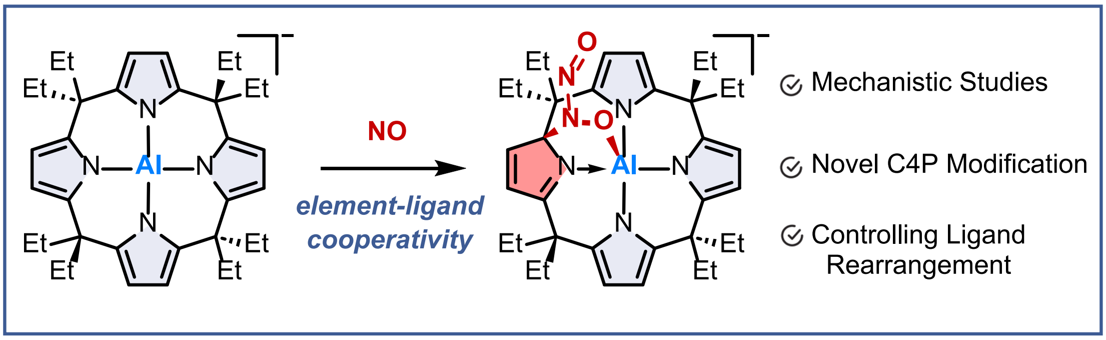
The dimerization of nitrogen monoxide (NO) to $(NO)_2$ plays a critical role in biochemical and environmental redox processes. However, the endergonic nature of this equilibrium has posed challenges in furthering our understanding of NO dimerization.[1]

We previously introduced meso-octaalkylcalix[4]pyrrolato aluminates, a class of anionic Lewis acids characterized by a unique square planar coordination of the aluminum center. The structural constraint enforced by the macrocyclic ligand framework leads to a biphilic reactivity towards polarized substrates.[2] In this study, we explore the reaction between calix[4]pyrrolato aluminate with nitrogen monoxide, a less polar substrate. Herein we describe the first dimerizing capture of nitrogen monoxide by element-ligand cooperativity. In doing so, we provide insights into the critical N-N bond formation in the NO-dimer and its impact on subsequent redox chemistry. By inhibiting the dimerization pathway through saturation of NO's unpaired electron with a phenyl group (nitrosobenzene), we trapped the 1,2-adduct as a key intermediate. Elevated temperatures led to an unprecedented and high-yielding calix[4]pyrrolato-based ring rearrangement. Kinetic and theoretical studies provide a comprehensive picture of the rearrangement mechanism, enabling future ring modifications of this macrocycle.[3]



✓ Mechanistic Studies
✓ Novel C4P Modification
✓ Controlling Ligand Rearrangement

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The First NIR-II Luminescent Vanadium(II) Complex with a 0.59 µs Lifetime in D_2O

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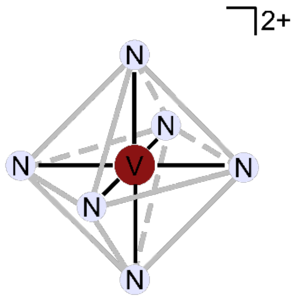
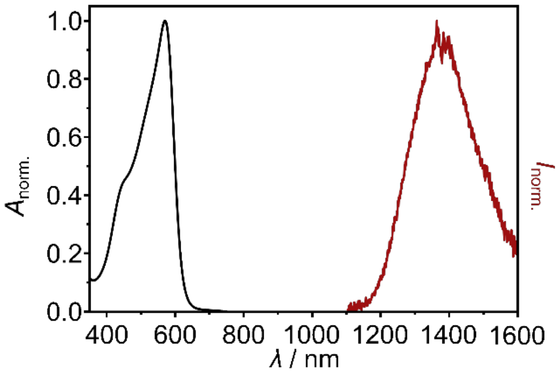
In contrast to isoelectronic chromium(III) complexes, known octahedral vanadium(II) complexes with d^3 electron configuration are non-emissive, for example with bpy, phen or ddpd ligands (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, ddpd = *N,N'*-dimethyl-*N,N'*-dipyridine-2-yl-pyridine-2,6-diamine).[1-3]

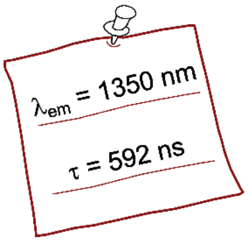
In this contribution, we present the first air- and water-stable vanadium(II) complex showing room temperature emission at 1350 nm. The emission lifetime is 0.59 µs in deuterated water and increases to 0.79 µs in deuterated acetonitrile, which approaches the ^{3}MLCT lifetime of the benchmark complex $[Ru(bpy)_3]^{2+}$ with 0.74-0.88 µs in acetonitrile.[4]

The vanadium complex is fully characterized by SC-XRD, vibrational spectroscopy, absorption and emission spectroscopy, transient absorption spectroscopy and quantum chemical calculations. The key to success appeared to be energetic separation of ^{2}MLCT and ^{2}MC states (MLCT = metal to ligand charge transfer, MC = metal centered).[5]

Singlet oxygen is generated via energy transfer catalysis after excitation of the complex with red light, which is exploited in low-energy photocatalysis. [5]







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$[Cr(tpPO)]^{3+}$ – a highly photooxidizing and photostable photoredox catalyst

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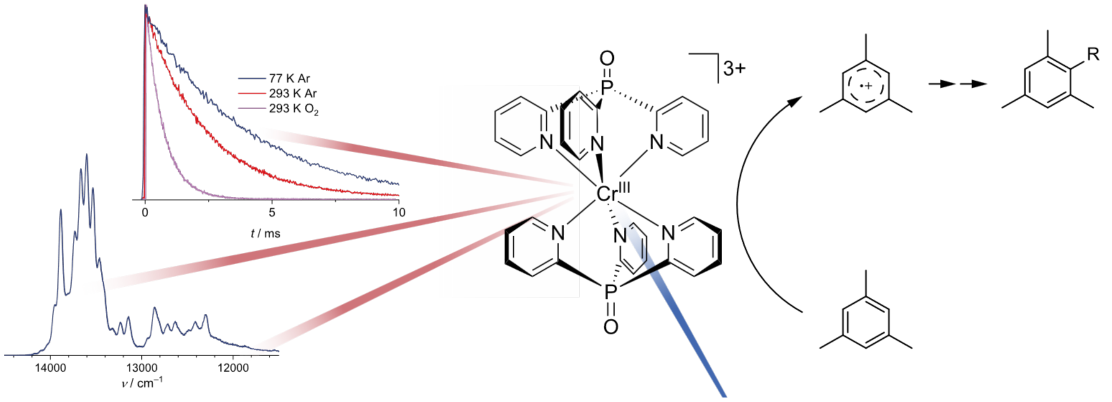
Due to their high excited state lifetimes up to milliseconds[1,2] and high excited state reduction potentials,[3–5] chromium(III) polypyridines have been shown to be versatile photoredox catalysts for reactions initiated by reductive quenching.[3–7]

In this work we present the synthesis, structure and comprehensive characterization of $[Cr(tpPO)_2]^{3+}$ (tpPO = tris(2-pyridyl)phosphane oxide). This complex is a highly photooxidizing chromium(III) spin-flip emitter with a tripodal trispyridyl ligand. The photophysical properties of the complex were determined by absorption spectroscopy as well as steady-state and time-resolved emission spectroscopy at ambient temperature and 77 K. Redox properties were measured using cyclic voltammetry.

We report the use of $[Cr(tpPO)_2]^{3+}$ as a photoredox catalyst. The outstanding combination of photophysical and redox properties of the complex permit the photoredox catalysis of reactions that have previously only been performed with 9-mesitylacridinium salts, a class of organic photoredox catalysts currently used in most challenging oxidative photoredox reactions.[8,9]



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New (chiral) heteroscorpionate copper-nitrene complexes for the aziridination of styrene

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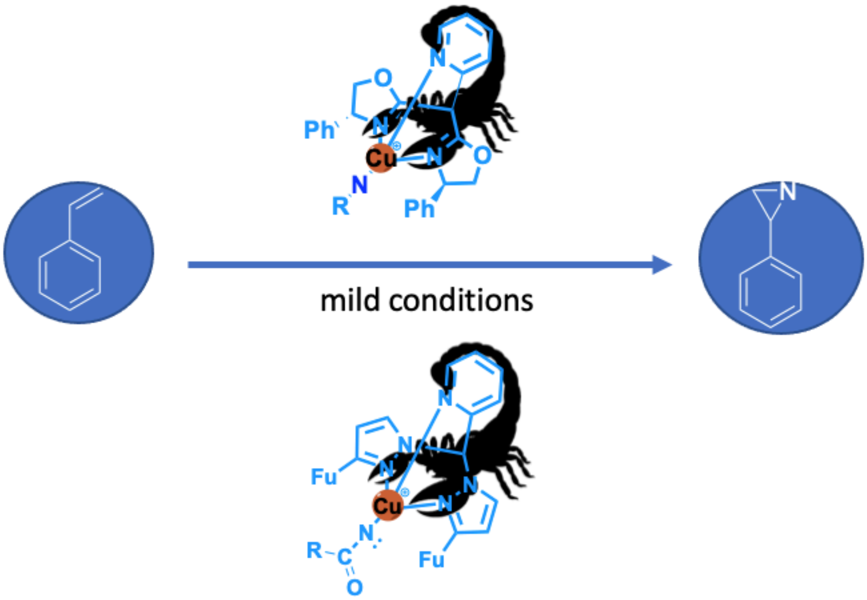
Copper nitrenes, as highly reactive intermediates, are pivotal in the direct synthesis of nitrogen-containing compounds through catalytic C-H aziridination[1] or amination[2]. In this research, terminal copper acyl nitrene complexes are synthesised using heteroscorpionate ligands of the bis(pyrazolyl)methane family and organic azide as environmentally benign nitrene sources. These complexes exhibit a high reactivity in the catalytic aziridination of styrene, achieving yields of approximately 70 % for all employed (hetero)aryl acyl azides under mild conditions. Additionally, a novel chiral heteroscorpionate copper tosyl nitrene complex, derived from the classical chiral bis(oxazoline) moiety, by reacting a copper(I) acetonitrile complex with ^{S}PhINTs, is developed. This complex indicted a high yield of 80 % in the enantioselective aziridination of styrene.

This study not only achieved a high yield in catalytic aziridination, but also provided new ideas for future research on the enantioselective C-H activation using heteroscorpionate copper-nitrene complexes.



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DFT- and ML-Supported Catalyst Design for the Ring-Opening Polymerization of Lactide

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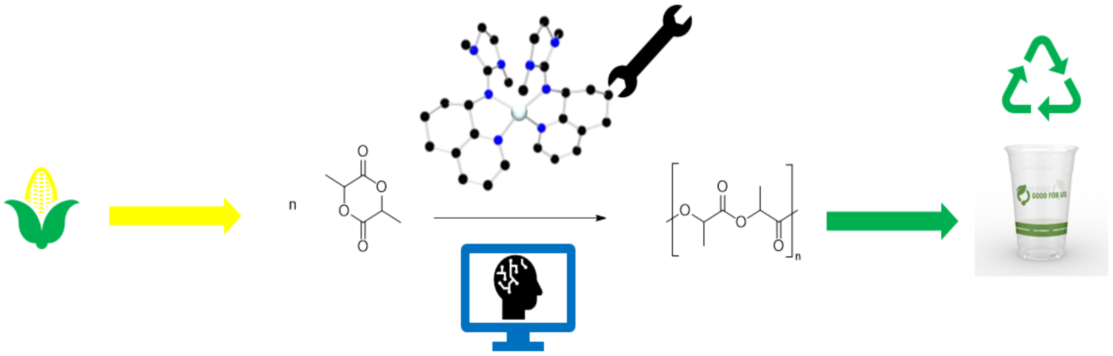
In recent years, people have become more aware of environmental issues and the resource limitations of today's plastics industry. Therefore, research highly focused on sustainable plastics such as polylactide (PLA).[1] As the catalyst for the industrial ring-opening polymerization (ROP) is the toxic tin(II) 2-ethylhexanoate, the need for more active and less toxic alternatives emerged in the past years.[2] Herein, zinc-guanidine complexes showed promising potential due to their non-toxicity as well as their functionality as single-site catalysts in the ROP of lactide.[3]

With the help of computational studies, the design of novel highly active catalysts for this purpose is accelerated: Activation energy calculations are carried out using density functional theory (DFT) methods.[4] These give insights about the influence of the ligand design towards the catalyst activity. Although this approach is resource-intensive, it can be feasible if the applied method is chosen carefully and in accordance with various experimental data. This leads to a faster prediction of the activity as only a few stationary points of the mechanism may be sufficient. However, these calculations can still come at a relatively high computational demand.

To circumvent this issue, the existing collection of known zinc-guanidine systems is examined using Machine Learning (ML) approaches with the aid of multiple GFN2-xTB-based features[5] to train and compare various ML models and quickly determine the activity of new catalysts. In addition, the importance of the features leading to efficient catalyst design is analyzed.



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Cyclodimerization of Internal Alkynes via Photoinduced Titanium Catalysis

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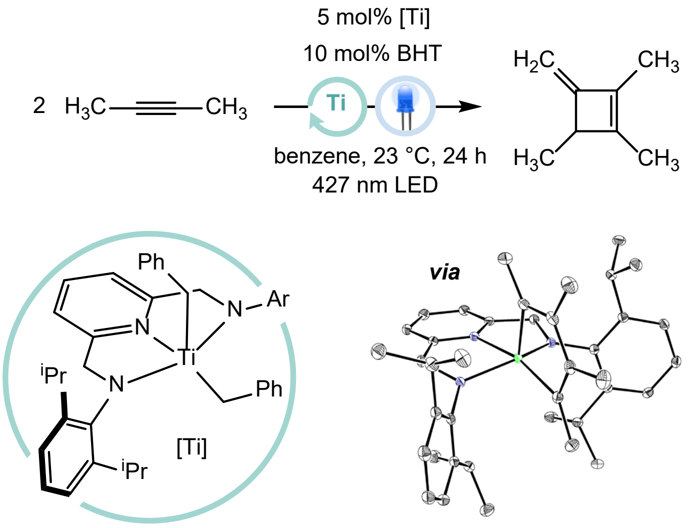
The oligomerization of alkynes is a well-known reaction in organometallic chemistry and provides useful building blocks from readily available chemicals. In the case of titanium, cyclotrimerization of terminal or internal alkynes to arenes is frequently reported.[1] Moreover, the dimerization of terminal alkynes to enynes is a well-precedented reaction.[2]
Using a pyridinediamido titanium dibenzylcomplex,[3] we present the catalytic cyclodimerization reaction of internal alkynes such as 2-butyne to afford methylenecyclobutenes. These molecules are complex building blocks containing an unsaturated four-membered ring, an exocyclic double bond and a new sp^3-hybridized carbon atom. Mechanistic investigations suggest light-accelerated formation of a titanacyclopentadiene, which is also the resting state during the reaction. Kinetic analyses give important insights into the rate-determining steps of the reaction. Substrate polymerization was successfully suppressed by addition of BHT as a radical inhibitor.



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New guanidino-functionalized aromatics (GFAs) with secondary amines as coordination spheres

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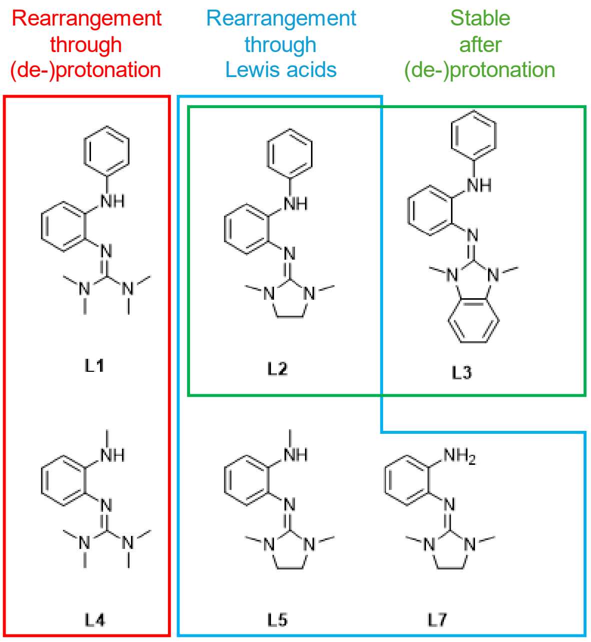
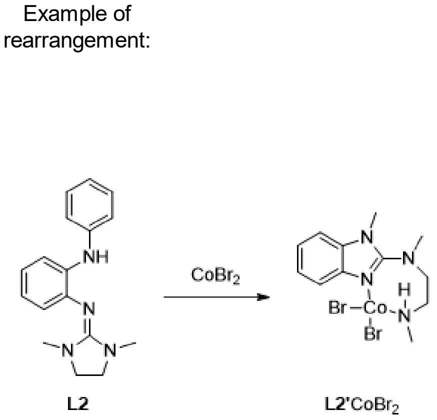
Coordination compounds with redox-active ligands are of interest for a variety of applications, e.g. for catalysis and the design of materials with switchable optical and magnetic properties.[1,2] Our group developed redox-active guanidines as a novel class of redox-active ligands and studied intramolecular electron transfer processes between the metal and the ligand in various mono- and dinuclear transition metal complexes with such ligands, and how they are influenced by the redox properties of the ligands, the coligands, the solvent[3], and the temperature.[4] Copper[5] and cobalt[3] complexes were in the center of these previous studies. The positive charge range of the oxidized ligands depends on the number of attached guanidino groups to the aromatic core.

In this work we extend our research to new guanidino ligands, that contain one guanidino function and a secondary amine as a coordination site. Accordingly, the charge shifts and includes a monoanionic redox state. Apart from the redox properties of these newly synthesized ligands; their rearrangement was studied including the effect of protonation, deprotonation and introduction of Lewis acids.





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Heteroleptic complexes with two different types of redox-active ligands

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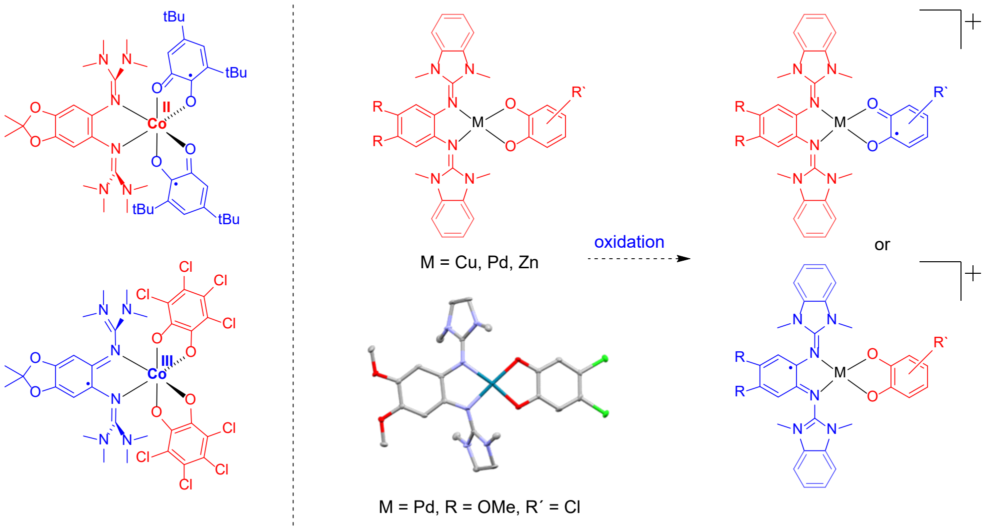
In our group, the coordination chemistry of complexes with guanidino-functionalised aromatic compounds as redox-active ligands is intensively studied. Upon coordination of redox-active metals as copper and cobalt, valence tautomerism of the complexes can be observed in many cases. Selective switching between the valence tautomers with distinctly different electronic or magnetic properties can be induced, e.g. by variation of the temperature, solvent or by coordination to a crown ether function serving as a secondary coordination sphere.[1-3]

By combining two different classes of redox-active ligands in heteroleptic complexes the possibility of forming valence tautomers is extended further. Previous studies focused on octahedral cobalt complexes comprised of a bisguanidine ligand and two oxolene-type ligands. The complementary charge regimes of those ligands lead to valence tautomers with distinctly different dipole moments. In these complexes with multiple redox centers redox isomerism can be observed.[4-5] This work focuses on the synthesis and properties of fourfold coordinated complexes of copper, palladium and zink.



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Catalytic Application of Rare-Earth/Group 10 and 11 Metal Complexes

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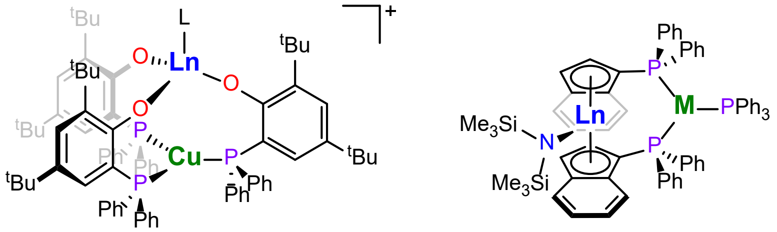
The investigation of complexes combining early and late transition metals, provided insight into aspects such as metal-metal interaction and cooperative reactivity. However, f-block/transition metal compounds have received significantly less attention with key examples being reported by the groups of Kempe and Roesky.[1-4] The first account of catalytic application of such complexes was reported only recently by Lu and co-workers investigating metal-metal interaction in the context of alkyne hydrogenation.[5]

In this contribution, our recent work on rare-earth/ group 10 and 11 metal complexes in the context of catalytic applications will be presented.[6],[7] We utilise phosphino-aryloxide as well as phosphine-functionalised indenly ligands to realise the heterodinuclear complexes (Figure 1). In our investigations, we explored the catalytic application of such complexes towards reactions such as alkyne oligomerisation, hydroamination, and ring-opening polymerisation.



$[B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4]^-$
Ln = La, Sm, Yb, Y; L = $(THF)_2$, DME

M = Ni, Pd; Ln = La, Sm

Figure 1: Selected examples of rare-earth/transition metal complexes investigated towards catalytic application.

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Electronic Structure of a Singlet Platinacarbene as Intermediate in an *in-Crystallo* Wolff Rearrangement

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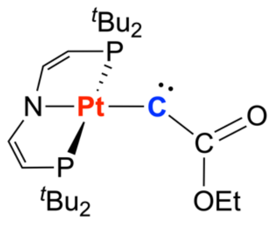
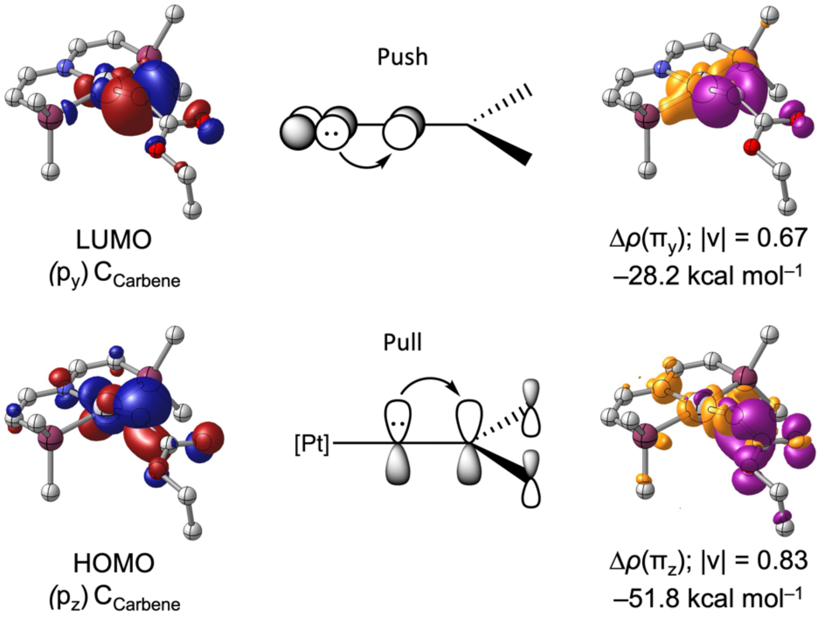
Previously, our groups established Pd/Pt metallocarbenes (i.e. M–C–$SiMe_3$) with triplet ground states, which are stabilized by spin-polarized push-pull interactions along both π-bonding planes.[1] We here report a platinacarbene that occurs as a fleeting intermediate in the photoinduced Wolff rearrangement of the corresponding PNP pincer diazoester complex (PNP)Pt($C(N_2)CO_2Et$).[2] Frozen solution and crystal matrix isolation experiments enabled structural analysis and UV/Vis spectroscopy. These results and quantum chemical investigations confirmed the singlet ground state of the carbene. The set screws controlling the electronic ground state of metallocarbenes are discussed. Natural orbitals for chemical valence (NOCV) analysis revealed a push interaction from the d_{xy}(Pt) orbital into the unoccupied $p_y(C_{Carbene})$ orbital and an orthogonal pull interaction between the doubly occupied $p_z(C_{Carbene})$ orbital and the unoccupied π* orbital of the neighboring ester group resulting in a push-pull stabilized singlet carbene.





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Excitation of a Ru(II) Polypyridine Complex with Red Light as a Photocatalyst in Cancer Cells

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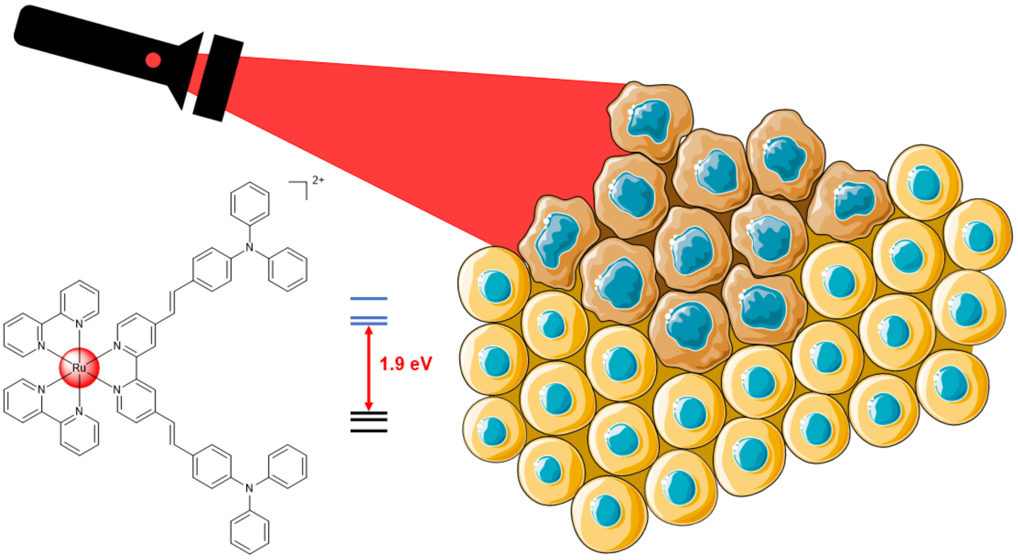
Chemotherapy for cancer is frequently constrained by significant side effects, limited specificity, and the risk of cancer cells developing resistance, which can make treatment less effective and more challenging. Light-activated therapies offer a precise approach to cancer treatment by targeting only cancer cells that both contain a light-sensitive substance (photocatalyst) and are directly exposed to light. This selective excitation minimizes side effects, as only the treated cells are affected, leaving surrounding healthy cells unharmed. Among the most promising class of compounds, Ru(II) polypyridine complexes are investigated as photocatalyst in cancer cells. Despite their promising properties, the majority of reported Ru(II) polypyridine complexes are excited by poorly penetrating UV or blue light, limiting their therapeutic potential to superficial tumors. [1]

Herein, the chemical synthesis, photophysical characterization, and biological evaluation of a Ru(II) polypyridine complex for light-activated anticancer therapy is reported. Using DFT calculations, we systematically modified the structure of the parent complex $[Ru(bipy)_3]^{2+}$ to design a novel compound with an excitation in the red region by minimizing the energy gap between the HOMO and LUMO orbital. The compound was found to highly efficiently catalyze the conversion of molecular oxygen to singlet oxygen. While being inactive in the dark, the metal complex was able to selectively eradicate cancerous cell upon irradiation with red light.[2]



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Synthesis of a Ru(II) Polypyridine Complex as a Synthetic Precursor for Photocatalysis

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Aldehydes are well-known for their high reactivity and functional versatility, making them indispensable tools in synthetic chemistry. This inherent reactivity has significant implications, such as facilitating the extension of ligand systems or enabling the conjugation of distinct molecules into a unified active conjugate. Herein, we envision to chemically extend the ligand scaffold of a promising Ru(II) polypyridine complex as a photocatalyst with aldehydes functionalities towards use as a synthetic precursor in photocatalysis. To ensure that the intrinsic chemical reactivity of the aldehyde group remains unaffected by the coordination to the metal center, a phenyl spacer was strategically introduced between the central ligand framework and the aldehyde functionality. Computational studies using density functional theory calculations were employed to investigate the photophysical mechanism. The results showed that the designed metal complex does undergo efficiently a metal-to-ligand charge transfer (MLCT) transition, yielding a reactive excited triplet state. The target compound was successfully synthesized and thoroughly characterized, revealing a high degree of stability both as a solid powder and in solution. Experimental analyses further demonstrated the compound's photocatalytic capabilities, specifically in the conversion of molecular oxygen to singlet oxygen. These findings highlight the potential of aldehyde-functionalized Ru(II) complexes as versatile platforms for advanced photocatalytic applications.

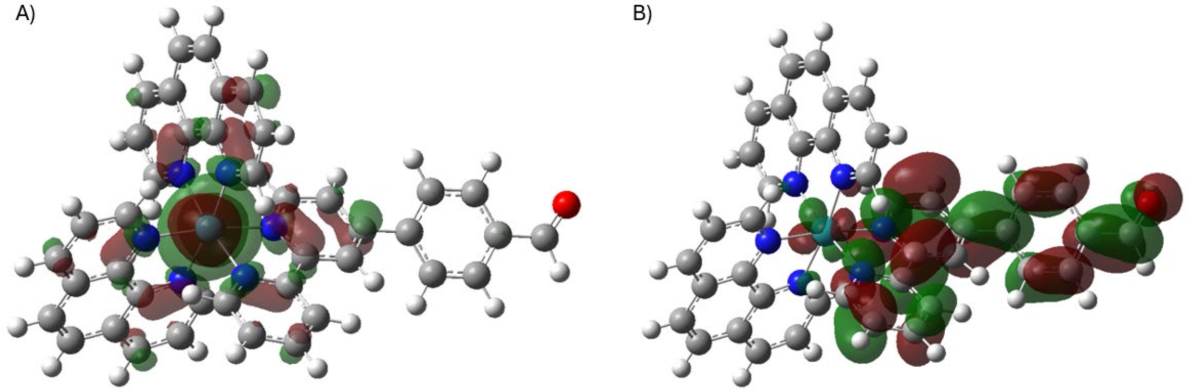

Figure 1. Molecular orbitals of the aldehyde-functionalized ruthenium polypyridine complex calculated using B3LYP functional with 6-31+G(d) basis set for organic atoms and LANL2DZ for metal atoms using CPCM solvent model for acetonitrile. A) HOMO. B) LUMO.

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Combining the Best of Two Worlds: Bichromophoric Cu(I)-Photosensitizers Based on Phenanthroline and BODIPY

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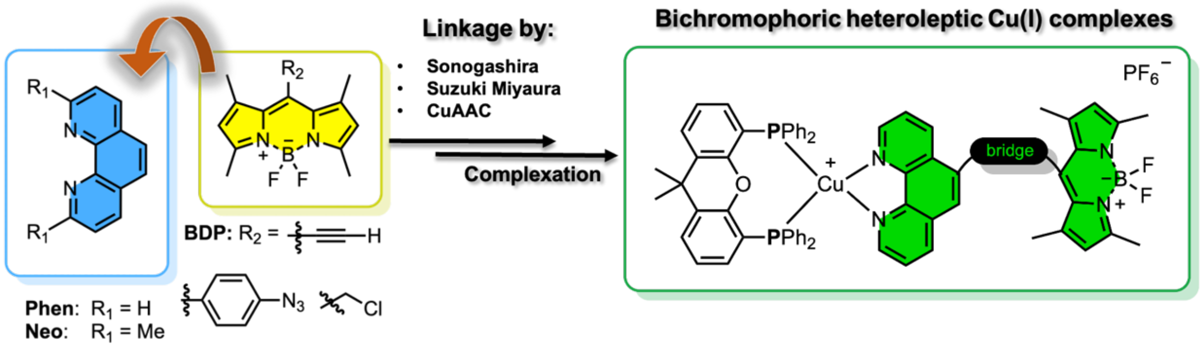
The design and study of bichromophoric Cu(I)-based photosensitizers offers a novel strategy for creating efficient light-harvesting molecules.[1] These systems consist of two linked chromophores, which often exhibit superior light absorption and energy transfer properties compared to single chromophore systems.[2] In particular, the class of BODIPY dyes is very promising for improving the light-harvesting processes of classical metal complexes, such as heteroleptic Cu(I) compounds.[3]

Heteroleptic Cu(I)-based photosensitizers already possess a variety of advantageous photophysical features like long-lived excited-states and high quantum yields, but suffer from a limited absorption in the visible.[1,4] This enables their use in different photocatalytic applications such as the production of hydrogen (H_2) from water or the generation of reactive singlet oxygen ($^1O_2$).[1,4]

We present the synthesis of a series of novel bichromophoric systems within different linkage possibilities between 1,10-phenanthroline (**Phen**) or 2,9-dimethyl-1,10-phenanthroline (**Neo**) and selected BODIPY derivatives (**BDP**). Subsequently, the corresponding heteroleptic Cu(I) complexes with the general formula [Cu(N^N)(P^P)PF_6] were prepared. Photophysical investigations, complemented by (TD)DFT calculations, are performed to elucidate the electronic communication between the two chromophoric units and to study the impact of the linker.



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Iron(III) Porphyrin π-Dications: the Bottleneck at Catalytic Crossroads

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Iron porphyrin catalyzed electrophilic chlorinations inspired by chloroperoxidase have the potential to provide environmentally benign avenues to functionalize molecules with chlorine.[1] Unlike chloroperoxidase, bioinspired[2] *meso*-substituted iron porphyrins do not form iron hypochlorite species from the reaction of Compound I with chloride.[3] However, electrophilic chlorinations can be accessed *via* an iron(III) isoporphyrin,[4] which is generated from the attack of chloride onto an iron(III) π-dication.[5] We have previously investigated the pivotal role of the iron(III) π-dication in such a catalytic cycle, showing that more electron rich porphyrins, which more readily form an iron(III) π-dication, are slightly more active catalysts.[6] Expanding on this work, we explored the viability of iron porphyrin catalyzed electrophilic chlorinations to be performed under practical conditions. Along the way, we identified a significant side reaction that stems from alternative reactivity at the iron(III) π-dication, leading to two different possible pathways at this point.[7]

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On the role of dinuclear Au(I) complexes with {$Ph_2PNHP(E)Ph_2$} (E = O, S, Se) ligands in cross-coupling reactions

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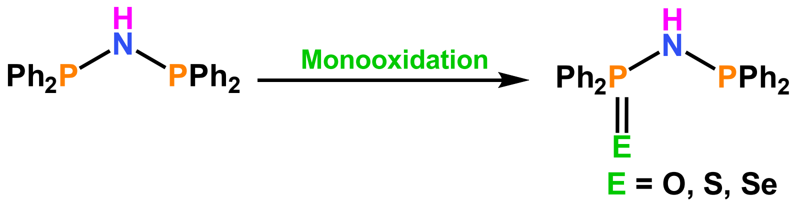
The application of gold(I) complexes in redox C-C coupling reactions has been widely studied during the last years.[1] Notably, most of the complexes employed in these transformations contain short-bite ligands, like bis(difenylphosphino)metane[2] or *N*-functionalized bis(diphenylphosphino)amine (dppa) derivatives.[3] Furthermore, dppa is a highly versatile ligand, and not only the nitrogen atom can be functionalized,[4] but also the phosphorus atoms can be selectively oxidized with different chalcogens affording hemilabile systems like {$Ph_2PNHP(E)Ph_2$} (E = O, S, Se), which exhibit several coordination modes, either in neutral or deprotonated form.[5] In this work we present the reactivity of {$PPh_2NHP(S)Ph_2$} towards chloro(dimethylsulfide)gold(I). The gold(I) derivatives containing these monosulfur ligand would provide the combination of a donor site that is tightly bound to gold, and a second hemi-labile donor atom, which in the end, we envision to guide its reactivity.



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DOTA-based photoswitchable ligands for lanthanoids

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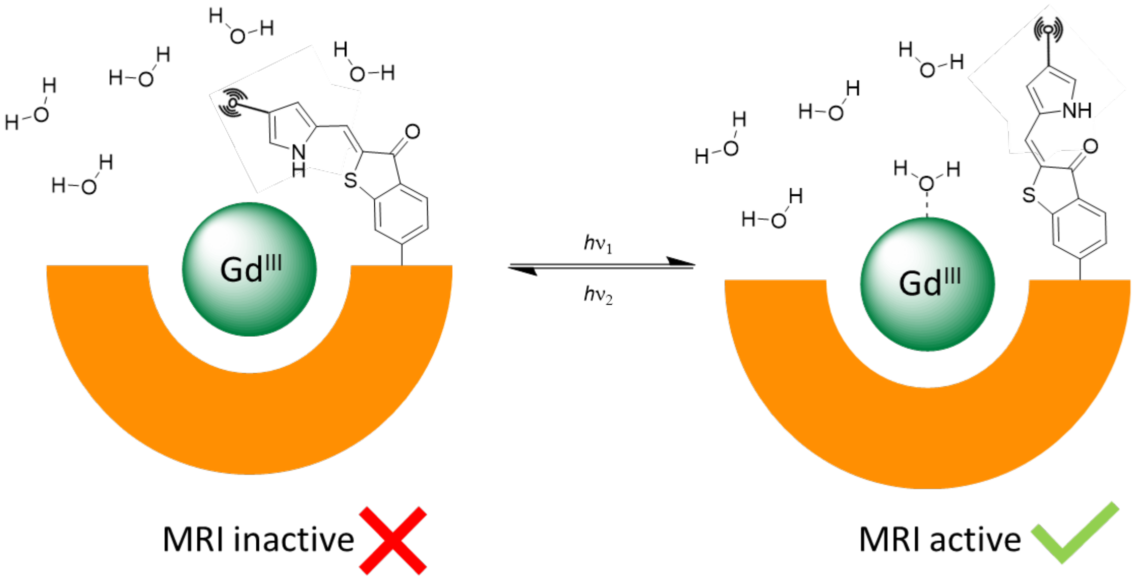
Particularly in the biomedical context, smart ligand design for lanthanoids is a powerful strategy to utilize their unique properties even better. While the lanthanoid provides the fundamental functionality, the ligand can support or modify the lanthanoid-centered properties and ensure compatibility with the specific application.[1,2] For example, for the realisation of europium-based emitters an organic antenna for indirect sensitization is required[3] and gadolinium-based contrast agents for MRI have to be extremely stable against decomposition, yet the ligand has to leave a coordination site vacant for water molecules to coordinate.[1] Such ligand-centered functionalities can in principle be manipulated with a large amplitude structural rearrangement of the ligand. This would, for example, pave the way to photoswitchable gadolinium-based contrast agents for MRI. Hemithioindigo is a photoswitchable building block which is a suitable candidate for the realisation of such ligands.[4] The combination of the particularly reliable DOTA-scaffold with the functionality of hemithioindigo-photoswitches promises a stimuli responsive utilisation of the unique properties of lanthanoids.



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Azobenzene Cryptates as Photoswitchable Ligands

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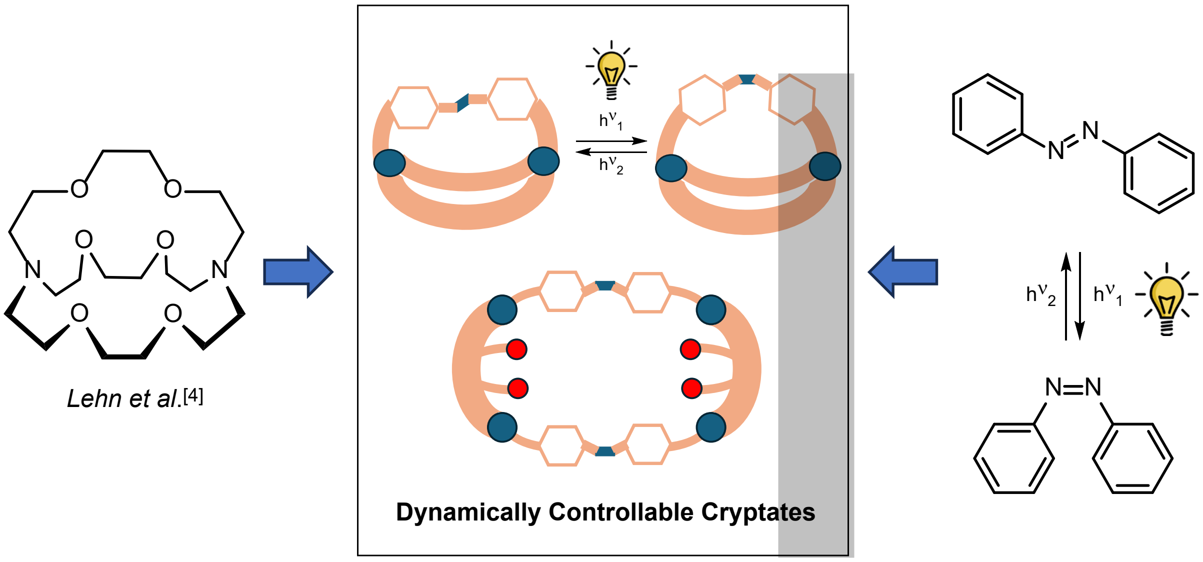
Due to their highly preorganized cavity, macrobicyclic cryptates form complexes of very high stability and exhibit excellent ion selectivity. Variation of size, donor atoms and rigidity of the building blocks connected by the bridge heads allows to fine tune their properties.[1] Applications include ion extraction, phase transfer catalysis and the use as ligand for metal ions, for example for luminescent lanthanoid complexes.[2]

A particularly interesting variant of cryptates results from the incorporation of photoswitchable building blocks, as it has been demonstrated by the pioneering work of *Shinkai et al.* [3] In such systems, the properties of the cryptates become dynamically controllable, paving the way for more elaborate applications. This requires fine tuning of the overall rigidity of the scaffold in both switching states and righteous choice of complementary building blocks.



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Thin films of a dinuclear Fe^{2+} complex on HOPG: Spin-crossover studies using X-ray absorption spectroscopy

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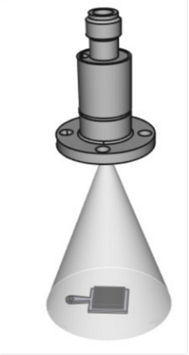
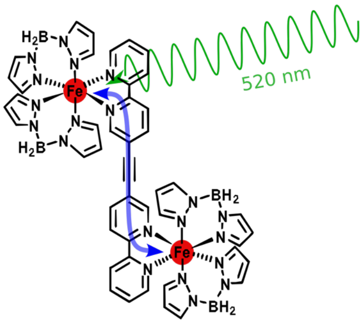
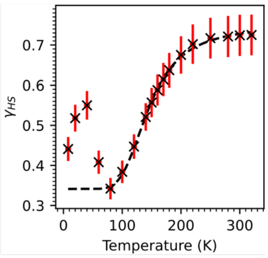
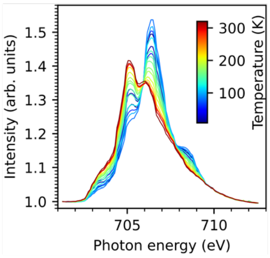
The spin-crossover (SCO) properties of the dinuclear complex $[\{Fe(H_2B(pz)_2)_2\}_2\mu\text{-}(ac(bipy)_2)]$[1] deposited as (sub)-monolayer and thin film by an ultra-high-vacuum liquid-jet deposition technique on highly oriented pyrolytic graphite (HOPG) were studied by X-ray absorption spectroscopy. A comparison of the SCO properties of thin films and a dropcast sample indicates that the spin-switching capability of the thin films is lower due to substrate–molecule interactions. The similar switching properties of the dropcast sample as of a bulk powder sample[1] confirm that the SCO properties are not affected by the presence of solvent necessary for deposition. The soft-X-ray-induced excited spin-state trapping (SOXIESST) effect is pronounced in all samples, although the light-induced high-spin (HS) fractions of the dropcast and the thin-film samples on HOPG are higher as compared to the HS fraction attained by SOXIESST, which confirms the sensitivity of the complex to light.









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H_2CTP als salzfreier Proligand für ein- und zweikernige Carbenaporphyrino-Zink-Komplexe

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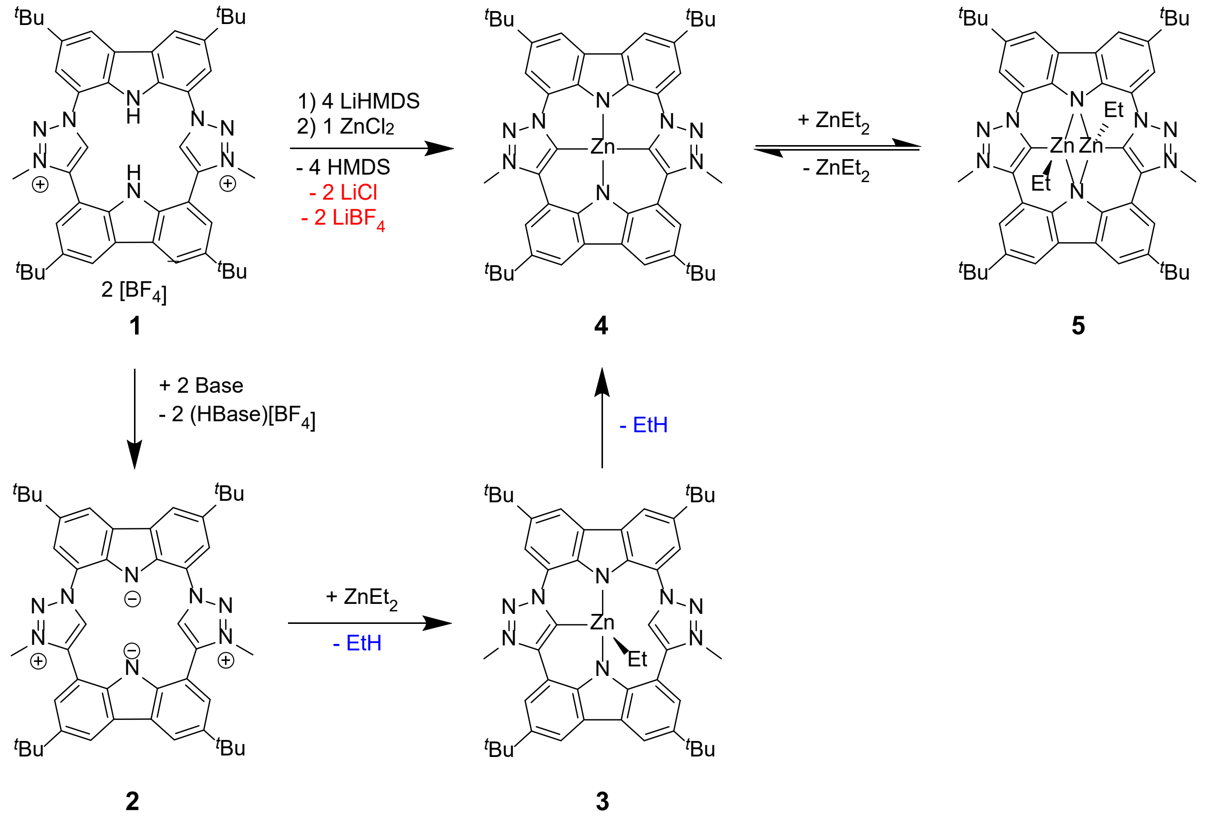
Der von uns entwickelte Carbazol-Triazolylidenporphyrin-Ligand (CTP) verfügt aufgrund der zwei mesoionischen NHC-Einheiten über einen starken Elektronendonor-Charakter, was die Reaktivität seiner Komplexe insbesondere von redoxaktiven Metallen beeinflusst. [1,2]
Für die Synthese der CTP-Komplexe nutzen wir bisher $H_4CTP(BF_4)_2$ (**1**) als Vorstufe,[1] bei der jedoch schwer abtrennbare Lithiumsalze anfallen. Um die Salzlast zu reduzieren, stellen wir nun die neutrale Verbindung H_2CTP (**2**) als alternativen Proliganden vor. Wir zeigen am Beispiel der Reaktion mit $ZnEt_2$, dass die Umsetzung von **2** mit basischen Metallverbindungen über die Zwischenstufe **3** zum gewünschten Metallkomplex ZnCTP (**4**) führt, wobei als Nebenprodukt nur Ethan entsteht.
Mit einem Überschuss an $ZnEt_2$ reagiert **4** in einer Gleichgewichtsreaktion zum zweikernigen Zinkkomplex **5**. Dieses sehr seltene Strukturmotiv wurde bei Zink-Porphyrinen bislang noch nicht beobachtet.[3]



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Intramolecular oxidative addition of halide-functionalized bimca-ligands

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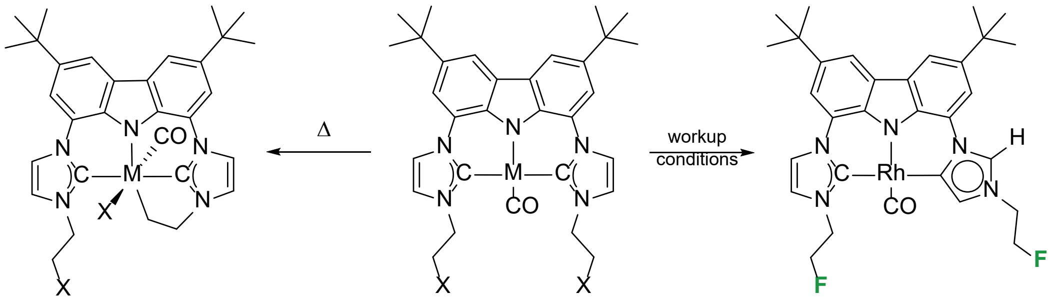
The oxdiative addition of methyliodide to Rh(I) or Ir(I) is one of the key steps in the Monsanto/Cativa process to produce acetic acid. In the case of Rh(I), this is the rate limiting step under the applied conditions (150 – 200 °C, 30 – 60 bar)[1]. We observe the facile intramolecular oxidative addition of typically unreactive ethylchlorides and ethylbromides in a Rh(I) and the corresponding Ir(I) complex under mild conditions. This reactivity occurs readily due to the strong electron donating effect of the used bimca-ligand leading to highly nucleophilic metal centers. In addition, the intramolecular reaction pathway enhances the reactivity compared to the intermolecular C-X-activation (X: Cl, Br)[2]. In contrast to the intermolecular reaction, the CO ligand is oriented *cis* to the carbazole moiety. The corresponding ethylfluoride complexes show no intramolecular C-F-activation under the tested conditions. However, the Rh(I) complex undergoes a partial isomerization into the thermodynamically less favored asymmetric abnormal carbene complex under the workup conditions.



[M^{III}(bimca^{EtX})CO]
X: Cl, Br

[M^{I}(bimca^{EtX})CO]
M: Rh, Ir
X: F, Cl, Br

[Rh^{I}(bimca^{EtF})CO] (abnormal)

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On the coordination chemistry of methylene-extended acridine chelators

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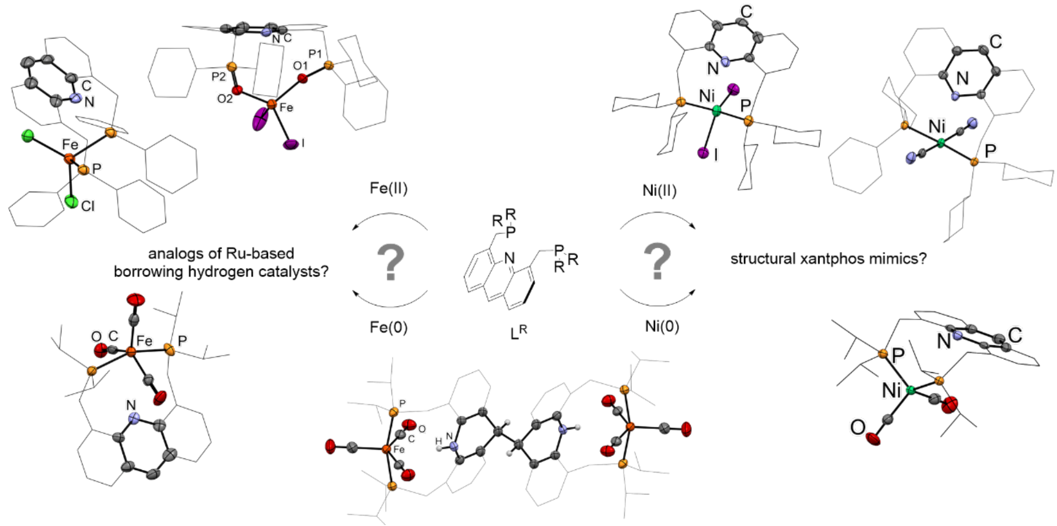
Inspired by flexible PNP pincer and scorpionate complexes of ruthenium and manganese derived from Milsteins methylene-extended acridine-based *4*,*5*-bis(methyl(di-*iso*-propylphosphino))acridine ligand, the fundamental coordination chemistry of potentially tridentate *4*,*5*-bis(methyl(organohetero))acridine ligands with first row transition metals was studied.[1-3] A main motivator was the search for iron analogs of the versatile borrowing hydrogen catalysts *trans*-*mer*-[RuHCl(CO)($R_2PCH_2acrCH_2PR_2$)].[1,2] The extension of the chelate rings by additional methylene groups prevents the coordination of the central nitrogen atom towards the first-row transition metals iron and nickel in contrast to the situation observed for manganese and copper,[3,4] mimicking the behavior of the popular xantphos ligand system.[1] Consequently, the acridine-based ligand acts as a *trans*-spanning diphosphine ligand in the square-pyramidal iron(0) tricarbonyl complexes [$Fe(CO)_3(R_2PCH_2acrCH_2PR_2)$] or as a *cis*-coordinating diphosphine ligand in tetrahedral [$Ni(CO)_2(R_2PCH_2acrCH_2PR_2)$]. In all cases, the nitrogen atom of the central acridine unit is in close proximity to the metal and may potentially allow hydrogen abstraction from substrates. The structural variety and reactivity of the complexes underlines the flexibility enabled by the methylene-extension in such ligands.



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Dual-Targeting UiO-MOFs: Functionalization with Cytotoxic Tumor-Targeting Ligands and Controlled Fluorouracil Release

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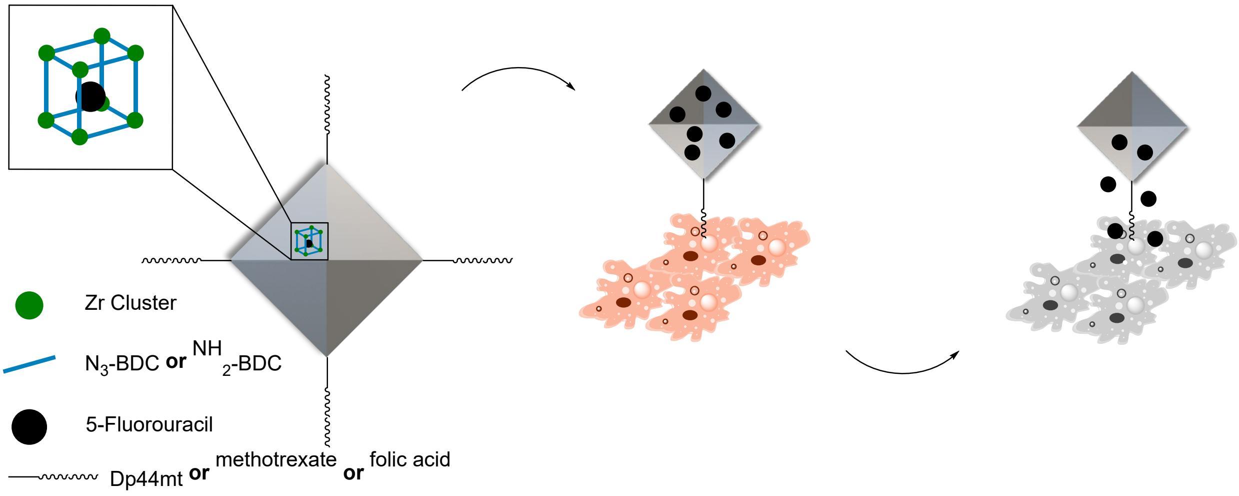
The development of metal-organic frameworks (MOFs) functionalized with tumor-targeting ligands and loaded with chemotherapeutic agents, such as fluorouracil (5-FU) offers innovative strategies for precise and effective cancer therapy.[1] This project focuses on combining intrinsic cytotoxic tumor-targeting ligands on UiO-MOFs with the controlled release of 5-FU. Specifically, the Zr-based MOF UiO-67-N_3 is functionalized with Dp44mT, an anti-cancer agent and iron chelator, using Click chemistry. Additionally, UiO-66-NH_2 is functionalized via amide coupling with methotrexate (MTX), a cytotoxic antifolate selectively taken up by cancer cells overexpressing folate receptors through the reduced folate carrier (RFC). To provide a meaningful comparison, UiO-66-NH_2 is also functionalized with non-cytotoxic folic acid, which is similarly taken up via the RFC pathway.[2] All functionalized MOFs are further loaded with 5-FU and tested for drug release and cytotoxicity against cancer cells. The functionalization processes and drug loading are characterized comprehensively using techniques such as PXRD, IR and qNMR spectroscopy, TGA, and physisorption. This work highlights the potential of functionalized MOFs as dual-targeting systems for precise delivery and controlled release of chemotherapeutic agents. Furthermore, their biological activity and specificity toward cancer cells will be investigated.



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Cu(II)-oxo Clusters as Click Catalysts with Application in a Biotechnological Cascade

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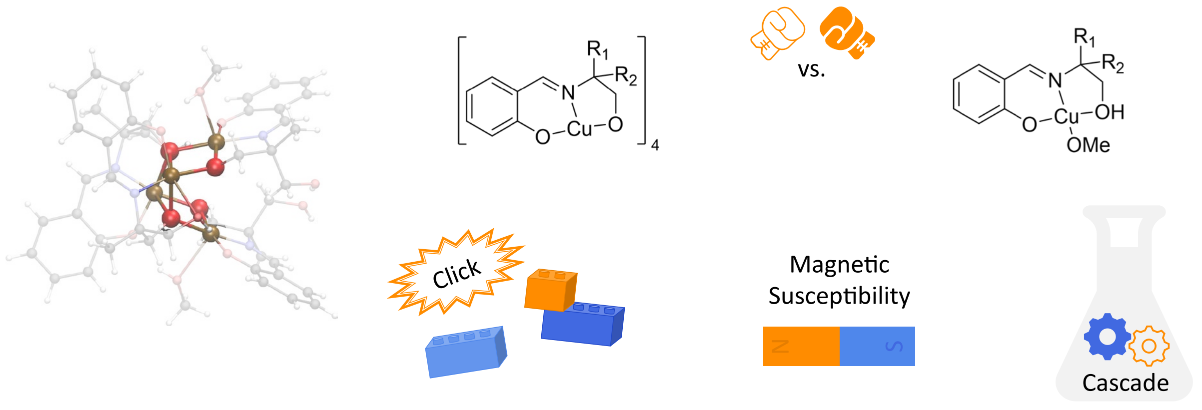
Metal clusters exhibit behaviour that is intriguingly different from free metal salts and metal complexes. For example, a μ-oxo bridged trimetric copper(II) oxo cluster is known to facilitate Click reactions.[1] Inspired by the catalytic activity of less biologically interfering Cu(ii), four chelated Cu_4O_4 clusters[2] and two corresponding Cu(II) monomers were selected. The hydrophilicity of these compounds varies, allowing the structural impact on catalytic performance to be investigated. The catalytic activity can be correlated to their unique magnetic properties, which were determined by magnetic susceptibility measurements. In addition, the bioorthogonality of all catalysts was evaluated by styrene monooxygenase (SMO) inhibition. To further investigate the applicability in biotechnological approaches, the most promising catalyst was chosen to further evaluate the activity in a chemoenzymatic cascade using a whole-cell approach. Again, a SMO was used as it produces the intermediate (*S*)-styrene oxide enantioselectively, which is subsequently functionalised by azidolysis and our designed bioorthogonal copper(II)-catalysed Click reaction.



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The hare and the hedgehog – Similar thermal expansion of argento- and aurophilic contacts for different reasons

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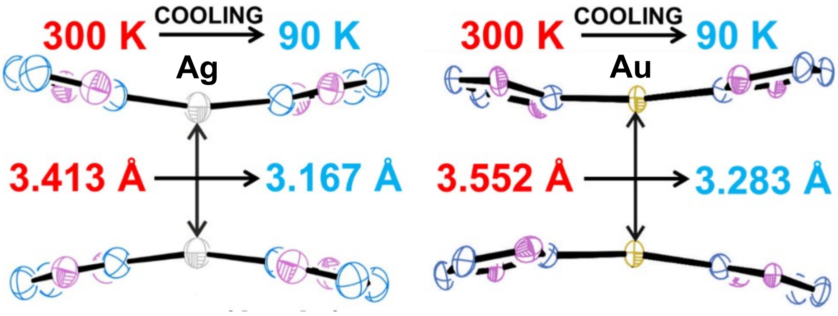
Metallophilic closed-shell interactions are an established concept in coordination chemistry of coinage metals with formal electronic nd^{10} configurations and play an important role in the self-assembly and supramolecular chemistry of such compounds. They are most prominent for linear two-coordinate Au(I) compounds with binding energies of the order of hydrogen bonds, and less pronounced for the lighter congeners Ag(I) and Cu(I). In 2008, a very large temperature dependence of the Ag···Ag distance was found in the Prussian Blue analogue $Ag_3[Co(CN)_6]$ which the authors coined "colossal thermal expansion" to describe this unusual behavior.[1] Later, we found an even larger temperature dependence of the intermetallic distances in metalorganic complexes of the form $[(NHC)_2Ag]A$ (NHC = N-heterocyclic carbene, A = weakly/non-coordination anion) and ascribed this behavior to a highly anharmonic, flat potential of argentophilic interactions.[2]

In this contribution, we will present a comparison of the thermal expansion properties of argentophilic and aurophilic contacts in the complexes of the form $[(^{iPr}NHC)_2Ag]ClO_4$ and $[(^{iPr}NHC)_2Au]ClO_4$. Using X-ray crystallography distinct structural changes and phase transitions at varying temperatures are revealed. Both complexes exhibit a similar strong temperature dependence of the metallophilic distances. Analysis shows that the shallower, more anharmonic aurophilic interaction is counterbalanced by the smaller vibrational amplitude of the heavier gold atoms, resulting in comparable thermal elongation despite differing atomic dynamics.[3]



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On the stabilization of potassium phosphides by the Terphenyl ligand

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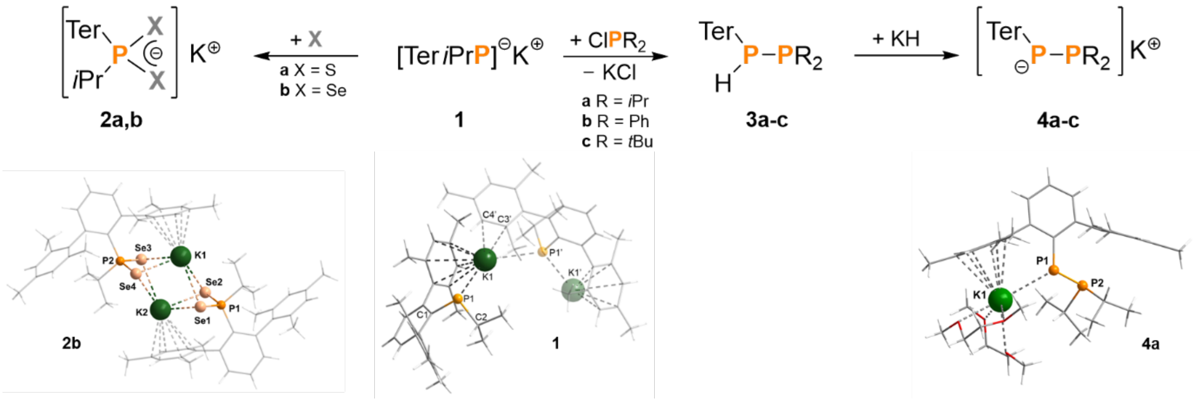
Potassium phosphides such as compound **1** can be synthesized by the deprotonation of Ter-stabilized (Ter = 2,6-bis-(2,4,6-trimethylphenyl)-phenyl) secondary phosphanes using KH in THF.[1] Due to the formation of side-products, the deprotonation of sterically demanding phosphanes can often be challenging. However, we found that for the presented approach, the deprotonation reactions are selective, and the products are stable at room temperature both in solution and in the solid state. Phosphide **1** reacts readily with several small molecules and elemental compounds like S or Se to yield dithiophosphinate **2a** or diselenophosphinate **2b**, respectively.[2]

Potassium phosphinophosphides of the type **4a-c** can analogously be synthesized by deprotonation of the corresponding H-substituted diphosphanes **3a-c** with KH in THF. The diphosphane moiety in compounds **4a-c** can be used for the functionalization with heteroatoms such as, *e.g*. PR_2 and SiR_3 in salt metathesis reactions.[3]

The solid-state structures of the isolated potassium phosphides and their reaction products show that the K^+ counterion is coordinated both by the P atom (in **1** and **4a-c**) or the S/Se atoms (**2a,b**) and by the Mes moiety of the Terphenyl substituent. We assume that the stability of the potassium phosphide species can be attributed to this coordination mode.



Scheme 1: Conversion of secondary phosphide **1** with S or Se, yielding **2a,b** (left) and synthesis of potassium phosphinophosphides **4a-c** by deprotonation of the corresponding diphosphanes **3a-c** (right).

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Ag-Nanocluster mit künstliche Nukleobasen enthaltender doppelsträngiger DNA als Templat

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Silber-Nanocluster (Ag-NC) am DNA-Templat bilden eine Schnittstelle zwischen der Chemie der Metallnanocluster und der DNA-Nanotechnologie. Ag-NCs bestehen aus bis zu 30 Ag-Atomen bzw. -Ionen.[1] Die geringere Größe und die damit einhergehende Abnahme der Elektronendelokalisierung der NC im Vergleich zu den entsprechenden Bulk-Metallen führen zu drastischen Eigenschaftsänderungen. Eine typische Eigenschaft zahlreicher Ag-NCs ist ihre intensive Lumineszenz.[2] Die DNA dient sowohl als Templat bei der Bildung als auch zur Stabilisierung der Ag-NC. Die Kombination aus NC und DNA führt zu Fluorophoren mit guter Biokompatibilität. So eignen sich DNA-Ag-NCs beispielsweise als Fluoreszenzsonden für biologische Anwendungen.[3]

In dieser Studie wird die Bildung von Ag-NCs an einem DNA-Templat spektroskopisch untersucht. Dabei werden die NCs verschiedenen externen Einflüssen sowie Reaktionsbedingungen ausgesetzt. Im Gegensatz zu vielen Ag-NCs aus der Literatur wird mit doppelsträngiger DNA gearbeitet, die 1*H*-Imidazo-[4,5-*f*][1,10]phenanthrolin als künstliche Nukleobase mit erhöhter Ag(I)-Ionen-Affinität enthält. Trotz der Nutzung nur einer Doppelhelix-Sequenz können mindestens vier verschiedene Ag-NCs am DNA-Templat nachgewiesen werden. Interessanterweise bleiben die Ag-NCs selbst nach einem 23-stündigen Erhitzen auf 80 °C (d.h. oberhalb des Schmelzpunkts der DNA-Doppelhelix) detektierbar.

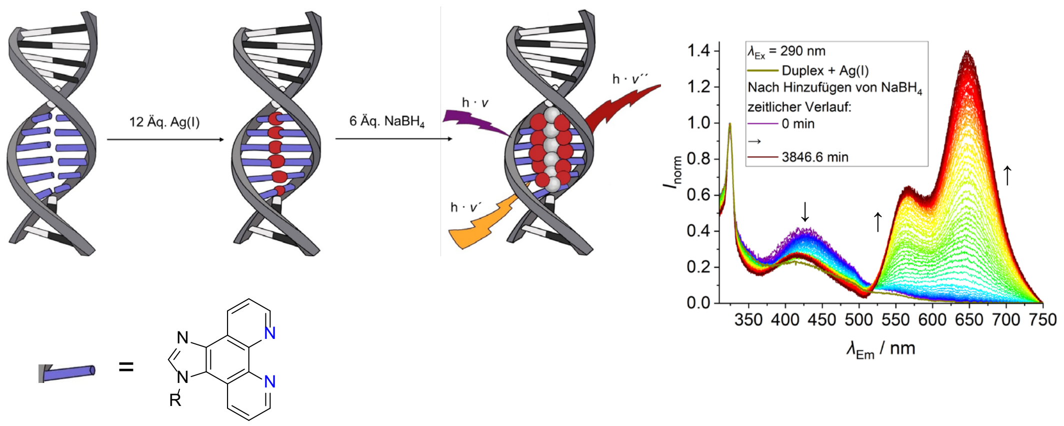

Abbildung: Schematische Synthese von DNA-Ag-NCs sowie zeitabhängige Änderung von deren Lumineszenzspektren.

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A Lead (II) Substituted Triplet Carbene

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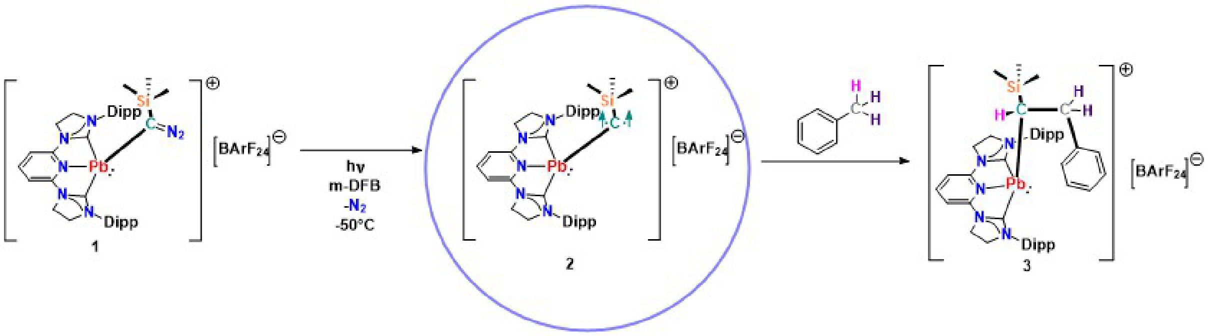
This poster [1] presents the synthesis of a C-N-C pincer-type ligand supported lead-diazomethanide complex $[L_3Pb(C(=N_2)TMS)][BArF_{24}]$ **(1)**, which is formed by the reaction of $[L_3PbBr][BArF_{24}]$ with $Li[(C(=N_2)TMS)]$ in cold diethyl ether . On irradiation, complex **1** releases dinitrogen and yields formal plumba-alkyne **2**, which is stable in cold fluoroarene solutions. Spectroscopic and quantum chemical calculations reveal that **2** is to be understood as a lead-substituted triplet carbene. The *in-crystallo* irradiation of **2** as well as irradiation in toluene leads to a C-H bond insertion into the benzylic position of toluene **(3)**.



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The Hexaphenyl-1,2-diphosphoniumdication
$[Ph_3P–PPh_3]^{2+}$

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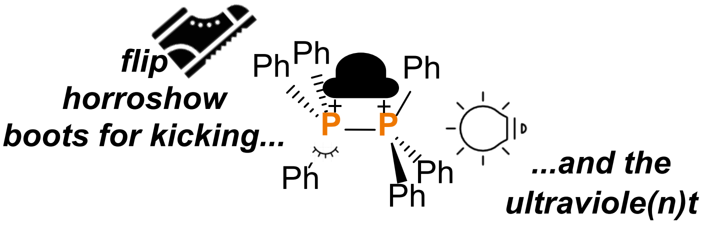
The long known trityl radical prefers to dimerize to GOMBERG's dimer,[1][2] rationalizing the elusive nature of hexaphenylethane[3] in respect to its heavier and isolable congeners. Herein we present the characterization and reactivity of the isoelectronic group 15 analogue, namely the hexaphenyl-1,2-diphosphoniumdication. Ambiphilic reactivity is demonstrated by its strong Lewis acidity, validated by fluoride abstraction from SbF_6, oxygen abstraction from $OPEt_3$, and Lewis donor substitution, thus substantiating hidden FLP-type reactivity. Under UV irradiation, it engages in H atom abstraction from dihydroanthracene and CH phosphoranylation of difluorobenzene. Further, we describe the activation of dihydrogen, oxidation of trimethylphosphine, and addition to a multiple bond.[4]



You have the choice!

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Evaluation of Non-Standard Radioisotopes in Coordination Chemistry

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Within the last few years, nuclear medicine entered a new era with precision radioligand therapeutics like Lutathera and Pluvicto. Both drugs are marketed by Novartis and are the highest grossing small molecule drugs, containing metal ions other than (alkali)earth ions. They harness their therapeutic efficacy by bringing Lu-177 into tumor cells, where the isotope decays and the emitted beta radiation causes apoptosis. [1]

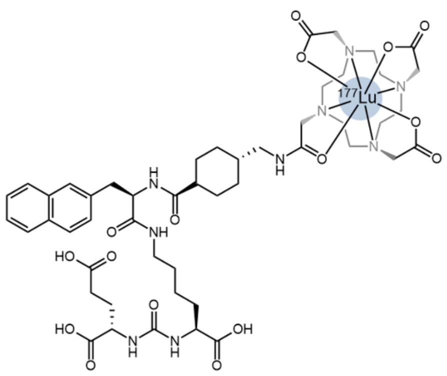
A major problem of both of these drugs, is their by-stander effect and nephrotoxicity. The energy of the upon decay emitted electron is about 500 keV, which translates to 2-3 mm or approx. 100 cells penetration depth. [2] By renal clearance of the drug, the kidneys are inherently damaged by that radiation. This too is the reason previous renal failure or kidney problems are contraindications for the use of these type of drugs. [3]

At the INM-5 we are investigating cyclotron produced non-standard radioisotopes for radiopharmaceutical purposes, leading to new therapeutic and diagnostic approaches for tumors. We employ our institutes IBA Cyclone 30XP, a multiparticle cyclotron capable of accelerating protons, deuterons and alpha particles to energies up to 30 MeV.

One of our focusses is the production of Pt-193m, an Auger-Meitner electron emitting radionuclide. The electrons emitted during the decay process have a very short penetration depth of less than one cell, and thus can lead to reduced radiotoxicological side effects and more precise therapeutics. [4]

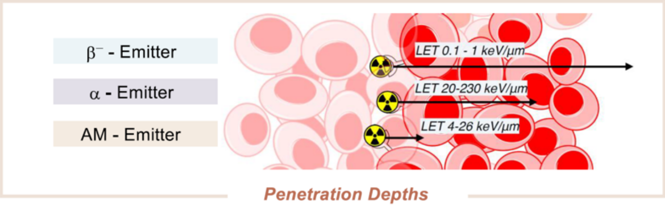
I will present our efforts in generating the radioisotope, isolation and recovery of the target material as well as the coordination of these non-standard isotopes in a nuclear medical context.

Pluvicto (#89 Top Selling Drug)



Non-Standard Radionuclides

Co 58m	Pt 193m	Pb 203
8.94 h	4.33 d	51.9 h
IT γ (25) e^- (8/decay)	IT γ (136...) e^- (30/decay)	ε γ 279, 401,... g



Penetration Depths

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Molecular Light-Driven Water Oxidation in Liposomal Assemblies

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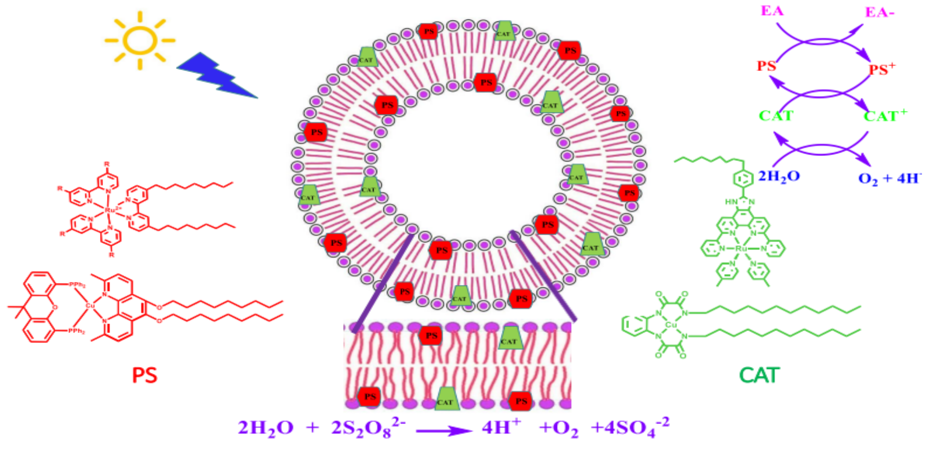
Photocatalytic water oxidation is a crucial step towards sustainable energy conversion, as it presents one half reaction of overall water splitting and can deliver electrons for productive reduction reactions. Inspired by the mechanism of Photosystem II in natural photosynthesis taking place in the thylakoid membrane, our study focuses on the development of liposomal assemblies to enhance the efficiency and stability of molecular light-driven water oxidation. We incorporate long alkyl tails on molecular photosensitizers and catalysts. Next to the established amphiphilic photosensitizer, based on Ru(II)-tris-bipyridine[1]. we apply earth abundant Cu-based photosensitizers. Additionally, hydrophobically functionalized Ru catalysts are being replaced by Cu-based catalysts.

The use of liposomes enables for light-driven conversion in water. To identify a suitable microenvironment for catalysis, we employ different lipids, such as DMPC and DPPC, combined with varying ratios of photosensitizers and catalysts in the presence of a sacrificial electron acceptor, $Na_2S_2O_8$. Liposome preparation is carried out using standard protocols, and their sizes were analyzed using dynamic light scattering (DLS). Oxygen concentrations are measured in both aqueous and gas phases using a FireStingO_2 optical oxygen meter, with blue light serving as the irradiation source.

This study highlights the essential role of lipid bilayers in modulating photocatalytic activity and provides valuable insights for optimizing light-driven catalysis within biomimetic interfaces. The membrane immobilization of our liposomal system not only facilitates enhanced photocatalysis but also establishes a versatile and efficient platform for future research.



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“Functionalized DNA as the Spatial Control of Photosensitizer and Catalyst in Light Driven Hydrogen Evolution”

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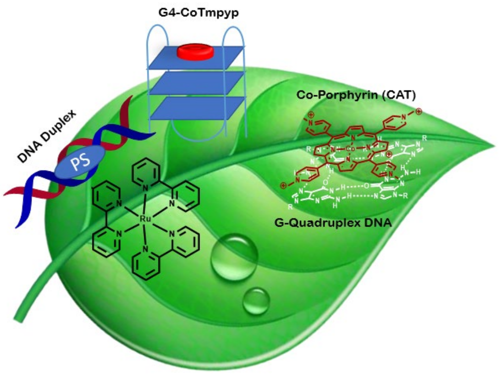
Hydrogen Evolution Reaction (HER) from water is one of the promising strategies to produce hydrogen. Because of the abundance of water on earth, hydrogen production offers a potentially scalable process for fuel generation. Artificial photosynthesis, the use of light to evolve hydrogen from water is the sustainable approach to replace electrolysis water splitting. In a study of hydrogen evolution using CoTmpyp (Tmpyp=meso-tetrakis(1-metyl-pyridinium-4-yl)-porphyrin) as catalyst (CAT) and $Ru(bpy)_3^{2+}$(bpy=2,2’-bipyridine) as photosensitizer (PS), found that the key processes triggering the photocatalytic hydrogen production is the electron transfer from the reduced photosensitizer to the catalyst[1].To overcome this problem, we are using DNA as the bridge to transfer electron from the PS to the CAT.

G4-quadruplex is a well-known DNA-structure that is rich in stacked guanine base. This architecture enables CoTmpyp to be intercalated because of the π-π stacking between the porphyrin ring and the guanine base. The combination of DNA duplex and G4-quadruplex in one strand can be a spatial control because $Ru(bpy)_3^{2+}$ can have hydrophobic intercalation with the major grooves of the DNA duplex. With this system, PS and CAT will always be at the same distance that makes the electron transfer more effective.

This study highlights the essential role of DNA in modulating photocatalytic activity and provides valuable insights for optimizing light-driven catalysis of hydrogen evolution. The CAT-PS-DNA conjugates not only facilitate enhanced photocatalysis but also establishes a versatile and efficient platform for future research.



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Guest-Encapsulation in Naphthalenediimide-Based Metal-Organic Framework for Enhanced Charge Transfer Interactions

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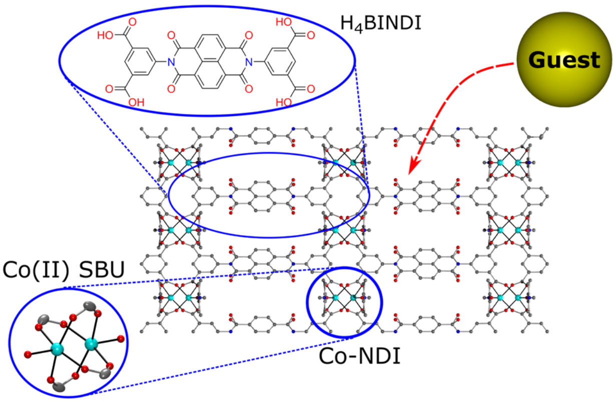
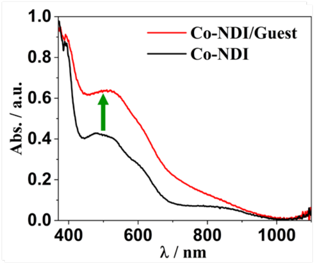
Metal-organic frameworks (MOFs) are versatile materials with promising applications in charge transfer chemistry due to their tunable porosity and chemical functionality. In this study, we present a cobalt(II)-based MOF incorporating naphthalenediimide (NDI)-based ligands as backbone to create an electron-deficient host framework.[1] By introducing an electron-rich guest molecule, we could construct a host-guest system that exhibits enhanced charge transfer interactions, as demonstrated by solid-state UV-Vis and ESR Spectroscopy. Analyses confirm that the structural integrity of the MOF is maintained after encapsulation, while new host-guest interactions could be effectively established. This strategy provides a robust and efficient approach for tailoring MOFs for advanced charge transfer applications, with implications for sustainable magnetic and electronic materials.





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Cobalt(II)-Based Single-Ion Magnets with Varying Counter Cations: Magneto-Structural Correlations, Relaxation Behavior, and Spin-Phonon Coupling

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Coordination compounds containing a single cobalt(II) ion are of current interest in the field of magnetochemistry.[1-2] In particular, the magneto-structural correlations of tetrahedral cobalt(II) complexes represent a promising avenue of research for the design criteria of single-ion magnets or the potential use in quantum computation.[3-5] This work focuses on homoleptic double anionic cobalt(II) compounds in an N4 donor coordination environment. The subtle exchange of counter cations enables the observation of slight structural changes around the cobalt(II) center, which can provide further insight into the magneto-structural correlations if linked with magnetic measurements. Moreover, alterations in the counter cation will result in changes in the structure of the vibrational spectra, which can also be explored using this series of cobalt(II) complexes. This investigation is based on a combination of structural analysis, SQUID, CW-EPR and THz-EPR measurements and *ab initio* calculations.

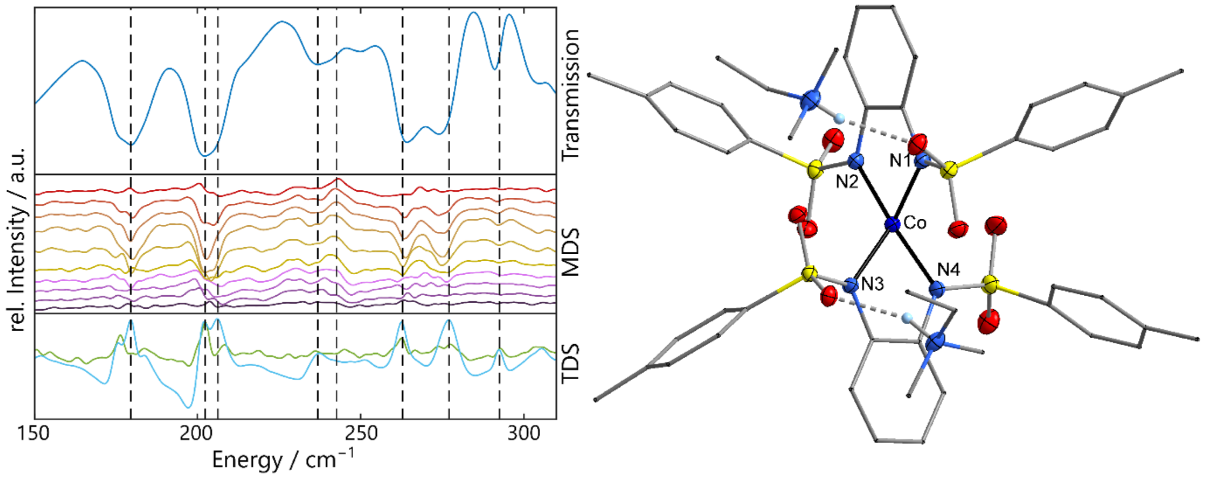

Figure 1: Right: Molecular structure of $[Co(L^{sulf})_2](HNMe2Et)_2$ **1**. All hydrogen atoms but the ones involved in hydrogen bonding are omitted for clarity. Left: THz-EPR spectra of $[Co(L^{sulf})_2](HNEt_3)_2$ **2**. The raw transmission spectrum (top), magnetic field division spectra (MDS) at 5 K (middle) and the temperature division spectra (TDS, 25/5 K and 50/25 K) at 0 T (bottom) are shown. For the MDS a spectrum at x T is divided by a spectrum measured at (x-1) T for fields up to 10 T. The broken lines mark some prominent phonons in the TDS and highlight the association to some of the magnetic signals in the MDS.

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Cucurbituril-based light switch assemblies with Ruthenium Complexes

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Aromatic N-based bridging ligands (e.g. dppz: dipyrrido[3,2-a:2',3'-c]phenazine)) of photocatalytic systems can suffer from other π-conjugated molecules through π-π-interactions.[1] The introduction of macrocycles (e.g. cucurbit[n]urils) results in the creation of artificial binding pockets that enable the light switch behavior of well-known ruthenium polypyridyl complexes.[2] In this study the host-guest interactions between [(bpy)$_2$Ru(dppz)]Cl$_2$ and cucurbit[8]uril as well as the light-switch capabilities were investigated.[3]

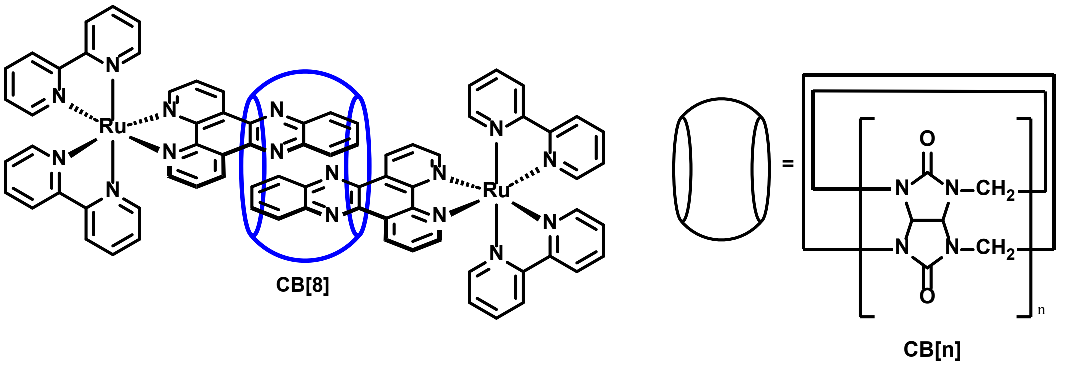

Figure 1: Host-guest complex between the dppz ligand environment and the binding pocket of cucurbit[8]uril.

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Synthesis and DNA intercalation of novel iron complexes

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The investigation of photoactive ruthenium complexes has shown their suitability for various applications, including photodynamic therapy (PDT). Using aromatic nitrogen-based ligands such as dppz (dipyrrido[3,2-a:2',3'-c]phenazine), ruthenium complexes have already been successfully intercalated into DNA thanks to the π-π-interactions.[1] However, increasing concern about sustainability has focused interest on iron as a more economical and environmentally friendly alternative. Recent advances in ligand design and synthesis have facilitated the development of more long-lived N-heterocyclic iron complexes.[2]

In this study, novel N-heterocyclic iron complexes with various dppz-related ligands were synthesized and their ability to intercalate into DNA was investigated.[3]

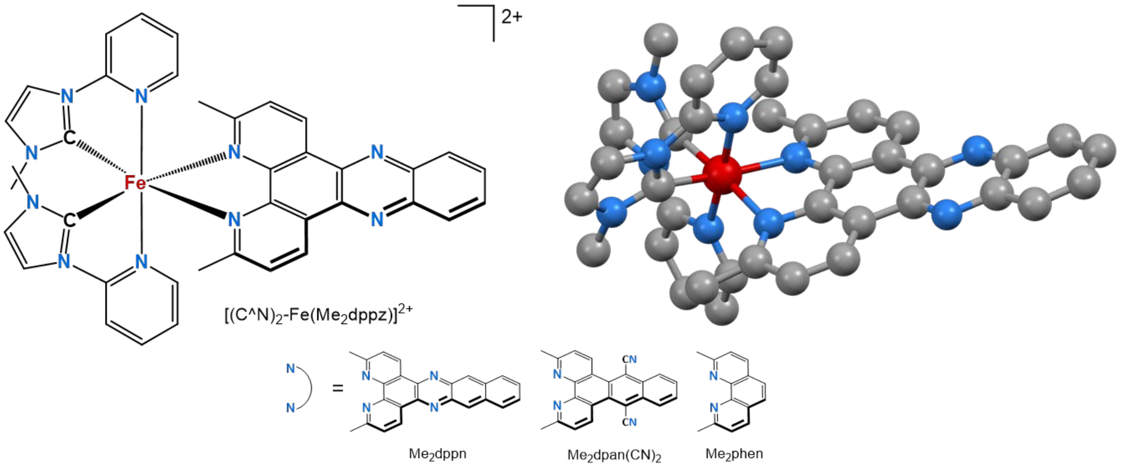

Figure 1: Chemical structure (left) of the iron-dppz complex and the corresponding crystal structure (right). Further dppz-related ligands that have been used to synthesize other iron complexes are also listed below.

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A Nonheme Perspective on Cytochrome c Oxidase: Investigating Key Iron-Copper Intermediates

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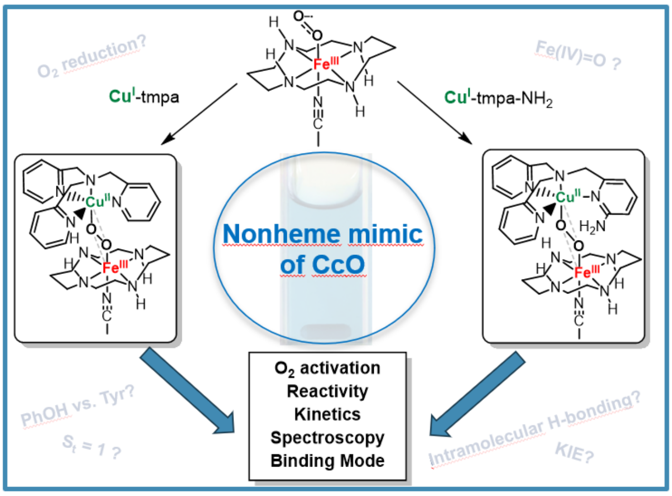
Cytochrome c oxidase (CcO), a heme-copper oxidase, catalyzes the final oxidative step in energy metabolism by transferring electrons to oxygen in the electron transport chain and generating water as a product.[1] The mechanism of O-O bond cleavage remains unclear and is proposed to involve a bridged iron-copper peroxo intermediate (I_p) with $S_t = 1$.[2,3] This intermediate is hypothesized to reduce overpotentials during O−O bond cleavage via tyrosine-driven electron transfer.[3] To date, numerous heme-copper peroxo systems have been developed as synthetic models of the I_p intermediate, but all of them are stabilized in the catalytically non-relevant $S_t = 0$ spin state. One example of a nonheme system has been reported, which stabilizes a $S_t = 1$ ground-state.[3] This study also adopts a complete nonheme approach, incorporating a previously reported Fe(III)-superoxo intermediate and two different Cu(I) precursors, Cu(I)-tmpa and Cu(I)-tmpa-NH_2.[4,5] By focusing on their reactivity as CcO mimics, it emphasizes the role of secondary coordination sphere substitutions, by comparing tmpa and tmpa-NH_2, to investigate the effects of intramolecular H-bonding on these systems. The findings provide mechanistic insights into the reductive cleavage of O_2 and enhance the understanding of the O-O peroxo core in CcO models.



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Synthesis and Characterization of Dioxygen Intermediates Employing a Pyridazine-bridged Dinucleating Ligand

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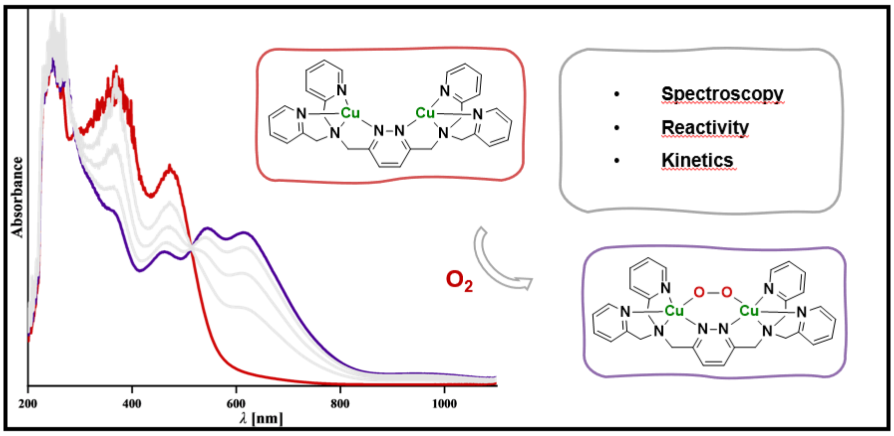
Dimetal-dioxygen complexes are key intermediates in biological oxidative reactions. Specifically, *μ*-1,2-peroxo-bridged dimetal intermediates are found in various enzymatic processes and have been proposed to directly oxidize a substrate or as an intermediate in the initial stage of dioxygen binding.[1,2]

By arranging a proximity of the metal centers in bioinspired model compounds through a rigid ligand scaffold, one can direct the binding mode of dioxygen at the metal centers and tune the reactivity of the adduct.

In this work, homobimetallic complexes are synthesized by employing a rigid pyridazine-bridged ligand scaffold as a dinucleating expansion of the widely employed tris(2-pyridylmethyl)amine (tpa) ligand, keeping a short metal-metal distance. The formation of dioxygen-adducts is followed by low-temperature UV-Vis spectroscopy and various spectroscopic techniques are used to identify the nature of the intermediates.



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Homogeneous *vs.* Heterogeneous Supported Electrocatalytic Hydrogen Production with Mononuclear Cu(II) and Ni(II) Complexes

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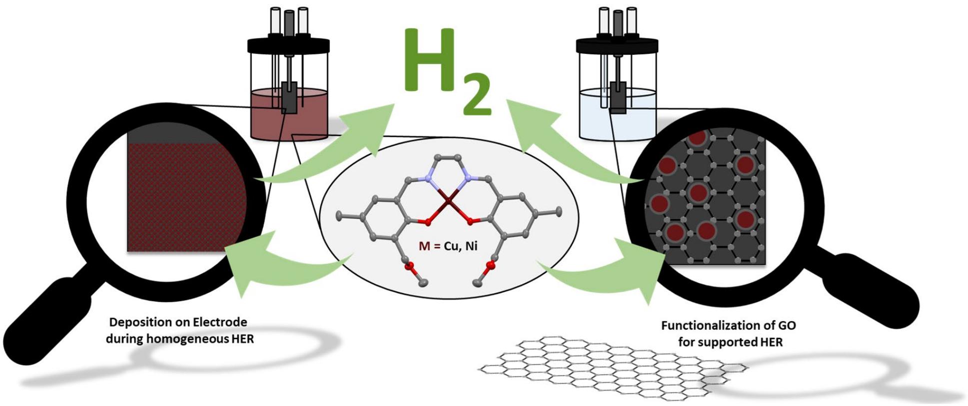
The rarity of platinum group metals has driven the search for alternative, cost-effective, and abundant catalysts for green hydrogen production.[1,2] This study focuses on investigating mononuclear salen-based copper(II) and nickel(II) complexes for homogeneous and heterogeneous graphene-supported electrocatalytic hydrogen evolution. The complexes $[\mathrm{Cu^{II}}(\mathrm{H_2L^{Me}})] \cdot 1.5\ \mathrm{H_2O}$ (**C1**) and $[\mathrm{Ni^{II}}(\mathrm{H_2L^{Me}})] \cdot 3\ \mathrm{H_2O}$ (**C2**) are characterized by single-crystal X-ray crystallography, infrared spectroscopy, and elemental analysis. Both complexes efficiently drive homogeneous hydrogen evolution at -1.9 V (**C1**) and -2.1 V (**C2**) in DMF with acetic acid as a proton source. Controlled potential electrolysis for 2 h results in charge accumulation of 33.95 C/cm² (**C1**) and 38.20 C/cm² (**C2**). Control measurements, rinse-and-repeat tests, and dynamic light scattering (DLS) analysis to exclude nanoparticle formation are used to further investigate the origin of catalysis.

Alongside this, the study of heterogeneous catalysis is being continued and includes a comprehensive electrochemical evaluation. The molecular catalysts are immobilized on Claisen graphene at different loadings and analyzed by linear sweep voltammetry (LSV) and controlled potential electrolysis to assess their activity and stability. The onset potential and overpotentials are determined, and the Faradaic efficiency is calculated by comparing the amount of hydrogen produced to the theoretical amount based on the charge passed.



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Exploring synthetic routes towards chiral metallacrown complexes for the investigation of CISS-related effects in spintronics

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Metallacrowns (MCs) are a group of polynuclear, macrocyclic coordination compounds. Their name is derived from crown ethers, organic macrocycles, which are able to coordinate a metal ion inside their central cavity.[1] MCs share this feature with their organic counterparts, but in addition to the capability of incorporating transition-metal ions as well as lanthanides, the surrounding macrocycle itself contains multiple transition metal ions. This leads to a multitude of interesting magnetic phenomena, ranging from tunable magnetic exchange interactions between ring metals and the central ion[2] to single molecule magnetic behavior.[3] Another feature of MCs is their planarity and stability. The combination of those features with their magnetic properties has made MCs the focus of intense research in the field of spintronics.

There is a rising interest in the application of the CISS (Chirality-Induced Spin Selectivity) effect in spintronics. The behavior of spin structures, like for example skyrmions,[4] can be influenced by chirality. Therefore, we are investigating different strategies to introduce chirality into the MCs. In this way, we want to make the vast number of MCs available for research related to the CISS effect.

Herein, we present three different strategies that have been successfully pursued to introduce chirality into MCs. In all cases, the different effects of the chirality on the structural and magnetic properties of the MCs have been investigated. It can be shown that MCs are a suitable platform to develop chiral, single molecule magnets.

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Improving Selectivity in Iron Promoted Catalysis of Azides *via* a Hemilabile σ-Donor in the Second Coordination Sphere

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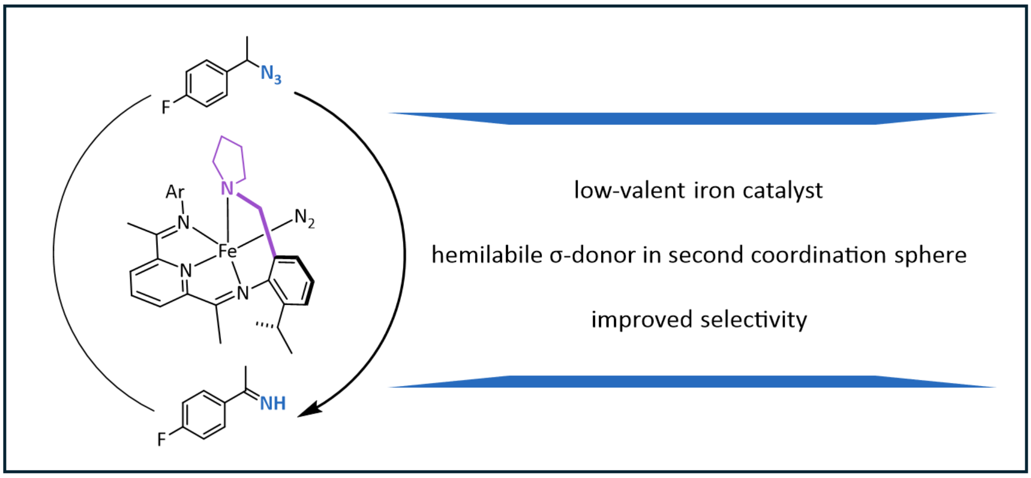
The addition of a σ-donor in the secondary coordination sphere of a low-valent redox active PDI-iron-complex improves the selectivity in the catalytic formation of N-unsubstituted imines from benzylic azides. While previously such imine-species could only be generated as *E/Z*-mixtures using established transition metal catalyzed approaches,[1,2] this study gives insight into the tunability of this reaction towards achieving higher selectivity through ligand-design.

The ligand design relies on the introduction of a hemilabile pyrrolidine-arm, which blocks the apical position of the iron catalyst, facilitating the preferred formation of the *E*-isomers. Crystallization and characterization of the pre-catalyst and catalytically relevant species allow the proposal of a mechanism.



low-valent iron catalyst

hemilabile σ-donor in second coordination sphere

improved selectivity

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Synthesis and characterization of low-valent phosphino-α-iminopyridine iron imido complexes

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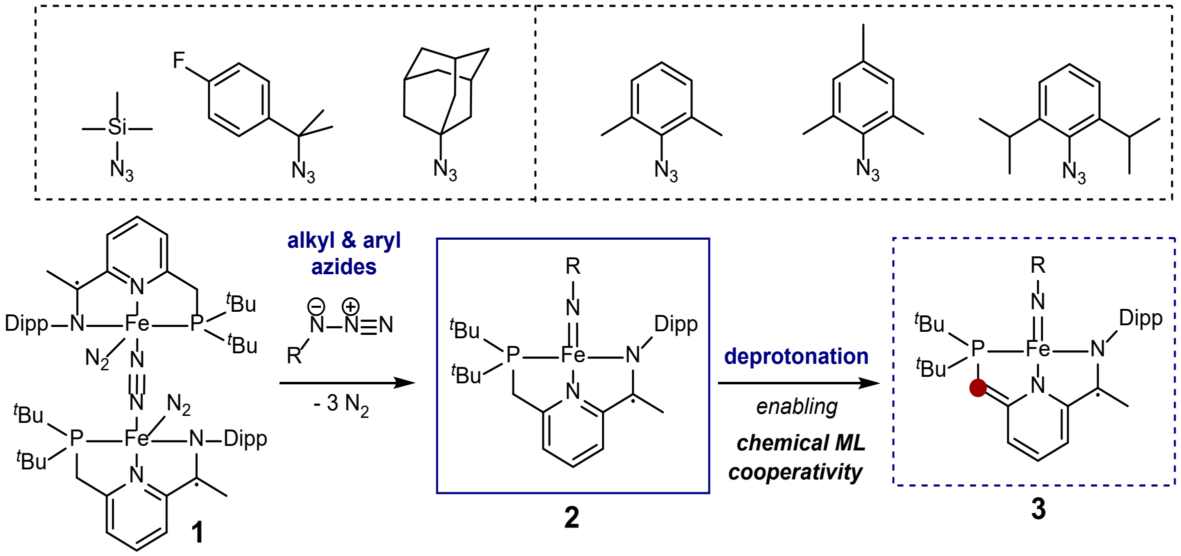
Terminal iron imides (Fe=N–R) exhibit interesting electronic structures and are the subject of intensive research, particularly with regard to their potential role as intermediates in the nitrogen fixation mechanism.[1] They are also of significant value due to their ability to undergo a range of reactions, including intramolecular[2] and intermolecular[3] C–H bond amination, olefin azidation[4] and aminohydroxylation.[5]

For our investigations, we have chosen di-*tert*-butylphosphine-α-iminopyridine ($^{t\mathrm{Bu}}$PNN) ligands - structural motifs amenable for different metal-ligand cooperativity (MLC) mechanisms. Firstly, the redox-active imine group can be used as an electron reservoir to "store" electrons and enter into redox MLC reactivity,[6] and secondly, the acidic benzyl group can be deprotonated to initiate a pyridine dearomatization, thereby enabling participation in chemical MLC.[7]

The target iron imido complexes type **2** were synthesized by reacting the $^{t\mathrm{Bu}}$PNN-based iron-nitrogen precursor **1** with various alkyl and aryl azides. The obtained $^{t\mathrm{Bu}}$PNN iron imido complexes **2** were found out to exhibit different reactivities depending on the *N*-substitution pattern of the azide reaction partner. In this contribution, these differences will be discussed.



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Cyclopentadienyl Cobalt Diamidobenzene Complex for Catalytic Ammonia Oxidation to Dinitrogen

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The rise in global energy demand and greenhouse gas emission necessitates sustainable energy source to reduce reliance on carbon-based fuels.[1] If energy can be retrieved efficiently then storing it in the form of chemical bonds is a good solution.[2] Ammonia is emerging as a promising alternative for carbon-free fuels due to its high density, easy transport and storage.[3] Ammonia oxidation converts ammonia (NH_3) into nitrogen (N_2) and water (H_2O), which is important for sustainable ammonia removal and nitrogen production. Molecular catalysts based on transition metals offers various insights into the spectroscopic, kinetic, electrochemical aspects of bond breaking and formation. Metal complexes, including iron,[4] manganese,[1] copper,[5] molybdenum,[6] and ruthenium,[7] have efficiently catalyzed ammonia oxidation. With this idea in mind we have synthesized a novel cyclopentadienyl cobalt complex with redox active diamidobenzene ligand, o-Bis(methanesulfonamido)benzene (H_2bmsab), which enhances electron deficiency and ammonia binding in its neutral state. This complex shows potential for electrocatalytic ammonia oxidation. We characterized its structure, redox behavior, electronic transitions, and magnetic properties using NMR spectroscopy, single crystal X-ray diffraction, cyclic voltammetry, UV/VIS/NIR (spectro-) electrochemistry, EPR and TD-DFT studies.

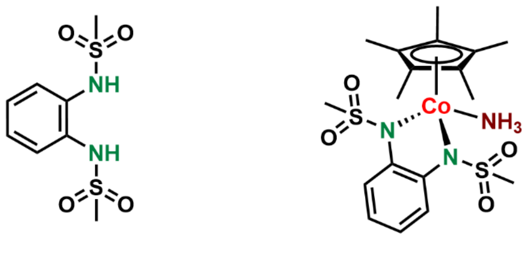

Figure 1. o-Bis(methanesulfonamido)benzene ligand (left) and cyclopentadienyl Cobalt Diamidobenzene Complex (right).

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New metal complexes for ruthenium-based photoactivated chemotherapy (PACT)

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Ruthenium-based photoactivated chemotherapy (PACT) refers to compounds that exhibit the ability to undergo a photosubstitution reaction with various solvents such as water, acetonitrile, or DMSO, with the resulting photoproduct then triggering cell death.[1]

Supported by theoretical calculations, it was shown that variation of the ligands in octahedral ruthenium complexes influences the photoactivation wavelength range.[2]

In this study, ruthenium-based [3+2+1] complexes were designed as novel potential PACT agents, to have their photoactivation range shifted to the red-light part of the spectrum. The monodentate ligand, which so far was mostly neutral, has been changed to a triazolato species in this new approach, which is then to be photosubstituted and released.

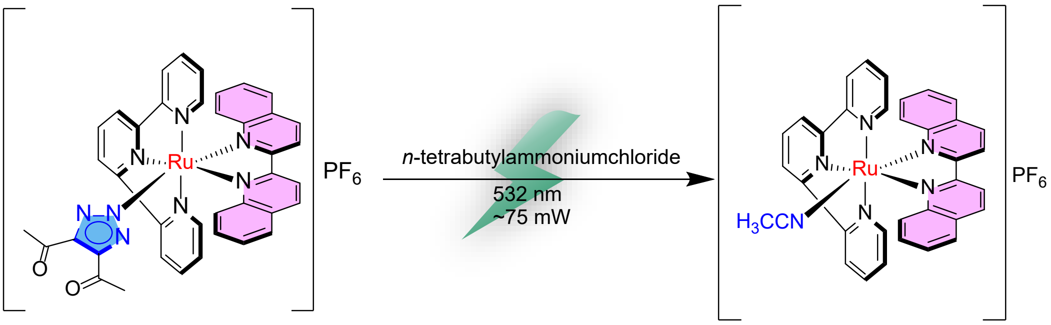

Figure 1: Ligand substitution in a [3+2+1] Ru(II) triazolato complex by green light as a novel approach to PACT.

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The Role of Ancillary Ligands in Cyclometalated Iridium(III) Complexes with a [3+2+1] Coordination Sphere

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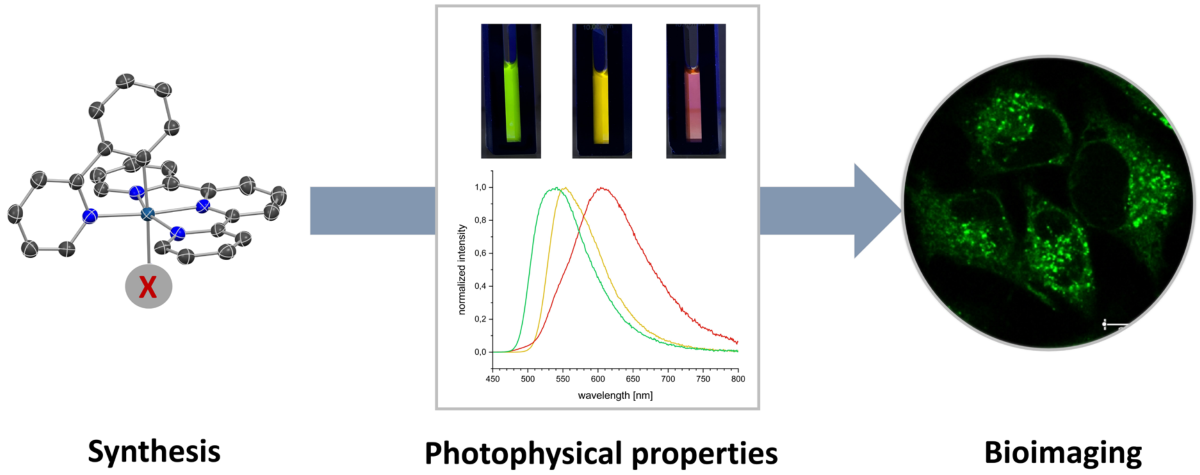
Cyclometalated iridium(III) complexes are of significant interest for applications in catalysis, materials science, and biology due to their exceptional photophysical properties, including high quantum yields, tunable emission profiles, and long-lived excited states.[1] This study explores cyclometalated iridium(III) complexes with a [3+2+1] coordination sphere, an attractive scaffold for modulating photophysical properties and reactivity through simple modifications of the monodentate ligand. A series of octahedral complexes were synthesized, systematically characterized, and their reactivity under both dark and light conditions was investigated. Furthermore, we aimed to demonstrate that, with the appropriate choice of ancillary ligand, this class of iridium(III) complexes can be used for potential biological applications.[2]



Synthesis

Photophysical properties

Bioimaging

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Synthesis and Redox Chemistry of Co_3E_4 (E = P, As) Clusters

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Due to their complex redox behaviors and confined coordination sphere, multi-metallic systems have attracted great attention not only for catalytic systems.[1] Despite their utilization in numerous fields, a controllable synthesis of many transition metal clusters remains a challenge and most of them are solely investigated by density functional theory calculations.[2] For the synthesis of $[(Cp^RCo)_nE_m]$ (E = P, As) cluster or cage complexes, only a few different routes are described in the literature via thermolysis or photolysis reactions with white phosphorus and yellow arsenic, respectively, or by utilization of *Zintl* reagents.[3] However, the subsequent reactivity of these transition metal clusters or polynuclear complexes, respectively, was not investigated. Within this work the synthesis of the cluster complexes $[(Cp'''Co)_3(\mu_3,\eta^2:\eta^2:\eta^2\text{-}E_3)(\mu_3\text{-}E)]$ (E = P (**3**), As (**4**)) starting from the anionic triple-decker complexes $[K(18cr6)(dme)_2][(Cp'''Co)_2(\mu,\eta^4:\eta^4\text{-}E_4)]$ (E = P (**1**), As (**2**)) by electrophilic quenching with the Co dimer $[(Cp'''CoCl)_2]$ is reported (Figure 1, left).[4] Both complexes can be described as *nido* clusters applying the Wade Mingos[5] rules exhibiting 9 skeletal electron pairs each. **3** and **4** show a distinct redox chemistry, which was first investigated by cyclic voltammetry (for compound **4**, Figure 1, right). We reduced and oxidized the cluster compounds **3** and **4** in a synthetic manner and performed DFT calculations to elucidate the structural features of the respective products.[4]

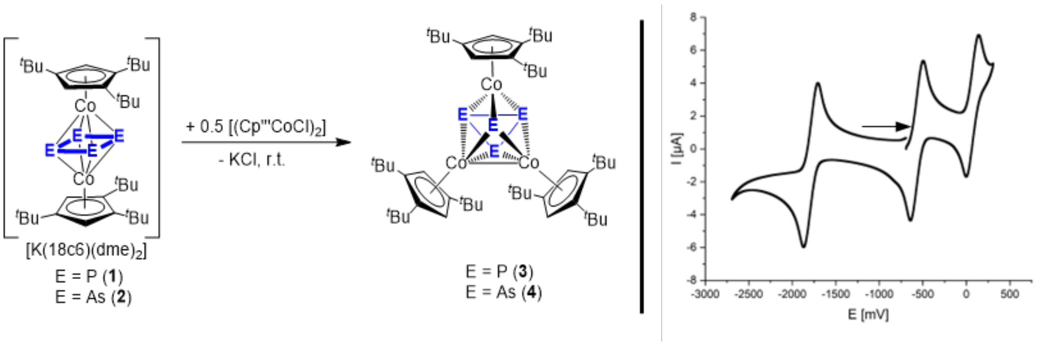

*Figure 12. Synthesis of the cluster compounds **3** and **4** (left) and cyclic voltammogram of **3** in thf against Cp_2Fe/Cp_2Fe^+ (right, electrolyte $[^nBu_4N][PF_6]$, rate of feed: 100 mV/s. temperature: r.t.).*

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Cationic group 13/14/15 element chain compounds with pnictogen-donor ligands

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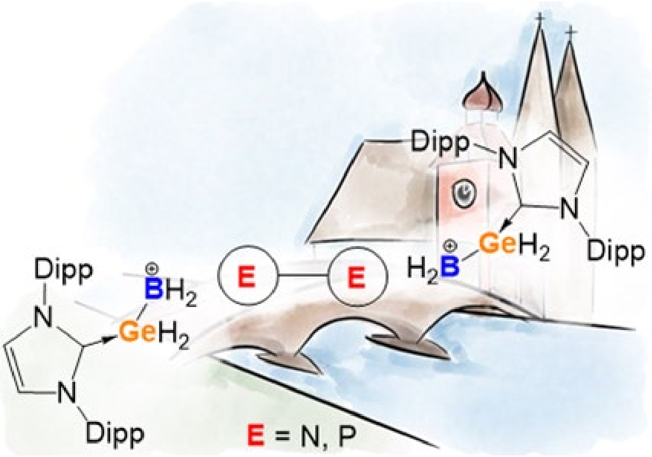
Mixed main group-element compounds have earned significant attention over the past decades e.g., as single-source precursor for semiconducting materials.[1,2] A recent advancement in this field was the synthesis of IDippGeH_2BH_2OTf (**1**), which features a cationic chain of group 13 and 14 elements.[3] The utility of compound **1** as a building block for extending main group-element chains has also been demonstrated.[4] Furthermore, the formation of both cationic and neutral group 13/14/15 element chains using P-donor ligands, as well as the formation of cationic chains with As-donor ligands, has been reported.[5]

In this presentation, the reactivity of **1** towards monodentate N-donor and bidentate pnictogen-donor ligands was studied. Tertiary amines and pyridine-type ligands form cationic adducts with **1**. In contrast, primary and secondary amines exhibit a proton transfer to the germanium center, resulting in the formation of IDippGeH_3^+ and IDippBH_2NHR'R''$^+$ adducts. Reactions with bidentate N- and P-donor ligands led to the formation of dicationic chains composed of two IDippGeH_2BH_2^+ units connected via the linker.

The synthesized compounds were characterized by SC X-ray crystallography, NMR spectroscopy and mass-spectrometry, providing insights into their structural properties.



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New Copper-Dioxygen Complexes for Photo-Assisted Oxidation of Toluene to Benzaldehyde

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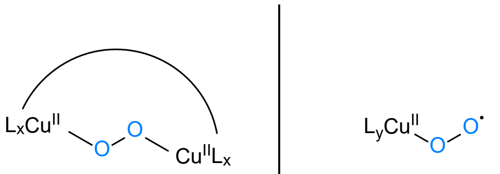
Selective oxidations of organic substrates using molecular oxygen under mild, enzyme-like conditions are of great interest for organic synthesis in terms of safety, efficiency, and economics. Model complexes provide precise control over the electronic and geometric properties of the ligands. These ligands stabilize the copper-dioxygen adducts, improve hydroxylation, and lead to the main goal of oxidizing C-H bonds.[1]
A model system based on the tetradentate ligand *tris*[(2-pyridyl)methyl]amine (TMPA) was developed by Karlin *et al*.[2]. TMPA can form a copper-dioxygen-adduct-complex when exposed to dioxygen and copper(I). The activated dioxygen can oxidize organic compounds, e.g., toluene to benzaldehyde. During the oxidation process, the copper(I) species is also oxidized to a redox inactive copper(II) species which is no longer able to oxidize further substrates. Thus, the recovery of the active copper(I) complex is of great interest to obtain a catalytic cycle.[2,3]
A recently developed approach is the use of photosensitizers to achieve the reduction of copper(II) complexes and therefore obtain a catalytic cycle.[4] To determine the most suitable copper-dioxygen species for this reaction, different polydentate ligand-systems were synthesized. Their respective copper(I) complexes have been investigated regarding their reaction with dioxygen. The focus is on comparing between intramolecular *end-on trans-μ*-1,2-peroxide- and an *end-on* η^1-superoxide species (Fig. 1) in their ability to oxidize toluene to benzaldehyde in a photo-assisted reaction cycle.



end-on trans-μ-1,2-peroxide

end-on η^1-superoxide

Figure 1: Intramolecular *end-on trans-μ*-1,2-peroxide species (left) and *end-on* η^1-superoxide species (right).

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Catalytic Photo-induced Proton Coupled Electron Transfer to Anthracene with Metalloporphyrin Hydride

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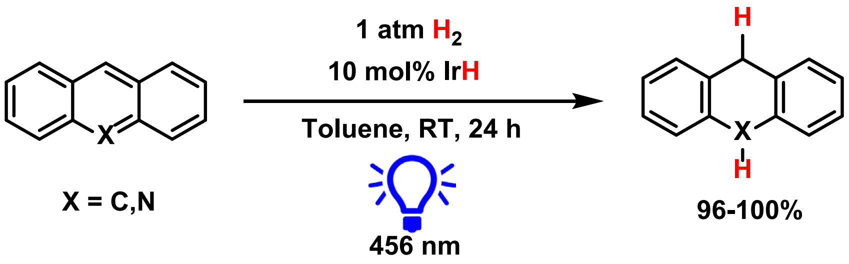
Photocatalysis is a potential strategy to overcome thermodynamic limitations that are associated with the formation of weak element-hydrogen (E-H) bonds as mechanistic bottlenecks during catalytic transformation. The concerted proton-coupled electron transfer (PCET) influenced by the photo-excitation has been an attractive method in field of photocatalysis. On the other hand, direct reduction of arenes and heteroarenes by visible light irradiation remains challenging, as the energy of single photon is not sufficient for breaking aromatic stabilization [1]. A representative example is the photoactive iridium(III) hydride which catalyzes the hydrogenation of challenging arenes like anthracene up to 61 percent under the photochemical conditions [2]. Here, we developed a porphyrin based iridium(III) hydride having decent excited state energy can able to perform quantitive hydrogenation of arenes and heteroarenes photocatalytically.



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Synthesis and Reactivity of a square-planar group 8 Complexes

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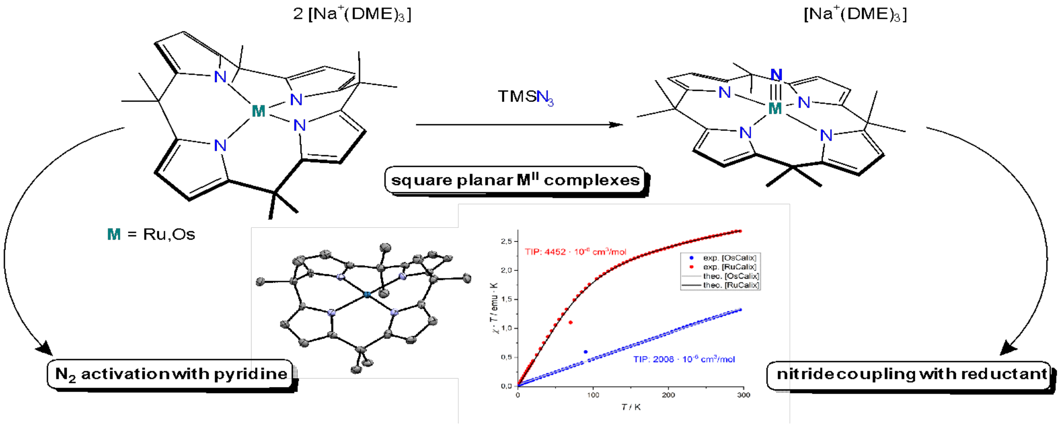
Four-coordinate Fe^{II} complexes are common and generally adopt tetrahedral ($S = 2$) or, in some cases, square-planar ($S = 1$) metal coordination.[1,2] In contrast, the coordination chemistry of the heavier, divalent group 8 metals (Ru^{II}, Os^{II}) is dominated by octahedral complexes, while four-coordinate Ru^{II} and Os^{II} tends to form seesaw structures ($S = 0$). Only a few examples for square-planar Ru^{II} have been reported,[3-5] and a single square-planar osmium(II) complex is known to date.[6]

Here, the synthesis as well as the spectroscopic, structural and magnetic characterization of square-planar ruthenium(II) and osmium(II) complexes is presented (Figure 1) and the reactivity towards dinitrogen splitting vs. reverse nitride coupling are discussed.



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Synthesis of bis(hydrosilyl)alkyne tungsten complexes

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α- Donor-substituted alkynes serve as versatile bridging ligands between two metal centers, adopting a μ-η^2–C,C‘-κ^2-E,E‘-bonding mode. The system has already demonstrated its flexibility and variability in tungsten complexes with a variety of different donor atoms (C, N, O, P, S). Both symmetrical and asymmetrical donor combinations are achievable. Silicon as the heavier homologue of carbon, has been introduced as a donor into this system, expanding its scope.[1-6] Starting from the η^2-acetylene tungsten complex, a hydrosilyl function is inserted through deprotonation of the alkyne ligand and subsequent addition of the chlorohydrosilane.

Bridging of the tungsten complex with a second metal center is achieved via oxidative addition of the Si-H bond to the second metal centre, resulting in the formation of a hydrido-metal complex. First success has been achieved with metals from the 7th and 8th subgroups, particularly iridium and platinum. Key areas of interest include the redox behavior of mononuclear tungsten complexes in comparison to their polynuclear counterparts, as well as the formation of silylium ions via hydride abstraction.

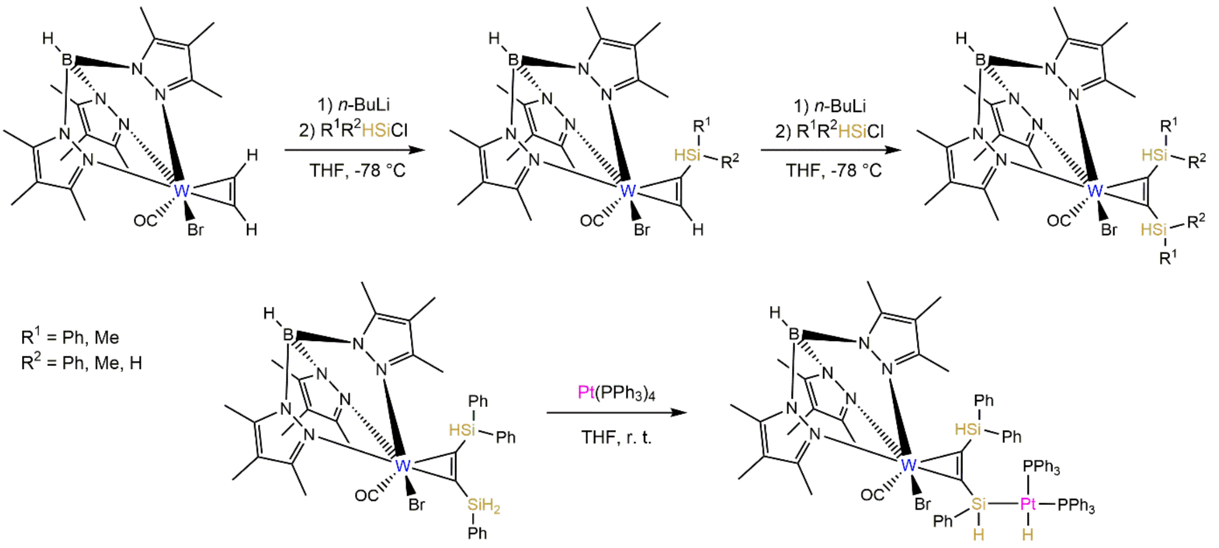

Figure 1: Syntheses of bis(hydrosilyl)alkyne tungsten complexes and an W-Pt dinuclear complex

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Triazole dithiolate as versatile building block in coordination polymers

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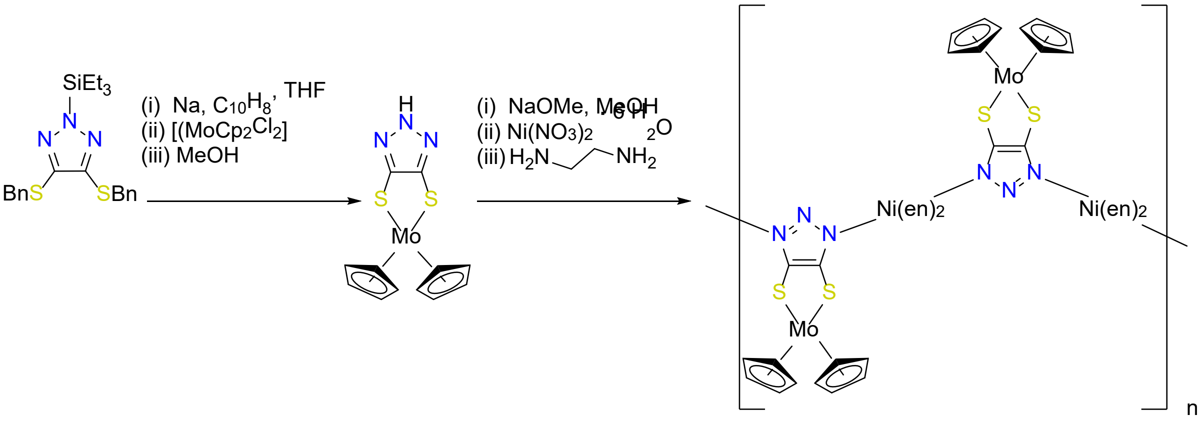
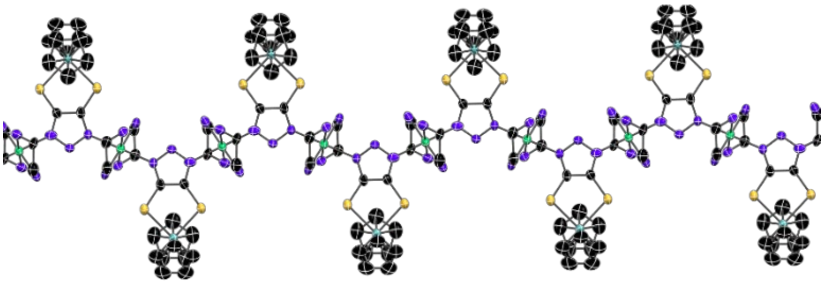
Dithiolenes are dithiolate ligands, which are unsaturated in the carbon backbone. The associated delocalisation of electron density renders the sulfur atoms very soft Lewis bases. Combining a dithiolene unit with a triazole creates a versatile ligand, in which the nitrogen atoms serve as relatively hard donors compared to the sulfur centers. However, both sulfur and nitrogen donors can coordinate metal ions, resulting in a variety of different linking modes. Due to the versatility of redox states in dithiolene complexes, transition metal complexes of triazole dithiolate are of significant interest in regard to the synthesis of electrically conductive MOFs (Metal-organic framework). Mononuclear complexes can be obtained by reacting various metal precursors with the dithiolene unit. The subsequent reaction of neutral molybdenum complexes with nickel(II) nitrate in the presence of ethylene diamine under basic conditions led to the formation of a 1D coordination polymer, in which the nickel(II) ion is coordinated by two triazole ligands in *trans*-position. The 1,3,-linkage mode of the triazole moiety resulted in a linear chain.





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Understanding Thermally Activated Delayed Fluorescence: A critical view on the Energy Gap

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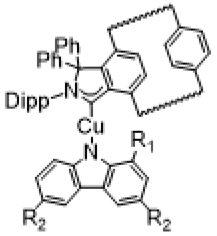
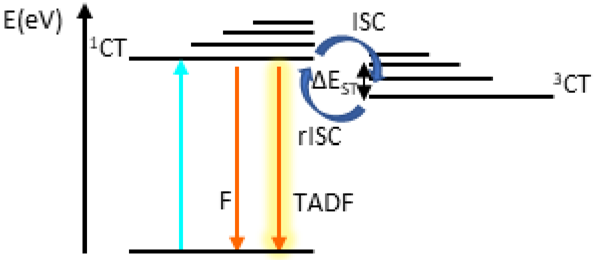
The efficiency of thermally activated delayed fluorescence (TADF) is assumed to dominantly depend on a small energy gap between the singlet and triplet excited states ΔE_{ST}, which can be overcome at room temperature, leading to an efficient reverse intersystem crossing (rISC) process (Figure). The dihedral angle between the donor and acceptor groups of linear copper(I) complexes determines the magnitude of the exchange integral, which directly influences ΔE_{ST}.[1] An extensively characterised series of copper(I) compounds with a [2.2]isoindolinophanyl-based carbene ligand (iPC), which differ only by the substituents on the donor scaffold, was investigated with regard to their TADF mechanism.[2] Using steady-state and time-gated emission spectroscopy, the energy levels of S_1 and T_1 of microcrystalline [CuX(iPC)] (X=Cbz (**1**), MeCbz (**2**), OMeCbz(**3**), and tBuCbz(**4**)) were determined and the energy gap was compared with the radiative rate constant. Compound **4** exhibits the largest radiative rate constant $k_{rad} = 1.4 \cdot 10^6\ s^{-1}$ with $\Delta E_{ST} = 62$ meV. Compound **3**, on the other hand, shows a smaller $k_{rad} = 1.1 \cdot 10^6\ s^{-1}$ despite an even smaller energy gap $\Delta E_{ST} = 55$ meV. A purely thermodynamic point of view cannot explain this behaviour, which is why the structurally very similar cyclic (amino)(aryl)carbene (CAArC) is used for comparison and the role of the density of excited states for the TADF mechanism is discussed.[3]



	k_r [$10^5 s^{-1}$]
(**1**) $R_1 = R_2 = H$	14
(**2**) $R_1 = H$; $R_2 = Me$	14
(**3**) $R_1 = H$; $R_2 = OMe$	11
(**4**) $R_1 = H$; $R_2 = tBu$	19



ΔE_{ST} vs. k_{rISC} vs. $f_{S_1} = k_{r(TADF)}$

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Ultrafast Photodynamics of an Azopyridine-Functionalized Cobalt(III) Complex

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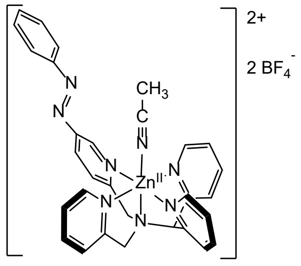
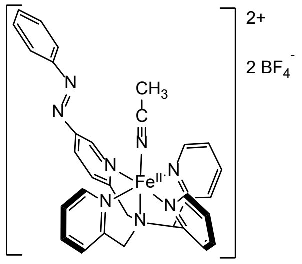
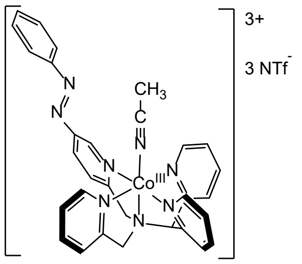
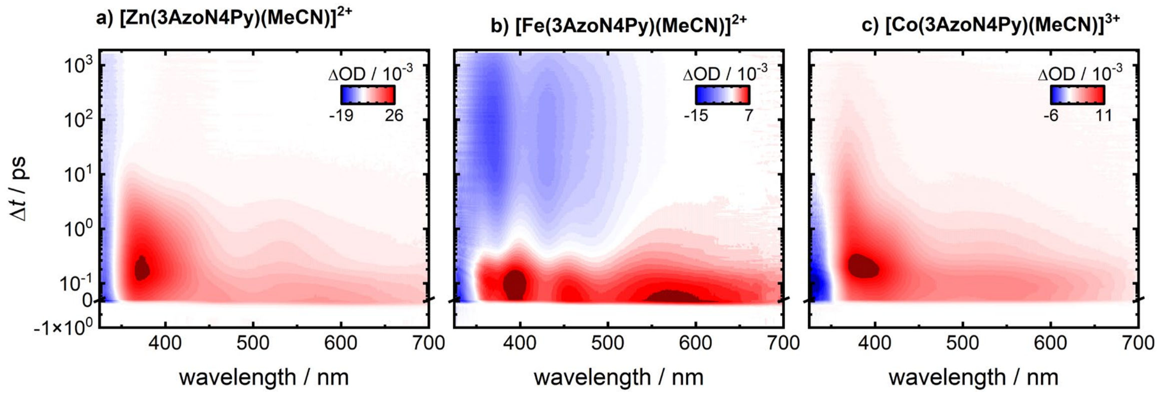
The concept of ligand-driven light-induced spin change (LD-LISC) of transition-metal complexes in solution holds great application potential for, e.g., spintronic devices.[1] In 2019 we published a study on an azopyridine-functionalized iron(II)-complex based on the N4Py ligand which was investigated using femtosecond transient electronic absorption spectroscopy (TEAS). The results suggest that the excited state of the azopyridine does not relax via *trans*-to-*cis* isomerization, but predominantly via energy transfer to the iron center, which explains the diminished *trans*-to-*cis*-isomerization observed in stationary experiments. The corresponding Zn(II) complex exhibits pure azo dynamics.[2] The system was then modified by replacing the metal center with cobalt(III). Since the MLCT bands are shifted to higher energies compared to iron(II), this excludes the relaxation pathway via MLCT bands and allows for a more efficient isomerization, as demonstrated by stationary UV-vis and NMR spectroscopy. When this system was investigated using TEAS apparent azo-related dynamics were observed, but also a long lived excited-state absorption, which is caused by a competing relaxation pathway. This potentially includes low-lying LMCT states, producing Co(II) and a ligand radical cation, or metal-centered excited states such as triplet states of Co(III).[3]









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Triazole group in charge-neutral zinc(II) containers - More than just connecting units

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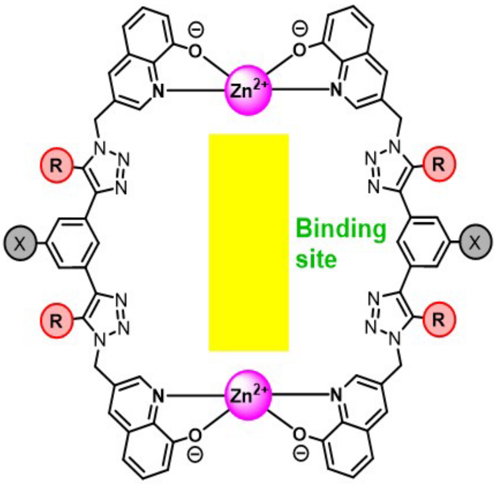
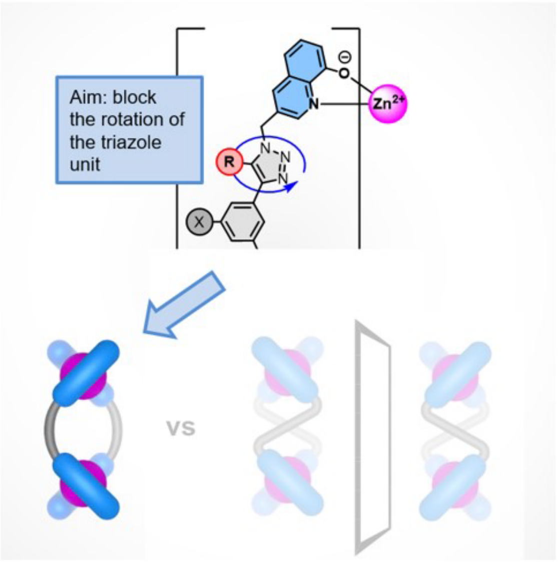
Charge-neutral metal-assembled organic cages that recognize anions have reduced competition from the counter anions that are usually associated with positively charged anion receptors and at the same time offer ease in the synthesis. Such a charge-neutral receptor that recognizes carboxylate anions has been reported from our lab [1]. Still, the solubility of the resulting complex was poor which makes it difficult to exploit the potential applications such as catalysis in confinement. Additionally, triazole can adopt two orientations which is hard to predict and mainly driven by the size of the guest. Here, we aim to substitute the proton at the triazole in the previously reported ligand with a suitable group that could prevent or facilitate the triazole rotation that can give more predictability to the receptor-anion complex [2] and increased solubility.




Aim: block the rotation of the triazole unit

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Tailored charge-neutral self-assembled L_2Zn_2 container for taming oxalate

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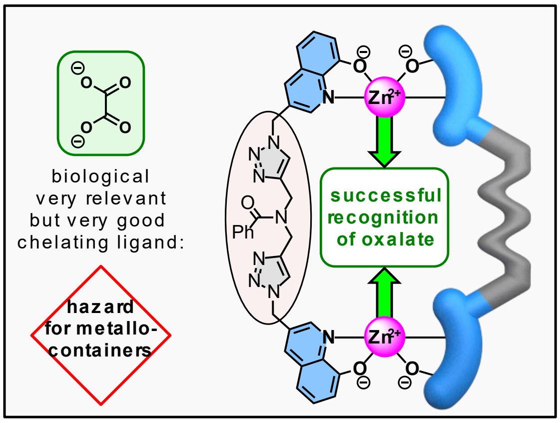
Dicarboxylic acids and their corresponding anions are involved in several industry processes and are omnipresent in nature. Many dicarboxylic acids are, for example, intermediates in the biosynthesis of proteins and environmental metabolites.[1,2] Oxalic acid, the simplest dicarboxylic acid, may cause a multitude of health problems including kidney stones and liver damage.[3-4] Thus, research tackling new receptors for especially oxalate is of great importance. Recently, our group published the first version of a charge-neutral metal-based self-assembled L_2Zn_2 helicate with the capability of binding dicarboxylates with astonishing binding affinities in competitive media.[5] Inspired by its size selectivity regarding the dicarboxylate length with naphthalene-2,6-dicarboxylate as aromatic and pimelate as aliphatic analyte being ideal matches for the receptor, the goal of this project is to bind now even shorter dicarboxylates. By modulation of the planar backbone with rather rigid bond angles to a more flexible backbone based on dipropargyl amine, the host-system increases its degree of freedom. Hence the system is capable of binding oxalate.[6]



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Aluminum complexes based on Aminophenol-Ligands

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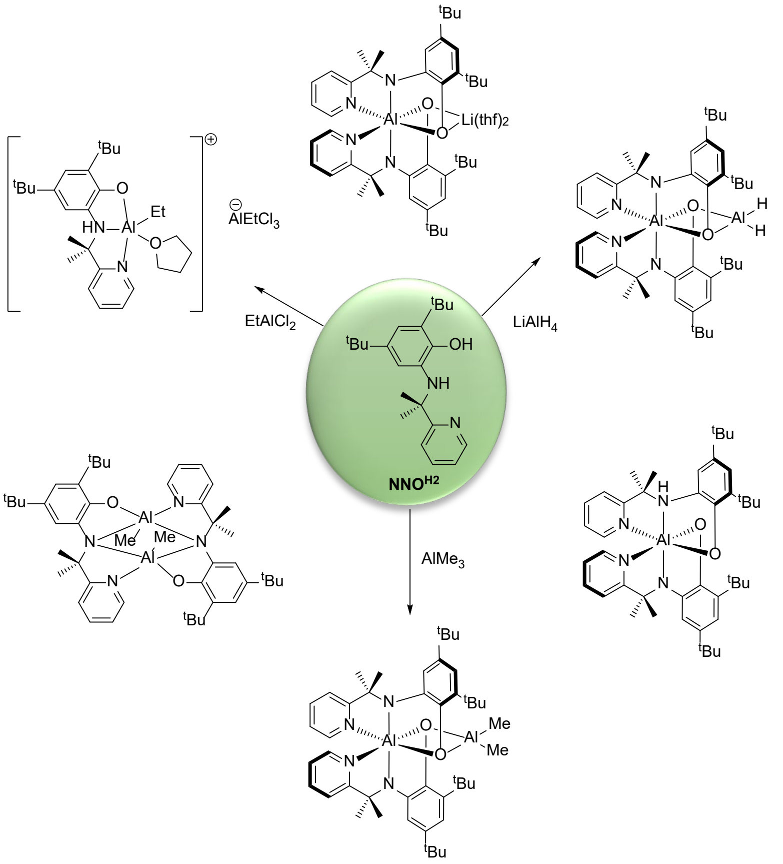
Within our working group the properties of redox-active, non-innocent ligands in transition metal complexes are investigated. Different transition metals including noble metals and earth abundant metals combined with a tridentate NNO^{H2} ligand are suitable for e.g. *C-H* amination catalysis.[1],[2] However, the combination of our tridentate ligands with p-block elements has not been investigated prior in our working group. Combining redox-active aminophenol ligands with Al^{III} led to the formation of complexes with varying coordination modes, heavily depending on the reaction conditions and different Al-precursors used within the synthesis. This diversity of accessible coordination modes may allow us to challenge the boundaries of the combination of Al^{III} and our redox-active ligands. We will report the first results on their synthesis as well as the characterization by NMR spectroscopy, EPR, XRD and electrochemical properties.



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Co-ordination Chemistry of Azole-Based Di- and Tridentate Ligand Scaffolds

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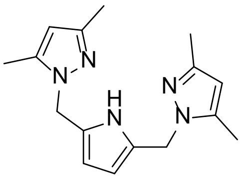
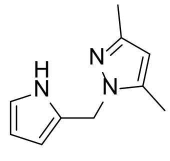
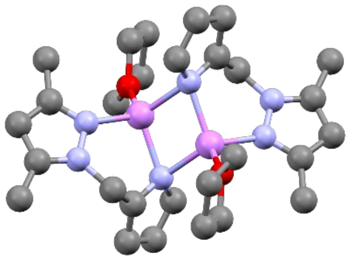
Pincer ligands are well known for their balance between reactivity and stability and their versatility.[1] Attributed to their modularity in steric and electronic parameters,[2] there are numerous examples of azole-based chelating ligands[3,4,5,6,7] with diverse potential applications, e.g., in catalysis[8] and medicinal chemistry.[9] This project aims to characterise the molecular and electronic structure of transition metal and lanthanide compounds of different ionic radii co-ordinated by the $(^{\mathrm{Me_2}}\mathrm{PzMe})_2$Py-NNN pincer ligand and its one-armed counterpart, the novel chelating $^{\mathrm{Me_2}}$PzMePy-NN ligand. A crystal structure of Li[$^{\mathrm{Me_2}}$PzMePy] was obtained that demonstrated formation of a binuclear complex similar to the known structure of $\mathrm{Li_2}[(^{\mathrm{Me_2}}\mathrm{PzMe})_2\mathrm{Py}]_2$.[10] While compounds of late transition metal complexes of the tridentate ligand with Cu, Ag and Pd are known,[10,11] there are neither reports of early transition metal and lanthanide compounds, nor of co-ordination compounds of $^{\mathrm{Me_2}}$PzMePy as yet, whose properties are to be elucidated during this project.

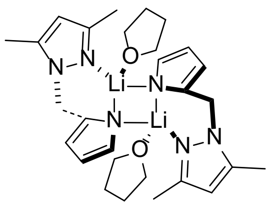


$(^{\mathrm{Me_2}}\mathrm{PzMe})_2$Py-NNN-Pincer



$^{\mathrm{Me_2}}$PzMePy-NN-Chelate





$\mathrm{Li_2}[^{\mathrm{Me_2}}\mathrm{PzMePy}]_2$

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Cooperative spin crossover leading to bistable and multi-inert system states in an iron(III) complex

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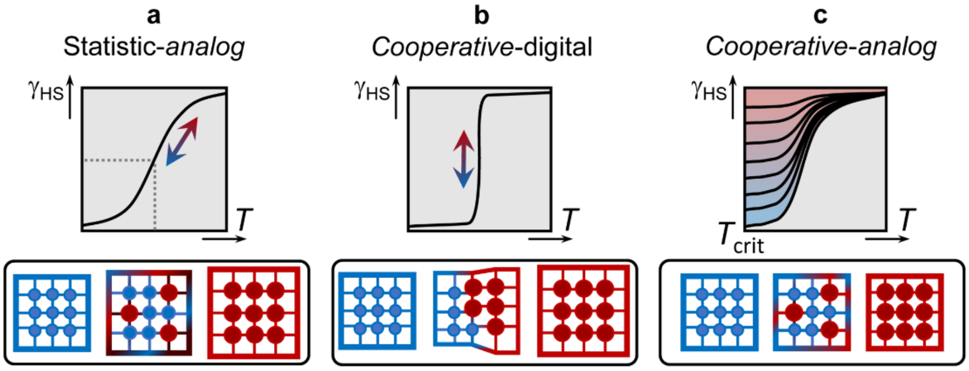
Cooperativity among spin centres has long been the royal road in spin crossover (SCO) research to impose magnetic bistability in terms of thermal hysteresis.[1,2] In this work we access magnetic multi-inert states of the iron(III) compound $\{FeL_2[B(Ph)_4]\}$ ≡ **FeB** at low temperature, in addition to thermal bistability. The packing of the low-spin and high-spin forms of crystalline **FeB** differs only marginally what ultimately leads to structural conservatism. This indicates that the SCO-immanent breathing of the complex cation is almost fully compensated by the anion matrix. The unique cooling rate dependence of the residual low-temperature magnetisation in **FeB** unveils continuous switching between the trapped high-spin (ON) and the relaxed low-spin state (OFF). The macroscopic ratio of the spin states (ON:OFF) can be adjusted as a simple function of the cooling rate.[3] That is, cooperative spin crossover can be the source of bistable and multi-inert system states in the very same material.



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Preparation of nanoparticles by incorporation of spin crossover coordination polymers in a block-copolymer matrix

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Synthesising nanostructured coordination networks (e.g. MOFs) or coordination polymers (CPs) is one key goal to lift this material class from fundamental research to application. Particularly interesting in that regard are spin crossover polymers and MOFs (SCOFs), where spin states of the material can be switched using different chemical or physical stimuli (e.g. pressure, temperature). This property makes them interesting especially for applications like sensing. In the past, the concept of CPs incorporated in block-copolymers was explored using in terms of magnetic properties, the influence of different bridging ligands[1] and micellular size and shape depending on the polymer composition.[2]

Upcoming studies will focus on the new spin crossover CPs and the exploration of compound exchange processes between the nanocomposite and its environment using a fluorescent marker.

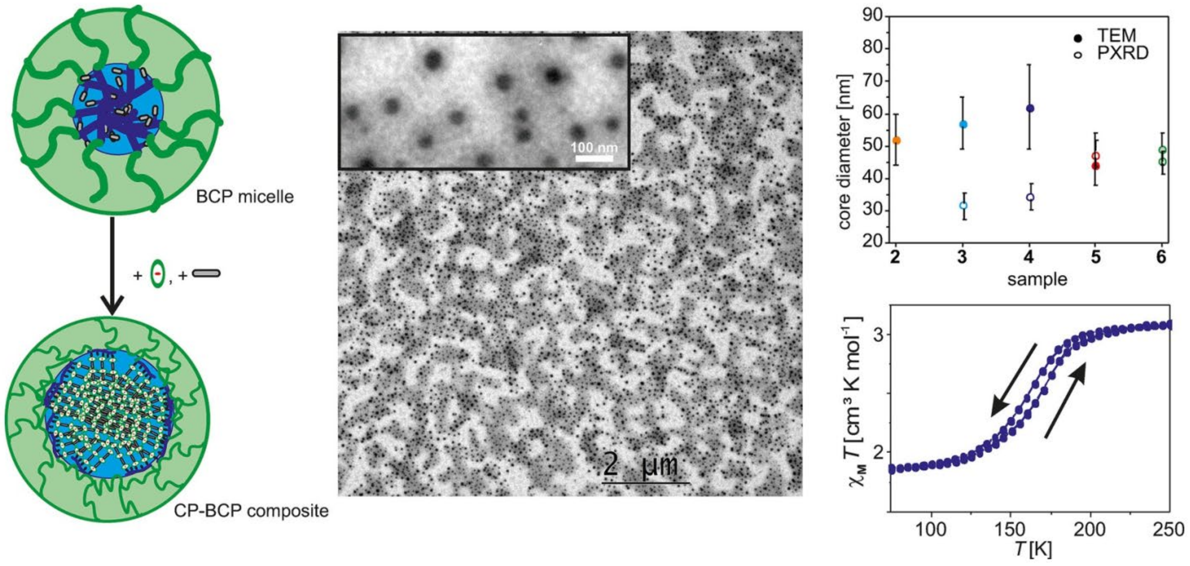

Figure 1: Schematic visualisation of Block-copolymer and the nanocomposite. Middle: TEM picture of the nanocomposite micelles. Right: Influence of the number of additions on the micelle core diameter. Magnetic measurements after the fifth addition.[3]

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Low-coordinate iron organoazide complexes

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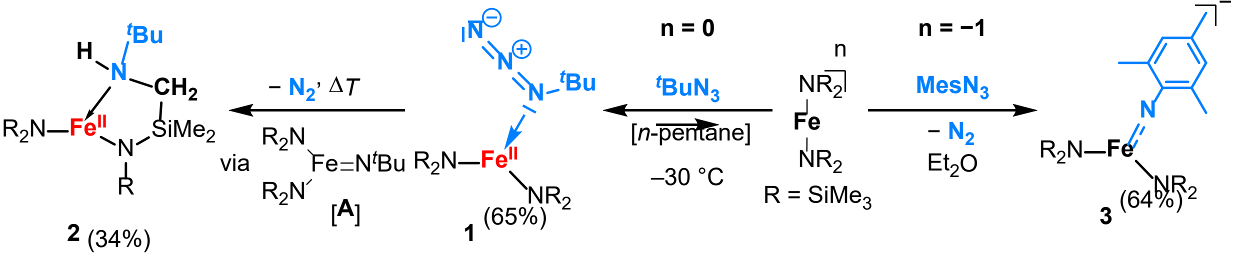
The 3d-metal catalysed amination of (un)-functionalized C–H bonds is under intense scrutiny as it is an atom economic and environmentally benign approach to secondary amines.[1] It is generally accepted that the reaction proceeds through a highly reactive imido metal intermediate [MNR].[2,3] The imido ligand is commonly described as a dianionic imide NR_2^{2-} as is the case for early transition metal complexes. In some of the recently reported late 3d-metal complexes, the electronic structure of the central [MNR] unit has been described as a metal bound imidyl $[NR]^{\bullet-}$ or a nitrene $[NR]^0$,[2] which rationalizes their H atom abstraction and/or nitrene transfer capabilities.

Recent examples show that isolable imido complexes can share substantial partial nitrene character, such as the trigonal arylimido iron complex $[Fe(NMes)(N\{Dipp\}SiMe_3)_2]$ reported by us.[4] It proved rather unreactive, which we attributed to the sterically encumbered ancillary $N(Dipp)SiMe_3$ ligands. As such we were interested in using the smaller $Fe(NR_2)_2$ ($R = SiMe_3$) as a platform for stabilisation of a more potent imido iron unit (Scheme 1). Reaction of the neutral iron(II) complex with the aliphatic azide $^tBuN_3$ yields the adduct product $[Fe\{N_3{}^tBu\}(NR_2)_2]$, **1**. Under ambient conditions, the azide adduct is subject to a dissociation equilibrium in solution, yet also undergoes intramolecular C–H bond amination. Single-crystal irradiation of the azide at 80 K leads to partial N_2 extrusion and formation of a putative imido iron intermediate **[A]**, which was computationally identified as a highly covalent $\{FeNR\}^8$ species.[5] Alternatively, the synthesis of the anionic trigonal arylimido iron complex $K\{crypt\}[Fe(NMes)(NR_2)_2]$, **3**, was achieved via the reaction of the linear, anionic iron(I) complex $[Fe(NR_2)_2]^-$ with $MesN_3$. **3** shows an ambiguous electronic structure as it reacts either as an iron(II) imidyl or as an iron(III) imido species [6]



Scheme 1: Synthesis of the trigonal iron(II) azido complex $[Fe\{N_3{}^tBu\}(NR_2)_2]$, **1**, and the C–H-insertion product $[Fe(\kappa^2N\text{-}N(R)SiMe_2CH_2NH^tBu)(NR_2)]$, **2** and the anionic iron(II) imidyl complex $[Fe(NMes)(NR_2)_2]^-$, **3**.

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Luminescent BOPHY platinum complexes

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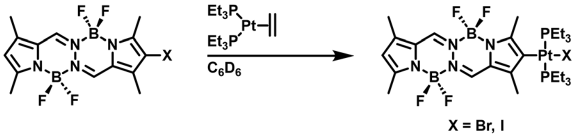

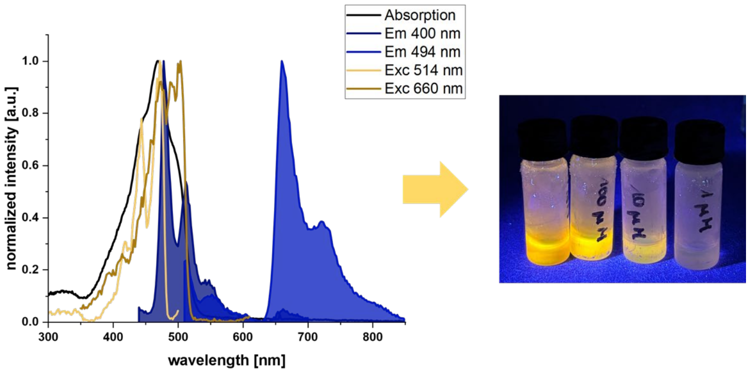

The term luminescence describes two distinct radiative transitions, namely fluorescence and phosphorescence. Phosphorescence emissions require intersystem crossing (ISC) from an excited singlet state S_n to an excited triplet state T_n.[1] Most prominent among the different mechanisms to promote the spin-forbidden process of ISC is the so-called heavy atom effect (HAE), which relies on spin-orbit coupling.[2] Drawing from the particularly large spin-orbit coupling constant of the Pt^{2+} ion,[3] numerous phosphorescent platinum complexes have been synthesized, which by means of the HAE, convert fluorescence of attached dye ligands into phosphorescence. In particular, Pt complexes with σ-bonded borondipyrromethene (BODIPY) dyes are dually emissive, exhibiting fluorescence and phosphorescence emissions.[4-6] We here report on four new mono- and dinuclear Pt complexes of highly emissive BOPHY ligands,[7] which feature two annealed BODIPY-like entities in their molecular structure. These complexes fluoresce at room temperature and display dual fluorescence and phosphorescence emissions at 77 K. Their emission behavior depends on complex concentration indicating enhanced aggregation-induced ISC rates at low temperature.

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Electrochemistry of a New Ni(I) Cofactor F430 Model

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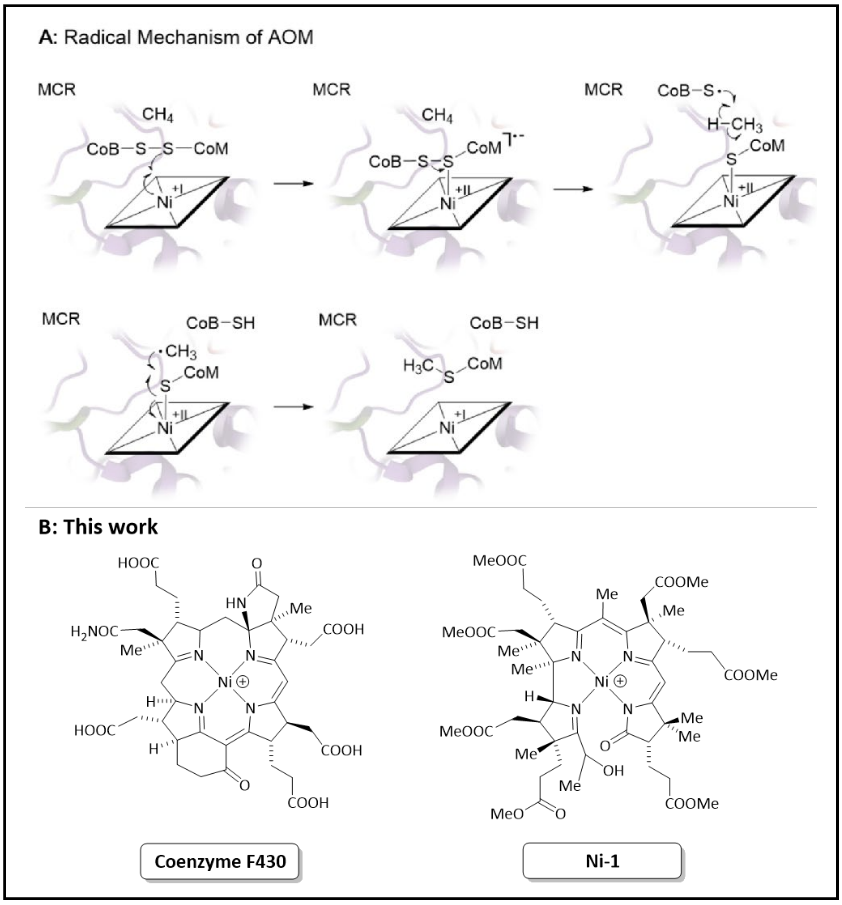
Cofactor F430-dependent methyl-coenzyme M reductase (MCR) catalyses the endergonic conversion of the heterodisulfide adduct of coenzymes M and B with methane to methyl-coenzyme M and coenzyme B. In a radical mechanism, the Ni(I)-induced formation of a transient thiyl radical of coenzyme B from the heterodisulfide has been proposed. Our group develops semi-artificial Ni-complexes derived from vitamin B12 as functional models of F430[1-2]. Herein, I introduce the synthesis and electrochemistry of a new seco-corrin **Ni-1** (Scheme 1B) and compare its chemistry to other models developed in our group.



Scheme 1. *A:* Proposed radical mechanism of AOM catalysed by F430-dependent MCR.[3-4] *B:* Structures of coenzyme F430 and its biomimic model **Ni-1**.

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