5th Lower Saxony Catalysis Symposium
(Niedersächsisches Katalyse-Symposium)

NIK∧S 2018

19th and 20th September 2018, Göttingen

GEORG-AUGUST-UNIVERSITÄT GÖTTINGEN

CASUS

CAROLO-WILHELMINA BRAUNSCHWEIG
Technische Universität Braunschweig

5th Lower Saxony Catalysis Symposium

September 19th-20th, 2018, Göttingen, Germany

ORGANISATION

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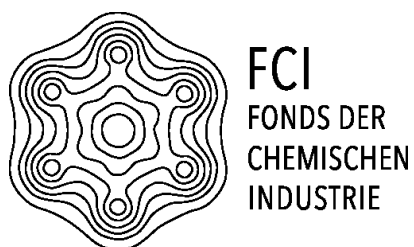
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5th Lower Saxony Catalysis Symposium

Wednesday, September 19th		
from 12:00	Arrival and Registration	
13:00 – 13:15	F. Meyer	Welcome/Introduction

Session 1		Chair: M. Morganti
13:15 – 14:00	M. Abu-Omar	Chemical Synthons and Recycable Materials from Lignin
14:00 – 14:45	M. Costas	Selective Oxidations Inspired in Non Heme Iron Dependent Oxygenases
14:45 – 15:00	Photo	
15:00 – 15:30	Coffee Break	

Session 2		Chair: M. Kolter
15:30 – 16:15	P. Chen	Carbene Complexes in Metathesis and Cyclopropanation
16:15 – 17:00	L. Gonsalvi	Carbon Dioxide Catalytic Conversion to Chemicals and Fuels with Non-noble Metal Complexes
17:00 – 17:20	M. Schütze	The Transformation of CO_2 into Polymeric Materials
17:30 – 19:30	Poster Session with Snacks and Drinks	

Thursday, September 20th		
Session 3		Chair: N. Sauermann
8:45 – 9:30	I. Larossa	Transition Metal Catalyzed C-H Activation: Reactivity, Selectivity Control and Late-Stage Functionalization
9:30 – 10:15	V. Derdau	C-H-Functionalization for Hydrogen Isotope Exchange and Modern Application for Life Science
10:15 – 10:45	Coffee Break	

Session 4		Chair: J.-P. Du
10:45 – 11:05	C. Kornhaaß	Process Development at Merck - From Laboratory to Large Scale
11:05 – 11:25	A. Wolpers	Controlled Radical Polymerization of Ethylene
11:25 – 12:10	E. Anxolabéhère-Mallart	Electrochemistry and Bioinspired Metallic Complexes for Reductive O_2 Activation
12:10 – 13:15	Lunch break	

Session 5		Chair: C. Schiwek
13:15 – 14:00	B. Plietker	Breathing In and Out - Fe-NO-Complexes in Catalysis
14:00 – 14:45	A. Dey	Managing Protons and Electrons in Small Molecule Activation
14:45 – 15:00	F. Meyer	Poster Awards & Farewells
15:00	Departure	

POSTERS

Number	Surname	Forename	Country	Title
1	Àrias	Òscar	Germany	Ligand Variation in Molybdenum Alkylidyne Complexes of the Type $[ArC\equiv Mo\{OCMe(CF_3)_2\}_3(L)]$
2	Auth	Thomas	Germany	A Gas-Phase Model for Dissecting Transmetalation Reactions at the Molecular Level
3	Chandra	Anirban	Germany	Nucleophilic vs Electrophilic Reactivity of Bioinspired Super-oxido Nickel(II) Complexes
4	Corona	Teresa	Germany	Characterization and Reactivity Studies of a Mononuclear non-heme Iron(II)-Superoxo Complex
5	Dammann	Wiebke	Germany	Synthesis of Bimetallic Zinc Pyridine Diimine Complexes
6	Du	Jia-Pei	Germany	Electrochemical CO_2 Reduction with Mononuclear Rhenium(I) Complexes – Influence of an Internal Proton Source
7	Enachi	Andreea	Germany	Trigonal NHC-Co(II) Dialkyl Complexes for Olefin Hydrogenation
8	Fritz	Maximilian	Germany	A Diazenido Bridged Dichromium Complex
9	Gathy	Robert	Germany	Cp*Co^{III} catalysed synthesis of planar chiral ferrocenes by ortho C-H activation
10	Glüer	Arne	Germany	Hydrosilane Synthesis via Catalytic Hydrogenolysis of Chlorosilanes and Silyl Triflates
11	Goursot	Pierre	Germany	Intramolecular Frustrated Dihydrogen Bond in a "Two-In-One" Nickel Complex and Water Assisted Reversible Splitting of H_2
12	Hackl	Ludwig	Germany	Complexes Bearing Four Membered Ring Cyclic Bent Allene Ligands Prepared From Dipiperidinoacetylene
13	Heinisch	Lauren	Germany	Synthesis of Cyclopentadienylalkylphosphide Nickel Chelates
14	Hümmer	Julian	Germany	Electrocatalytic Production of H2 from Water With f-Element-Based Molecular Catalysts
15	Keilwerth	Martin	Germany	From High-Valent Iron Nitrides to a Pentad of Low-Valent Iron Nitrosyls
16	Kollmann	Jiri	Germany	Visible-Light-Mediated Efficient Metal-Free Catalyst for Oxygenation of Tertiary Amines to Amides
17	Kolter	Marlene	Germany	Organopalladates as Intermediates in Cross-Coupling Reactions
18	Kothe	Thomas	Germany	Compartmental Bimetallic Complexes of New Pyrazole/Pyrrole Hybrid Ligands
19	Kreft	Alexander	Germany	Donor-Acceptor Cyclopropanes: A Kinetic Study of Their Reactivity
20	Kuhn	Vitali	Germany	Synthesis and Protonation Studies of 10-Azacorroles
21	Kunal	Kureja	Germany	Catalysis with Carbene Complexes Based on Mesoionic Compounds

| 22	Li	Ming	Germany	Catalytic Silylation of Dinitrogen by Dinuclear Cobalt Complexes Based on the Two-in-one Pincer Ligand
23	Lücken	Jana	Germany	Mechanistic Studies of a Highly Active Molecular Diruthenium Water Oxidation Catalyst
24	Müller	Thomas	Germany	1,4-Iron Migration for Expedient Allene Annulations through Iron-Catalyzed C–H/N–H/C–O/C–H Functionalizations
25	Munz	Dominik	Germany	A Palladium Terminal Imido Complex
26	Paesch	Alexander	Germany	Synthesis of Novel *N*-Heterocyclic Silylenes
27	Peters	Marius	Germany	Cationic NHC-Phosphinidene Ir(I) complexes and their application in Hydrogen Isotope Exchange Reaction
28	Resch	Stefan G.	Germany	Sulfide redox and protonation interconversions at a preorganized dinickel site and HAT reactions of a nickel-bound thiyl radical with organic substrates
29	Rieger	Rene	Germany	Utilization of Aerial Oxygen as an Abundant Oxidation Agent in Selenium-π-Acid and Photoredox Catalysis
30	Riemer	Daniel	Germany	CO_2-Catalyzed Oxidation of Benzylic and Allylic Alcohols with DMSO
31	Rode	Katharina	Germany	Aerobic Allylation of simple Alcohols via Dual Organocatalysis
32	Sang	Sier	Germany	Mechanistic Investigation of Olefin Hydrogenation Catalyzed by Cobalt(II) Pincer Complexes
33	Sauermann	Nicolas	Germany	Base Metal-Catalyzed C–H Alkynylation
34	Schiller	Carl	Germany	The Reactivity of Terminal Nitrido Iridium- and Rhodium Complexes
35	Schilling	Waldemar	Germany	Metal-Free Catalyst for Visible-Light-Induced Oxidation of Unactivated Alcohols
36	Schiwek	Christoph	Germany	Experimental confirmation of a new intermediate for the reductive disproportionation of CO_2
37	Tröndle	Sabrina	Germany	Transition Metal Complexes and Heterogeneous Catalysis Employing Phosphane-Substituted Troticenes
38	Valero	Mégane	Germany	Highly Selective Directed Iridium-Catalyzed Hydrogen Isotope Exchange Reactions of Aliphatic Amides
39	van Alten	Richt	Germany	Mechanism of (electro)Chemical N_2 Splitting by a Rhenium Pincer Complex
40	Völker	Max	Germany	Metal vs. Ligand Protonation
41	Wagner	Jannik	Germany	Catalyzed Chain Growth Polymerization: A Versatile Tool for End-group Functionalization and Surface Modification
42	Waldecker	Bernd	Germany	Dibenzothiophenium Salts as Alkynyl-transfer reagents

PLENARY LECTURES

Chemical Synthons and Recyclable Materials from Lignin

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Transition metal catalysts have been an integral part of the success story of the petrochemical industry in the past century. For this century and the future, we must advance developments in renewable energy and the utilization of sustainable resources to make chemicals and materials. Approximately 1.4 billion tons of lignocellulosic biomass is an annually renewable source of energy and chemicals in the U.S. alone. The major components of biomass are cellulose, xylan, and lignin- all polymeric and contain high percentage of oxygen. Current biomass processing underutilizes lignin. We have developed selective reaction chemistries that convert lignin selectively into phenolic molecules/synthons. We have coined this process chemistry CDL for Catalytic Depolymerization of Lignin. Spectroscopic data coupled with mechanistic investigations revealed the roles of solvent and catalyst in this unique reactive-separation, which provides selective molecules from lignin. Renewable triphenol motifs (TPs) have been synthesized and converted to polymers with advanced thermo-mechanical properties that rival those from petroleum. A fully biobased epoxy thermoset has been prepared by esterification of lignin-derived TP with vegetable oil to yield materials with tunable mechanical properties and glass transition temperature. The implication and use of lignin synthons to make renewable, recyclable, and self-healing thermoset polymers will be discussed.
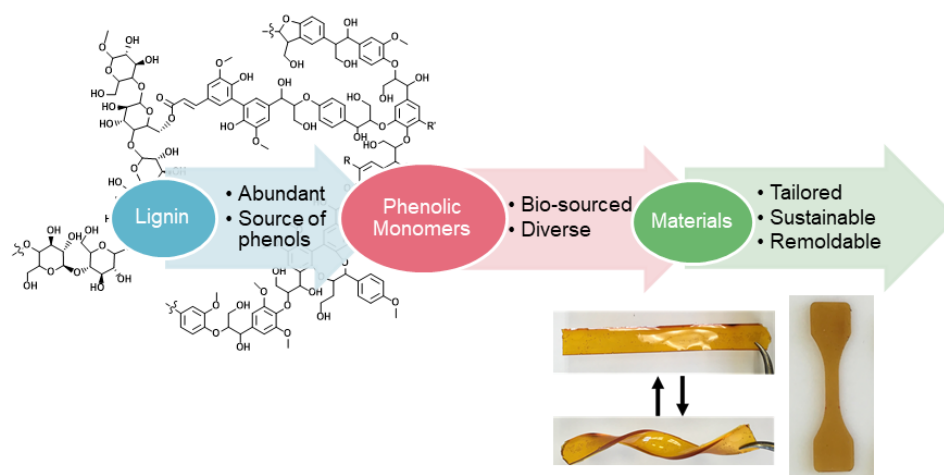
Selective Oxidation Catalysts Inspired in Nonheme Iron Dependent Oxygenases

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Biologically inspired catalysts are currently explored with the aim to produce selective oxidation reactions. The quest for catalytic methodologies that provide novel reactivities and selectivities that could complement those attained with traditional oxidants, or that could represent a more efficient alternative constitute major reasons of interest for this approach.[1-3] Towards this end, iron and manganese coordination complexes ligated to amine and oxygen containing functionalities, and that could be viewed as a minimalistic model of iron coordination sites in non heme iron dependent oxygenases, are employed as catalysts for the oxidation of organic substrates. By control of their structure and electronic properties, catalysts have been designed that engage in controlled O-O lysis of H_2O_2 to form highly electrophilic high valent metal-oxo species that are finally responsible for enzyme-like selective oxidation chemistry.[4] Principles of catalyst design and use of these catalysts in selective oxidations, and reaction intermediates involved[5] will be discussed.

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Carbene Complexes in Metathesis and Cyclopropanation: De Novo Mechanistic Design, Mechanistic Studies, and a Historical Twist

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While catalysts have typically been discovered, not designed, we present mechanistic work directed towards the rational design of new reactivity. The mechanistic tools start with elementary reactions of reactive intermediates in the gas phase, and quantum chemical calculations, and proceed with reaction kinetics in solution to generate a new catalyst. The target transformation, a catalytic, electrophilic cyclopropanation without diazo compounds, fills a gap in synthetic methodology. Three new catalytic cycles were built, of which one—a nickel-catalyzed reaction—has a historical connection of considerable pedagogical value. Another one, based on palladium catalysis, has the scope and robustness to replace the Simmons-Smith reaction in industrial synthesis of cyclopropanated compounds. For both the Ni and Pd-catalyzed reactions, detailed mechanistic studies reveal aspects of the catalytic cycle which show how challenging it is to construct new reactivity *de novo*.

Carbon Dioxide Catalytic Conversion to Chemicals and Fuels with Non-noble Metal Complexes

Luca Gonsalvi

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Among the major challenges for scientists in the current times, the search for renewable, continuous and portable sources of non-fossil based fuels, combined with the reduction of greenhouse gases such as carbon dioxide, are at the forefront of worldwide attention, both from academic and industrial point of view. [1] Global CO_2 emissions reached 35.7 Gt in 2014, translating into an atmospheric CO_2 concentration of 408.84 ppm, a 56% increase since the 1990s. [2] The use of hydrogen as energy vector is now considered as a valuable alternative to fossil fuels if produced from renewable sources and combined with low or zero emissions of carbon dioxide. The catalytic reduction of CO_2 is a possible answer due to its potential as hydrogen storage method and use of this abundant substrate as C-1 feedstock. [3] An overview of the main developments in homogenously catalysed processes leading to the current state-of-the-art will be here discussed.

Another important issue to address is the economical viability of the processes, that are now mainly based on precious metal catalysts. Many research groups worldwide are studying how to replace these catalysts with non-precious counterparts, without affecting the overall process efficiency. Examples of recent contributions, including results from our research group, [4] will be here summarised.

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The transformation of CO_2 into polymeric materials

Mike Schütze, Aurel Wolf* Christoph Gürtler*

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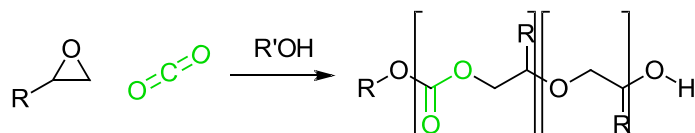
Covestro has developed an innovative technology enabling carbon capture and utilization (CCU) by partly substituting oil-based raw materials with CO_2. The obtained polyol blocks, commercially now available under the trade name cardyon™, are applied for the production of polyurethane flexible foams used in mattresses and furniture. The progress of catalysis-research towards the CO_2-containing polyols is illustrated; starting from the very beginning of the investigation of CO_2 based polycarbonats towards the scale-up and the LCA.

Transition metal catalyzed C-H activation: reactivity, selectivity control and late-stage functionalization

Professor Igor Larrosa

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The development of greener and more efficient synthetic methodologies is essential for organic chemistry to reach its full potential in its application to many applied and fundamental scientific problems. Biaryls are structural motifs predominant in numerous pharmaceuticals, agrochemicals, chiral catalysts, liquid crystal displays, and even molecular switches and motors. The most common methodology for their synthesis involves the traditional cross-coupling between an organometallic compound, Ar-M, and a haloarene, Ar-X. In the last few years, two promising alternatives to these cross-couplings have emerged: *direct C–H arylation*, where a readily available Ar-H is coupled with Ar-X, and *oxidative double C–H activation*, where two different Ar-H are cross-coupled. These approaches use non-prefunctionalized starting materials, thus eliminating several synthetic steps and consequent chemical waste associated to traditional cross-couplings. However, several challenges have to be resolved before this new approaches can be widely applied: 1) the development of mild reaction conditions with a broad scope, 2) the control of the regioselectivity of C–H activation and, in the case of oxidative couplings, 3) the control of the selectivity of homo- versus cross-coupling, and 4) the development of conditions that can be safely used in industry.

In this talk I will present some of our group's approaches towards addressing these challenges. In particular, we will discuss the use of bimetallic Pd/Ag,[1] Pd/Cr[2] and Au/Ag[3] synergistic systems and the development of novel Ru-catalysts for late stage functionalization.[4,5]

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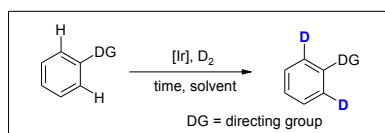
C-H-Functionalization for Hydrogen Isotope Exchange and Modern Application for Life Science

Volker Derdau,[a] Mégane Valero,[a] Daniel Becker,[b] Kristof Jess,[b] Annina Burhop,[a] Remo Weck,[a] Jens Atzrodt,[a] Matthias Freytag,[b] Peter G. Jones,[b] Matthias Tamm,[b]
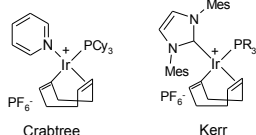
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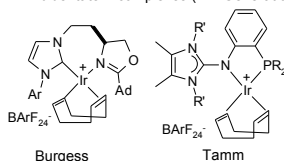
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Hydrogen isotope exchange (HIE) allows the direct substitution of hydrogen by its isotopes (deuterium and tritium) at the target molecule itself and thus circumvents the need for additional chemical synthesis steps (e.g. precursor synthesis or a stepwise preparation from isotopically enriched starting materials).[1] Thus, HIE is commonly employed to insert deuterium (D) atoms into pharmaceutical drug candidates for use as internal standards for mass spectrometry, for metabolic pathway elucidation and to alter ADME properties ("heavy drugs"). Additionally, tritium (T) atoms can be incorporated by HIE labelling to provide radioactive tritium tracers, which are important drug discovery tools for e.g. radioligand, protein- and covalent binding assays, for photoaffinity labeling and for ADME profiling of new drug candidates.
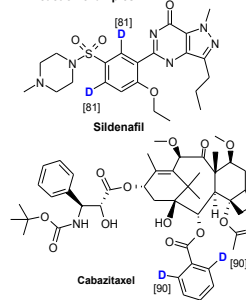

Nowadays, the most efficient methods for selective ortho-directed HIE reactions (selective hydrogen isotope introduction at the ortho-position next to a directing group) are based on homogeneous iridium(I) complexes. Recently we have identified a new generation of Ir-catalysts with bidentate P,N or NHC,N ligand structure which allow to overcome some of the limitations associated with commonly utilized monodentate Crabtree's[2] and Kerr's catalysts[3]. The talk will discuss HIE reactions with Burgess[4] and Tamm catalysts[5] and related applications of resulting labelled compounds in drug discovery.

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Process Development at Merck - From Laboratory to Large Scale

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The transfer of chemical reactions from laboratory to large-scale production is the most important step on the way of making bulk quantities of speciality chemicals, active pharmaceutical ingredients (API) and their precursors in an economical fashion.

The upscale of chemical reactions and downstream processing requires the assessment of the thermal safety parameters and must comply with quality standards to result in safe and robust industrial processes. It has to be taken into consideration that transfer of several operations, that are common on laboratory scale, to large scale is not possible or too expensive.[1–3]

The Merck site in Buchs (SG) produces a large variety of chemical products ranging from organic and inorganic reference materials and analytical standards to APIs and pharmaceutical precursors. Therefore, our process development department and our safety lab are equipped with the latest technology, such as automated reactors, parallel equipment and state-of-the-art calorimeters in order to develop and improve chemical processes in a highly efficient and effective way.
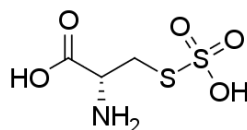

Figure 1: S-Sulfo-(*R*)-Cysteine

For instance, lately we developed a process for the GMP-production of a cysteine-derivative (Figure 1). This material can be used to replace unfunctionalized cysteine in cell-feeds as it shows an enhanced performance due to its water-solubility and, in contrast to cysteine, can be added to the feed at neutral pH.[3]

The development of a process for large scale production proved to be challenging. Optimization of the process conditions [4] lead to an increased space-time-yield and to a drastic reduction of the overall production costs.

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Controlled radical polymerization of ethylene

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Polyethylene (PE) is one of the most widely used plastics in the world and is industrially produced from ethylene mainly by either radical polymerization or catalytic coordination polymerization. Controlling the chain growth during a polymerization enables property fine-tuning of established materials as well as the development of completely new ones that might be composed of block copolymers or even more complex architectures. In the field of catalytic polymerization, coordinative chain-transfer polymerization (CCTP) is the only industrially relevant technique to produce olefin block copolymers. As it is the case for coordination polymerizations in general, however, this technique is limited to apolar polymers. Insertion of polar groups into polyolefins is indeed feasible by radical polymerization; a prominent example would be the statistical copolymers of ethylene and vinyl acetate (EVAs). However, similar to PE, the radical production of EVAs is claimed to be only effective under rather harsh conditions (100–300 °C, 1000–4000 bar of ethylene), which makes it impossible to control the macromolecular architecture through techniques like the indeed well-established controlled-radical polymerizations (CRPs). Being able to polymerize ethylene, and with it polar monomers, seems like a worthwhile endeavour.

In 2009, the C2P2 group revisited milder conditions for radical polymerization of ethylene and demonstrated that it can be effective also at less than 80 °C and less than 250 bar if the solvent system is chosen wisely.[1] These conditions were subsequently applied to using reversible addition–fragmentation chain-transfer (RAFT) with xanthates as chain-transfer agents, which yielded the first radical polymerization of ethylene with chain-growth-controlled characteristics (see Scheme).[2] While showing interesting polymerization properties, however, the system suffered from an inherent side reaction, reducing chain-end functionality and thus potential for further processing of the produced PE.

At the NiKaS 2018, the peculiarities of both radical polymerizations and CRPs of ethylene on a laboratory scale will be described. In addition, the research conducted in the C2P2 group following the first successful RAFT polymerization of ethylene will be presented.
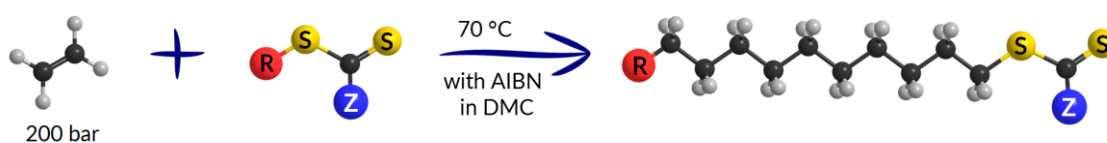
Scheme: Schematic representation of the first successful RAFT polymerization of ethylene conducted in the C2P2 group.[2] R = CH$_2$C(O)OCH$_3$, Z = OEt, AIBN = 2,2'-azobis(2-methylpropionitrile), DMC = dimethyl carbonate.

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Breaking and forming bonds with electrons and protons using earth abundant metal complexes as catalysts

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Our work relates to the development of processes for energy storage or newsynthesis processes. Our major goal is to develop efficient electro-catalysts for O_2 activation, CO_2 reduction or H_2 evolution based on earth abundant transition metal catalysts. This requires deciphering the parameters that control the factors that govern the reactivity of the catalysts and the nature of the intermediates. We address this question through electrochemical methods coupled to spectroscopies (UV-vis, EPR, IR, XAS) which provide insights into the mechanism of these fundamental catalytic reactions. In the present talk, we will show how our approach can give insights into the involved mechanisms. We will illustrate our work with recent examples of O_2 reductive activation using Mn[1][2] or Fe[3][4] complexes and of molecular catalysis of CO_2 electrochemical reduction using Fe and Co complexes.[5][6] Example of H_2 evolution using Co complexes will also be introduced.[7][8]
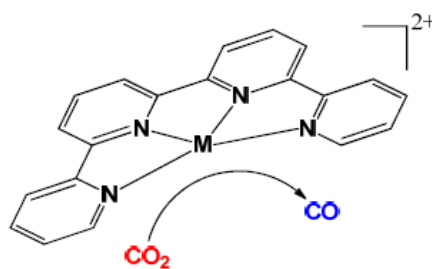
**Scheme:** [M(qpy)]$_{2+}$ (M= Co, Fe) complex

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Breathing in and out: Fe-NO-complexes in catalysis

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The field of Fe-catalysis has witnessed an impressive development both when it comes to reactivity but also to understanding fundamental aspects of Fe-complexes in action. In particular the interaction between iron-center and substrate but also between iron-center and ligand through shared molecular orbitals has been shown to be one of the key elements in developing catalysts with unique and novel reactivities. One of the smallest redox-active ligands, the NO-ligand, is in the center of our research. In this talk, catalytic methods using Fe-NO-complexes ranging from allylic substitution,[1] carbene-[2] and nitrene-transfer[3] over borylative cyclization to cycloisomerizations[4] will be presented. The role of the NO-ligand as an "electron lung" within the catalytic cycles will be highlighted.[5]
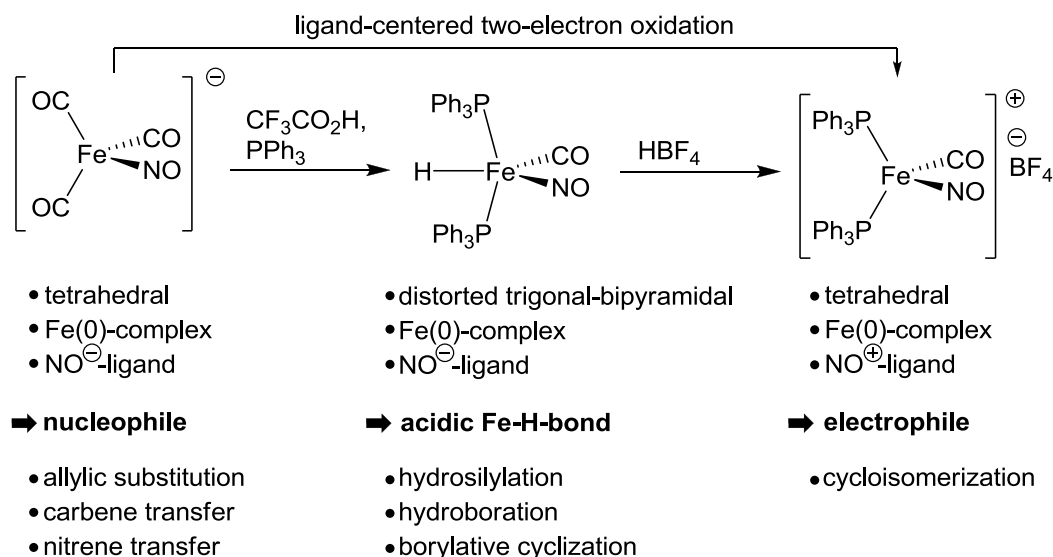
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Managing Protons and Electrons in Small Molecule Activation

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Small molecule activation often requires both protons and electrons. This includes chemical transformations key to sustainable energy and environment e.g. reduction of H^+, O_2, CO_2 and N_2. Similarly, mono-oxygenation of organic molecules using molecular oxygen, a process often described as the Holy grail of chemistry, requires protons and electrons. Erstwhile mechanistic investigations on metallo-enzyme active sites which catalyses these reactions have revealed that the proton and electron delivery often occur in distinct chemical steps and in many cases, coupled, in the same steps. This talk to focus on control of proton and electron delivery in synthetic inorganic molecular catalysts to achieve efficient catalysis using a combination of synthesis, self-assembly, in-situ spectroscopy and electrochemistry. This includes catalysts for hydrogen generation, oxygen reduction, organic substrate oxidation using oxygen and CO_2 reduction; all under aqueous environment and ambient conditions.

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September 19th-20th, 2018, Göttingen, Germany

POSTERS

Ligand Variation in Molybdenum Alkylidyne Complexes of the Type [ArC≡Mo{OCMe(CF₃)₂}₃(L)]

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Alkyne metathesis has received increasing attention in the past decades as an efficient tool for the reorganisation of C–C triple bonds.[1] In particular, the admirable progress in the development of highly active, well-defined catalysts has led to an expansion of the reaction scope including natural product synthesis, material sciences and polymer chemistry. Yet the potential of the alkyne metathesis is limited to some extent by the relatively exigent working conditions, especially caused by the instability of the catalysts towards air or moisture. Hence, catalyst design is crucial in order to improve the robustness of the alkylidyne complexes.

In our group we focused on the variation of the ligand environment in the mesitylidyne complex [MesC≡Mo{OCMe(CF₃)₂}₃] (**1**, Mes = 2,4,6-trimethylphenyl),[2] which is characterised by its outstanding activity in both internal and terminal alkyne metathesis. For example, a series of complexes showing different degrees of fluorination at the alkoxide ligands has been published recently.[3] In the present contribution, the modification of the benzylidyne unit (≡CAr) (**2a–e**) or the addition of a coordinating ligand (L) (**3a–g**), which results in complexes of the type [Mo(≡CAr){OCMe(CF₃)₂}₃(L)], will be discussed in more detail, including structural characterisation and catalytic investigations.

1: Ar = Mes, L = —
2a: Ar = Ph, L = —
2b/c: Ar = 4-(MeO)C₆H₄, L = —, thf
2d/e: Ar = 2,4,6-(MeO)₃C₆H₂, L = —, thf
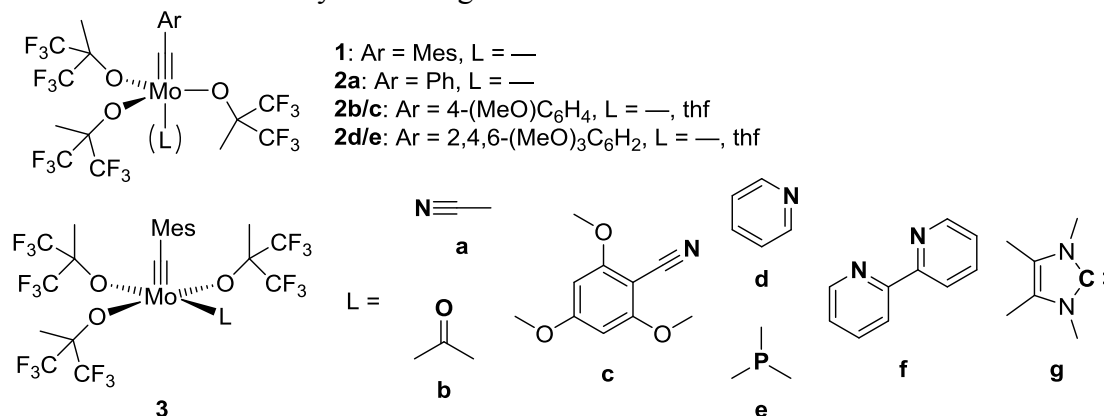
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A Gas-Phase Model for Dissecting Transmetalation Reactions at the Molecular Level

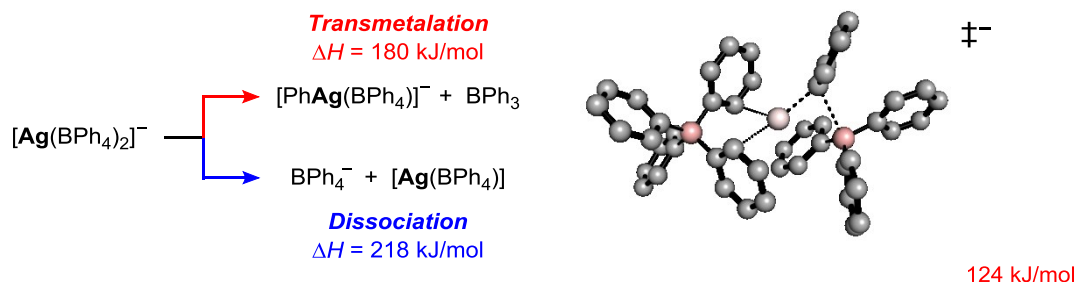Thomas Auth,[a] Konrad Koszinowski,[a] Richard O'Hair [b]

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Transmetalation is a key elementary step for both the stoichiometric preparation of organometallic reagents and transition-metal catalyzed cross-coupling.[1,2] Despite this great importance of transmetalation reactions, only little is known about their fundamental mode of operation and mechanistic details.[3]

Inspired by crystallographic data related to the transmetalation of silver salts with tetraarylborates,[4,5] we have studied solutions of AgOTf and LiBPh$_4$ in MeCN with ESI mass spectrometry in order to obtain information at a strictly molecular level. The ESI mass spectra showed $[M_n(BPh_4)_{n+1}]^-$ and $[M_n(BPh_4)_{n-1}]^+$ species (M = Li, Ag), whose unimolecular reactivity was probed by collisional activation. In line with the results from quantum chemical calculations, we observed transmetalation for anionic and cationic tetraphenyborate-containing silver complexes whereas the lithium counterparts merely dissociated. Moreover, the quantum chemical calculations revealed that the transmetalation steps are energetically less demanding than the subsequent dissociation of the corresponding product complexes.

In conclusion, by means of the powerful combination of gas-phase experiments and quantum chemical calculations, we were able to tackle the questions of how transmetalation depends on the metal, the charge and the oligomeric state for tetraphenylborate-containing complexes. The versatility of this approach holds great promise for a systematic and comprehensive inve   eactions.

Transmetalation
ΔH = 180 kJ/mol

$[\mathbf{Ag}(BPh_4)_2]^-$ ⟶ $[Ph\mathbf{Ag}(BPh_4)]^-$ + BPh_3

BPh_4^- + $[\mathbf{Ag}(BPh_4)]$

Dissociation
ΔH = 218 kJ/mol

‡⁻

124 kJ/mol

Gas-phase reactivity and transmetalation transition structure of $[Ag(BPh_4)_2]^-$.

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Nucleophilic vs Electrophilic Reactivity of Bioinspired Super-oxido Nickel(II) Complexes

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Mononuclear metal-dioxygen species are proposed to be key intermediates in biocatalytic cycles of dioxygen activation by metalloenzymes.[1] Generally metal-peroxo species are known to show oxidative nucleophilic reactivity(e.g. aldehyde deformylation), whereas metal-superoxo species are known to show electrophilic reactivity(e.g. HAT, OAT, C-H activation etc.).[2] Superoxido metal complexes showing nucleophilic reactivity are very rare in literature.[3] Herein we show the formation and detailed spectroscopic characterization of the first biuret-containing monoanionic superoxido-Ni^{II} intermediate $[LNiO_2]^-$ as Li salt **2** [L = MeN[C(=O)NAr]$_2$; Ar = 2,6-iPr$_2$C$_6$H$_3$)]. It results from oxidation of the corresponding [Li(thf)$_3$]$_2$[LNi^{II}Br$_2$] complex with excess H_2O_2 in the presence of Et$_3$N. The $[LNiO_2]^-$ core of **2** shows an unprecedented nucleophilic reactivity in oxidative deformylation of aldehydes, in stark contrast to the electrophilic character of the previously reported neutral Nacnac-containing superoxido-Ni^{II} complex **1**, [L'NiO2] (L' = CH(CMeNAr)$_2$).[4] According to Density Functional Theory (DFT) calculations, the remarkably different behaviour of **1** vs **2** can be explained by a two-state reactivity, in which a doublet ground state and a nearby spin-polarized doublet excited-state both contribute in **1** but not in **2**.

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Characterization and Reactivity Studies of a Mononuclear non-heme Iron(II)-Superoxo Complex

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Iron-containing mentalloenzymes are throughout the natural world and they participate in vital oxidative processes involving the activation of O_2. Thanks to the efforts carried out by many research groups, the structures of many of these enzymes (e.g. cytochrome P450, Rieske dioxygenases, …) are now well established.[1] Moreover, extensive mechanistic studies have been carried out on synthetic iron-oxygen adducts (e.g. iron(IV)-oxo, iron(III)-hydroperoxo and iron(III)-peroxo), which are mostly formed by using artificial oxidants such as iodosylarenes (PhIO), peroxy acids (*m*CPBA) and hydroperoxides (H_2O_2).[2] Alternatively, Münck, Que, Banse and co-workers reported the formation of an iron(IV)-oxo complex via O_2 activation with electron and proton or Lewis acid donors.[3-5] We now show that by tuning the equatorial donation of the ligand to the iron center it is possible to stabilize a novel and unprecedented binding mode of dioxygen, thereby underlining the importance of subtle electronic changes in the stability of the biologically relevant metal-dioxygen intermediates.[6]

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Synthesis of Bimetallic Zinc Pyridine Diimine Complexes

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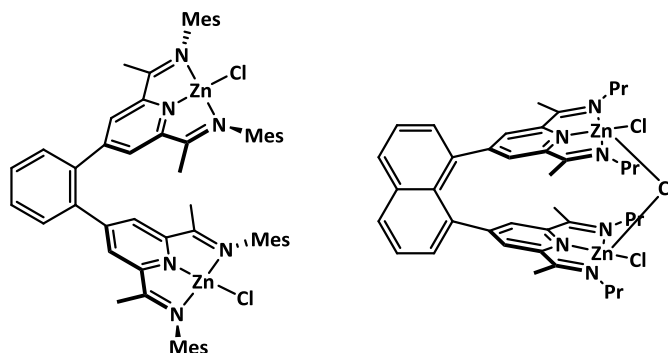e-mail: dammann@chemie.uni-hamburg.de

Figure 1: Zinc-PDI-complexes.

It is well established that cooperative effects can facilitate the activation of small molecules. An important parameter is the metal-metal distance in the dinuclear metal complexes. Here, we present an extension of the ubiquitous pyridine, diimine ligand system to PDI ligands, which are tethered by an aromatic linker. This allows to access dinuclear PDI complexes with different, well-defined metal-metal distances, yet, a very flat potential for the variation of the M-M distances according to DFT calculations.

For the initial study of this type of ligand system, dinuclear zinc-pyridine-diimine-complexes (Zn(II)-PDI) were studied.[1] Reduction of these zinc complexes [2] leads to formal zinc(I)-PDI complexes with different binding motifs (Figure 1). A main aspect of these investigations is the reactivity of these paramagnetic compounds towards oxygen and other small molecules like CO_2, CO, O_2 and H_2.

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   Nikonov *Dalton Trans* **2016**, 45, 13440-13448 (mononuclear complexes).

Electrochemical CO$_2$ Reduction with Mononuclear Rhenium(I) Complexes – Influence of an Internal Proton Source

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The electrochemical reduction of CO$_2$ has always been of great interest over the last few decades since it represents a key step towards the use of CO$_2$ as chemical feedstock and fuel source.[1] The products of the multi electron reductions of CO$_2$ exhibit similar potentials, therefore a catalyst is needed that selectively forms only one of the products and additionally bypasses the high-energy radical CO$_2^{\cdot-}$. In the past rhenium complexes bearing an α-diimine-tricarbonyl motif were used and have shown to be highly active in the electrochemical CO$_2$-to-CO conversion.[2]
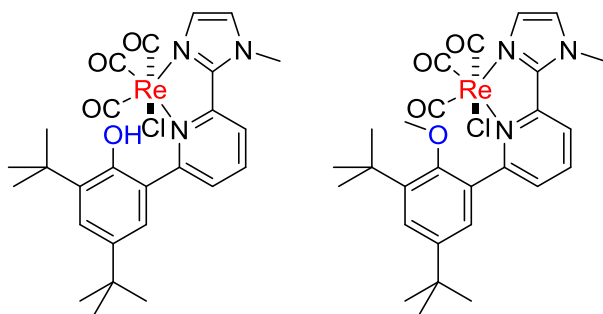

Figure 2: Mononuclear Rhenium(I) Complexes

A possible mechanism of the rhenium catalysed CO$_2$ reduction has been proposed by Meyer and co-workers. In a two-electron reduction pathway CO$_2$ is doubly reduced, and protonation induces C-O bond cleavage and formation of CO and water.[3] Thus, protons seem to play a crucial role in catalysis. Savéant and co-workers showed that the introduction of a local proton source into the ligand backbone of an iron tetraphenylporphyrin complex leads to a drastic enhancement of the catalytic activity.[4] In order to address the question whether an internal proton source can speed up the electrochemical CO$_2$ reduction and to probe its influence on the catalysis, we synthesized mononuclear rhenium(I) α-diimine-tricarbonyl complexes bearing either a OH- or a OMe-moiety in the ligand.

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Trigonal NHC-Co(II) Dialkyl Complexes for Olefin Hydrogenation

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Transition metal alkyl complexes are among the most reactive species in organometallic chemistry, therefore their preparation and isolation is challenging.[1] However, we are able to synthesize dialkyl cobalt complexes (**1**) in good yields using [(tmeda)Co(acac)$_2$] as Co^{2+} source and MgR'$_2$ (R'= CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph, CH$_2$CMe$_3$) as the alkyl transfer reagent. Furthermore, the tmeda ligand can be easily displaced by tunable bidentate phosphines and *N*-heterocyclic carbenes (NHCs) [2] which are good σ-donors and act as 'spectator' ligands and confer good stability to the low coordinated Co(II) atom (**2**).

Complexes containing earth abundant transition metals such as the 3d elements have become an important goal in catalysis.[3] They are being regarded as alternatives to the traditional catalysts based on precious metals such as iridium, rhodium and ruthenium in the area of homogeneous catalysis.[4]
Our complex **2** proved to be catalytically active in the hydrogenation of sterically hindered unactivated olefins and alkynes. Furthermore, during catalytic investigations on the hydrogenation of diphenylacetylene complex (**3**) was isolated.
Studies on reaction mechanism and the catalytically active species are ongoing.

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A Diazenido Bridged Dichromium Complex

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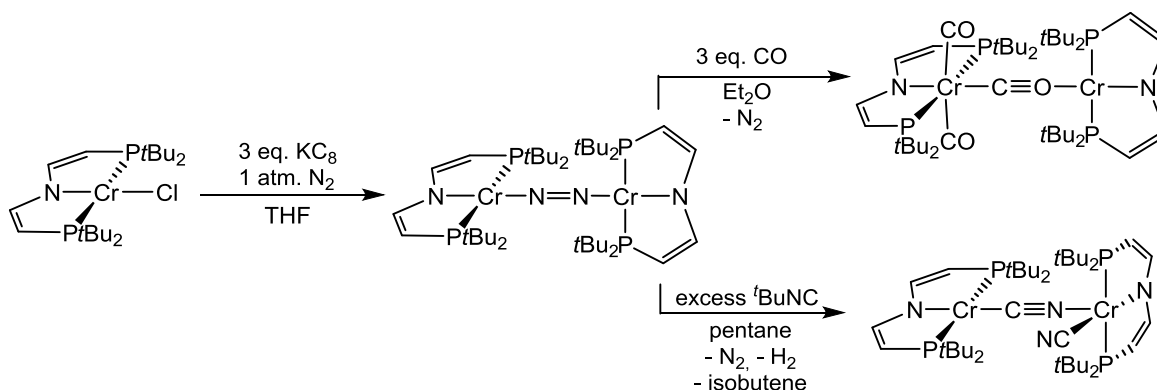a) Georg-August University, Department of Chemistry, 37077 Göttingen, Germany

Figure 1. Follow-up reactivity of [CrCl{N(CHCHPtBu$_2$)$_2$}].

Strong N_2 activation and functionalization with chromium complexes is less well explored in comparison to the heavier homologue molybdenum. For example, Cr-mediated N_2 splitting into nitrides remains unknown,[1] and diazenido bridged key species for such reactivity are scarce.[2-4] We here report the isolation of an N_2 bridged dichromium complex upon reduction of the square-planar chromium(II) chloro complex [CrCl{N(CHCHPtBu$_2$)$_2$}] under N_2 atmosphere (Figure 1). Crystallographic, spectroscopic and magnetic characterization indicate high-spin chromium(II) bridged by a diazenide ligand. This compound serves as a chromium(I) synthon as demonstrated by reactions with CO and isonitrile, which will be discussed.

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Cp*Co[III] catalysed synthesis of planar chiral ferrocenes by ortho C-H activation

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Recently, 1,2-disubstituted, planar chiral ferrocene derivatives have attracted increasing attention, e.g. in the fields of medicinal chemistry[1] and asymmetric catalysis.[2] They are mainly synthesized by *ortho*-metallation reactions, for example with Li, Pd, Pt and Rh.[3,4] In the last years, the bench-stable complex Cp*Co(CO)I$_2$ has been utilized in a variety of different reactions with aryls bearing oxygen- and nitrogen containing *ortho*-directing groups.[5] The advantages of Cobalt compared to the noble transition metals are its abundancy as well as its low cost. In this work, the dimethylcarbamoyl group was identified as a suitable ODG for the selective monoalkenylation of ferrocenes with terminal arylethynes, yielding substituted ferrocenyl analogues of stilbene. Intermediates of the catalytic cycle were investigated by DFT calculations, which explain the high selectivity of the chosen ODG.[6]
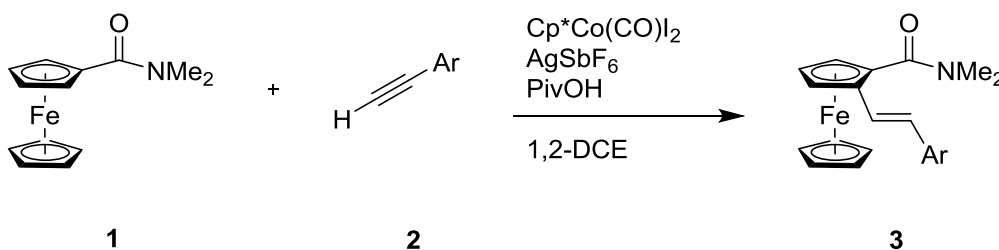
Further investigations will focus on the development of enantioselective variations, as well as investigations of the catalytic cycle. Due to the known versatility of the Cobalt catalyst, more experiments with different electrophiles will be conducted, aiming for the generation of planar chiral ferrocenes with other interesting structural motifs.

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Hydrosilane Synthesis via Catalytic Hydrogenolysis of Chlorosilanes and Silyl Triflates

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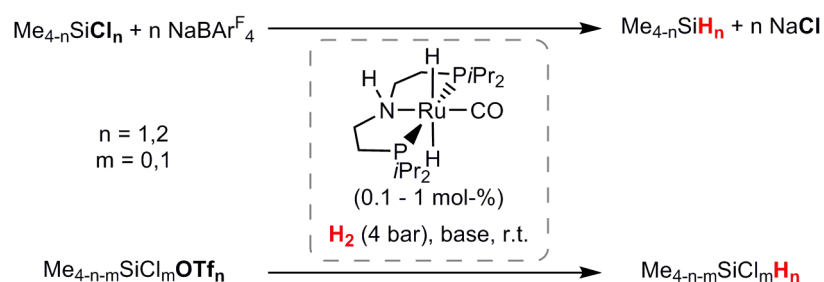
Organohydrosilanes are important reagents for olefin hydrosilylation and other applications such as C-H bond silylation, desulfurization of fuels, or dehydrogenative oligo/polysilane formation.[1] Most organohydrosilanes are conventionally obtained using stochiometric amounts of metal hydrides such as $LiAlH_4$, producing large amounts of metal-containing waste. Thus, utilizing H_2 as (atom)economic reducing agent is highly desirable. Recently, Shimada and coworkers pioneered in the hydrogenolysis of silyl triflates and halides ($R_{3-n}SiX_{n+1}$, X = OTf, I, Br, Cl).[2] However, only moderate dihydrosilane yields of 53% and 58% were obtained for the hydrogenolysis of silyl bistriflate Me_2SiOTf_2 and two step hydrogenolysis of Me_2SiCl_2, respectively, despite high iridium catalyst loadings (5-10 mol%) and long reaction times (2-7 days).

We present hydrogenolysis of chlorosilanes and silyl triflates (triflate = trifluoromethanesulfonate, OTf⁻) $Me_{3-n}SiX_{1+n}$ (X = Cl, OTf; n = 0, 1) to hydrosilanes at mild conditions (1-4 bar H_2, room temperature) using low loadings (1 mol%) of the bifunctional catalyst [$RuH_2CO(HPNP^{iPr})$] ($HPNP^{iPr}$ = $HN(CH_2CH_2P(iPr)_2)_2$). Direct endergonic chlorosilane hydrogenolysis can be driven by chloride removal, e.g. with $NaBAr^F_4$ ($BAr^F_4{}^-$ = B(C₆H₃-3,5-(CF₃)₂)₄⁻). Alternatively, conversion to silyl triflates enables facile hydrogenolysis with NEt_3 as base, giving Me_3SiH, Me_2SiH_2 and $Me_2SiHOTf$, respectively, in high yields. An outer-sphere mechanism for silyl triflate hydrogenolysis is supported by DFT computations. Additionally, the valuable bifunctional hydrochlorosilane Me_2SiClH can be obtained in yields over 50% by hydrogenolysis of chlorosilane/silyl triflate mixtures with 2,6-lutidine as base.

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Intramolecular Frustrated Dihydrogen Bond in a "Two-In-One" Nickel Complex and Water Assisted Reversible Splitting of H₂

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Metal ligand cooperativity (MLC) is a concept that is currently receiving much attention in homogeneous catalysis, exemplified by the "*Milstein Catalysts*" that exploit reversible (de)aromatization at the {PNN} ligand backbone.[1] Metal metal cooperativity (MMC) is a complementary concept, often inspired by oligonuclear active sites found in metalloenzymes, that makes use of the synergy of several metal ions for substrate transformations and offers new perspective for catalytic processes. Pyrazolate bridging ligands represent useful scaffolds for preorganizing two metal ions in close proximity, which has proven valuable for achieving bioinspired MMC reactivity.[2]

In recent work, we presented a pyrazolate-based ligand that can be viewed as composed of two {PNN} pincer-like compartments, which potentially allows for dual (MLC + MMC) cooperativity. A diiron(II) complex of that "*Two-In-One*" pincer ligand was shown to undergo reversible spin state switching in solution associated with ligand exchange processes.[3] Here we report a novel hydrido-hydroxido dinickel complex **3** that can host and stabilize a frustrated dihydrogen bond by MMC and split H₂ by MLC.
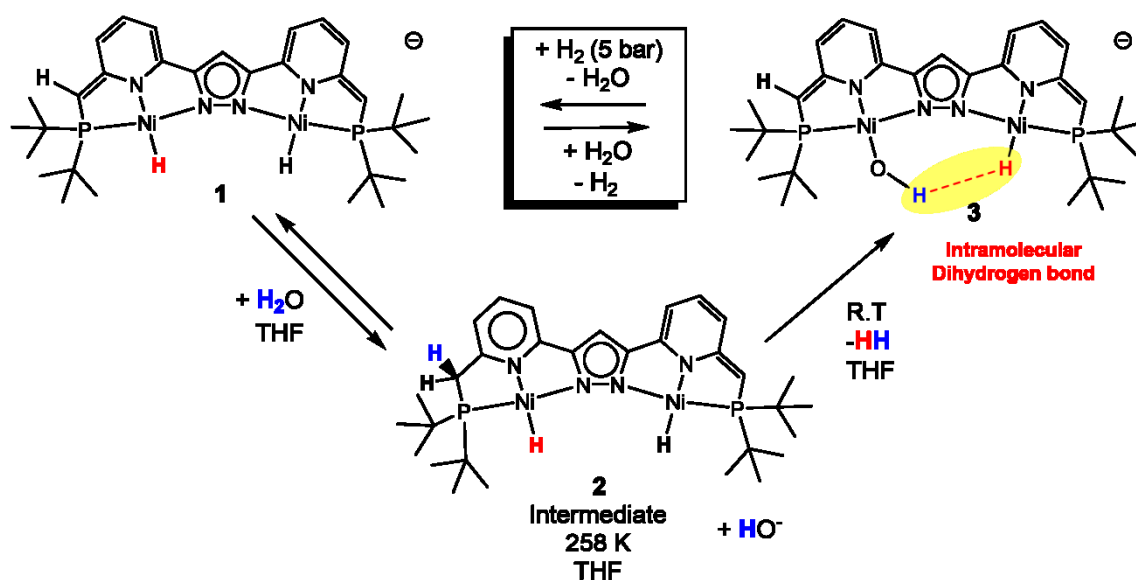
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Complexes Bearing Four Membered Ring Cyclic Bent Allene Ligands Prepared From Dipiperidinoacetylene

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Diaminoacetylenes, which are highly electron-rich alkynes, have only been used in a few applications in organometallic chemistry. In 2010, a novel synthetic protocol for the preparation of diaminoacetylenes has been developed by our group, allowing for a more convenient access of, e.g., dipiperidinoacetylene,[1] which has been used in the synthesis of a variety of organometallic compounds, mostly focusing on its dicarbenoid character.[2] Herein, we report the thermal dimerization of dipiperidinoacetylene yielding the enyne **1**. This enyne can be reacted with different main group element and transition metal precursors (e.g. gold, copper, rhodium, iridium and tungsten), giving complexes with a cyclic bent allene ligand, a class of ligands for which only few examples exist.[3] Ligands of this class have been successfully used in complexes for olefin hydrogenation.[4] Further investigations revealed the exceptional high donor-strength of this ligand, which makes it an interesting addition to the library of auxiliary ligands in organometallic catalysis.

e.g. ML_n = AuCl

e.g. E = Ge
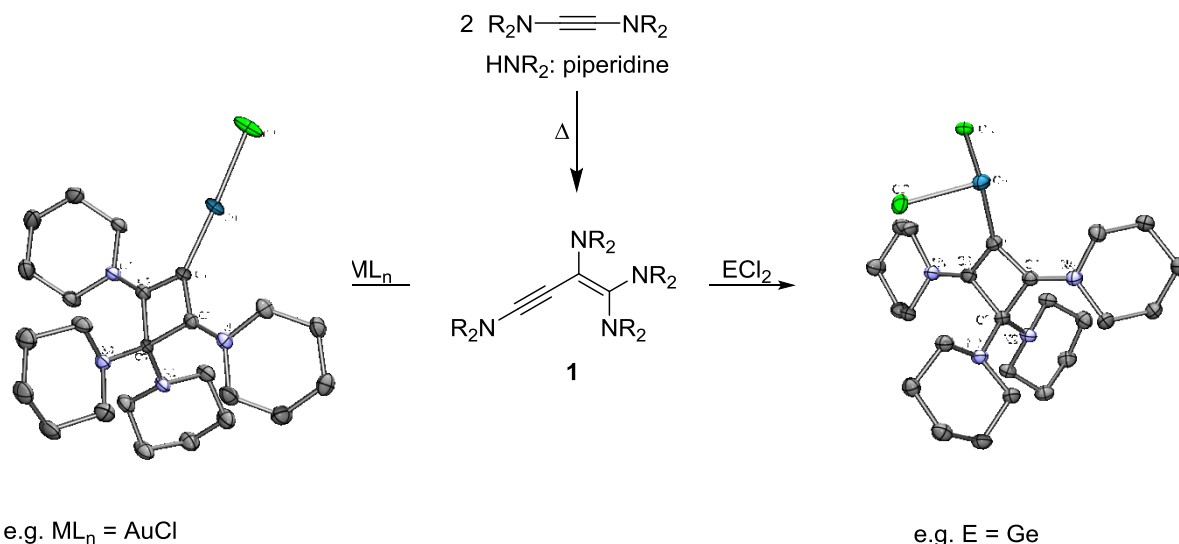
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Synthesis of Cyclopentadienylalkylphosphide Nickel Chelates

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Cyclopentadienylalkyl nickel complexes bearing a secondary phosphine chelating side chain are of interest as they should allow for a deprotonation reaction resulting in the formation of phosphide chelates. Such compounds could be attractive for catalytic reactions such as hydrosilylation reactions.

The first cyclopentadienyl nickel complexes with a secondary phosphine ligand were synthesized in our group.[1] New isocyanide complexes **2-7** could be obtained through ligand exchange reaction of complex **1** with an isocyanide in the presence of stoichiometric amounts of InBr$_3$. Current work is focused on deprotonation reactions to afford their corresponding phosphide complexes.
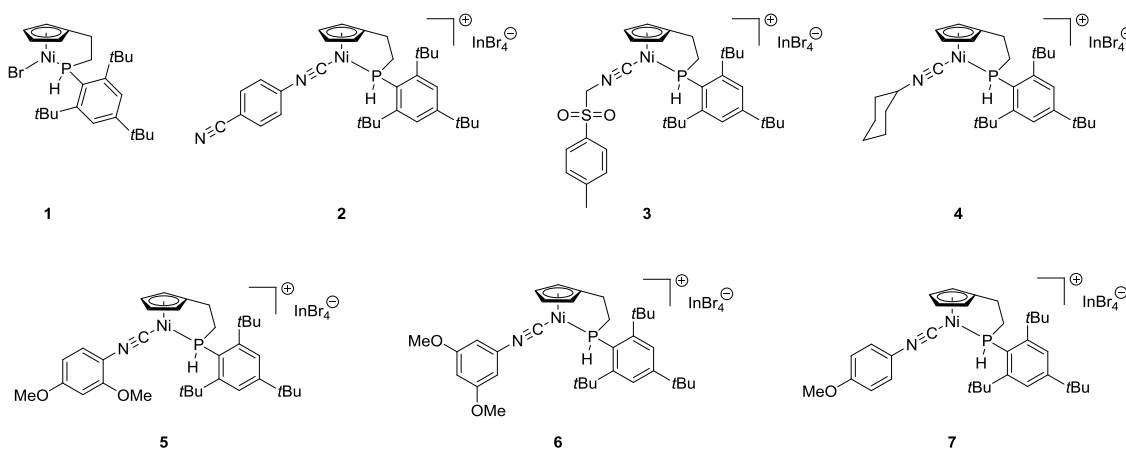
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Electrocatalytic Production of H$_2$ from Water

With f-Element-Based Molecular Catalysts

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Research on renewable energies and energy storage, such as H_2 production from H_2O, has become a key challenge for our society. The low efficiency of conventional H_2O electrolysis precludes large-scale applications. Thus, catalysts are desired to make this otherwise convenient strategy more applicable. Due to the high reactivity and oxophilicity of trivalent uranium complexes, as well as the large-scale availability of depleted uranium (^{238}U, DU), uranium complexes are widely discussed as effective and economic catalysts for stable substrates.

In our previous studies of the uranium-monoarene complex $[(^{Ad,Me}ArO)_3mes)U]$ (**1**), unique electrochemical and well defined synthetic behavior were found, rendering **1** a perfect candidate for electrocatalysis.

Indeed, trivalent uranium coordination complex **1** was found to be the first molecular uranium catalyst for electrocatalytic H_2 production. Utilization of **1** during H_2O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance of the reaction by 3 orders of magnitude. Isolation of key intermediates and *in situ* EPR experiments allowed to determine the reaction mechanism of H_2O reduction with low valent U(III). This reactivity was then studied in a series of lanthanide complexes $[(^{Ad,Me}ArO)_3mes)Ln]$ (**2–Ln**), which allows for fine-tuning of overpotential and reactivity of the catalyst by choice of the lanthanide ion.
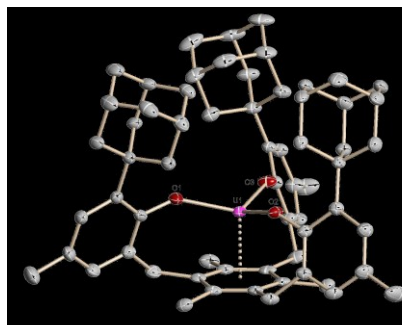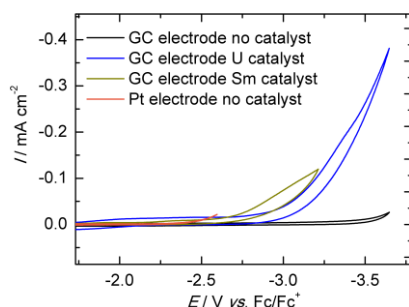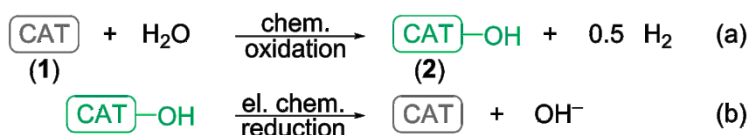
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From High-Valent Iron Nitrides to a Pentad of Low-Valent Iron Nitrosyls

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We present our work on the synthesis and reactivity of iron nitrido and nitrosyl complexes, stabilized by sterically encumbered, tripodal tris-*N*-heterocyclic carbene chelates. Based on the iron nitrido complex $[(TIMEN)Fe^{IV}(N)]^+$, we asked ourselves to what extent the complexes' electronic and structural properties change when – formally – atomic oxygen is added to the nitrido ligand; thus, transforming a high valent metal nitrido to a low valent metal nitrosyl complex.

$[(TIMEN)Fe(N)]^+$ $\xrightarrow{[O]}$ $[(TIMEN)Fe(NO)]^+$ or

$\{Fe–N\}^n$ $\{Fe–NO\}^n$ with n = 6 - 10
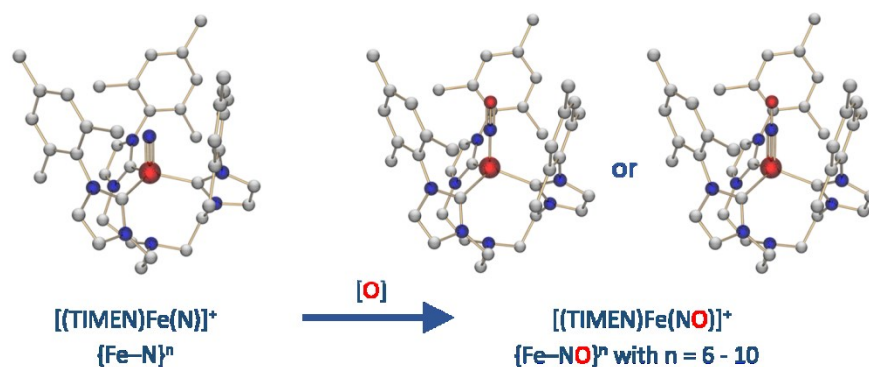
This discussion was proposed by Bendix & Wieghardt in 1998,[1] using the $\{M–N\}^n$ formalism approach for nitrido complexes – similar to the Enemark & Feltham $\{Fe–NO\}^n$ nomenclature for nitrosyl species. Formally, the transformation of $\{Fe–N\}^4$ to $\{Fe–NO\}^6$ or $\{Fe–NO\}^{10}$ would have to be considered a two- or even six-electron reduction, which is expected to be associated with striking structural changes. Accordingly, and independently, a series of iron nitrosyl complexes $[(TIMEN)Fe(NO)]^m$ (m = 3+ to 1−) was synthesized. Treatment of the coordinatively unsaturated $[(TIMEN)Fe]^{2+}$ with $NOBF_4$ yielded the corresponding $\{FeNO\}^6$ precursor complex. Subsequent reduction with Zn, Mg, and Na/Hg gave access to $\{FeNO\}^7$, $\{FeNO\}^8$, and $\{FeNO\}^9$, respectively. Finally, reaction of $\{FeNO\}^9$ with the electride Cs(2.2.2cryptand) • e⁻ provided the highly reduced $\{FeNO\}^{10}$. All compounds were thoroughly characterized, including temperature and field-dependent (VT-VF) SQUID magnetization as well as VT-VF ^{57}Fe Mössbauer, IR vibrational, UV/vis/NIR electronic absorption, multi-nuclear NMR and multi-frequency EPR spectroscopies and single-crystal X-ray diffractometry; except for the $\{FeNO\}^{10}$, for which a solid-state structure remains elusive (as of now). The study was complemented with computational analyses to provide insight into the electronic structure of the currently most complete series of iron nitrosyl complexes with an $\{FeNO\}^{6–10}$ core unit.
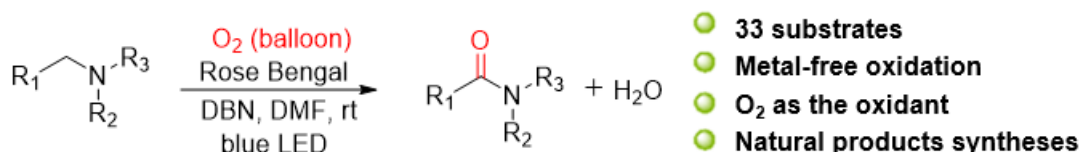
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Visible-Light-Mediated Efficient Metal-Free Catalyst for Oxygenation of Tertiary Amines to Amides

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A metal-free system has been discovered for the efficient oxygenation of tertiary amines to the corresponding amides using oxygen as an oxidant. This visible-light-mediated oxygenation reaction exhibited excellent substrates scope under mild reaction conditions and generated only water as the by-product. The synthetic utility of this approach has been demonstrated by applying onto drug molecules. At the end, detailed mechanistic reactions clearly showed the role of oxygen and the photocatalyst.

- 33 substrates
- Metal-free oxidation
- O_2 as the oxidant
- Natural products syntheses

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Organopalladates as Intermediates in Cross-Coupling Reactions

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Anionic Pd^0 species are suggested to be important intermediates in sp^3-sp^3 cross-coupling reactions utilizing palladium complexes with diene ligands as catalysts. Supposedly, these reactions follow a catalytic cycle beginning with the transmetalation step yielding an anionic intermediate, followed by the oxidative addition of the electrophile and subsequent product formation.[1,2] Herein, we used electrospray-ionization (ESI) mass spectrometry to characterize the palladate complexes which form in the transmetalation of palladium diene (1,3-butadiene and isoprene) complexes with organometallic reagents and to investigate their tendency to undergo oxidative addition reactions with organyl halides. Secondly, we also combined the electron-poor palladium phosphine complex PdL_3 (L = tris[3,5-bis(trifluoromethyl)phenyl]phosphine) with organometallic reagents and examined the reactivity of the resulting palladate(0) complexes towards oxidative addition via ESI mass spectrometry.

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Compartmental Bimetallic Complexes of New Pyrazole/Pyrrole Hybrid Ligands

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Bimetallic complexes are of significant interest in many fields of coordination chemistry. Inspired by nature the investigation of bimetallic model systems provides a deeper understanding of active sites in enzymes and other metalloproteins.[1] Research on this topic also motivated various applications for such compounds and therefore contributed to fields of catalysis, activation of small molecules and general coordination chemistry. However, synthetic approaches for ligand scaffolds that are designed to bind two metal centres remain a challenge.

Providing two N-donors for two metal ions, the pyrazolate moiety is a suitable bridging unit in ligand scaffolds for bimetallic complexes, resulting in metal-metal distances of 2.6-4.5 Å. This can be further elaborated by adding chelate substituents to the bridging unit to provide two oligodentate coordination sites.[2] Following this approach, we recently reported a pyrazole-based binucleating system that can be described as a fused version of two pincer like subunits.[3] Pyrroles have been beneficially used as central donor units in pincer ligands,[4] and therefore we have now developed a family of new pyrazole/pyrrole hybrid ligands that feature two pincer-type compartments (see figure). The accessible coordination sites in bimetallic complexes with these ligands, located trans to the pyrrole, are directed into the bimetallic cleft, suitable for potential metal-metal cooperativity. Here we report first insights into the coordination chemistry of these new ligands.
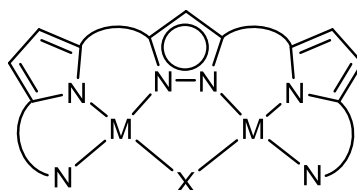
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Donor-Acceptor Cyclopropanes: A Kinetic Study of Their Reactivity

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Donor-Acceptor-substituted (D-A) cyclopropanes have become versatile building blocks in organic synthesis due to their high ring strain (~115 kJ·mol^{-1}) and their substitution pattern bearing an electron-donating and an electron-withdrawing group in vicinal positions. Because of their formal 1,3-zwitterionic character, they are able to undergo reactions with a broad scope of nucleophiles, electrophiles or dipoles to generate functionalised alkanes or (hetero)cyclic compounds.[1,2]

Although the field has been rapidly evolving, there is still a great lack on physical-organic data regarding reactions of these special three-membered rings. In this study, we present a comparative analysis of kinetic data for different D-A cyclopropanes and demonstrate that the rate constants range over more than three orders of magnitude.[3]

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Synthesis and Protonation Studies of 10-Azacorroles

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The class of 10-heterocorroles can be considered as intermediate between porphyrins with the dianionic character and the ring-contracted, trianionic corroles. 10-Heterocorroles offer the opportunity to vary the size of the binding cavity while maintaining comparable electronic and steric conditions. Representatives of that class with an oxygen, sulfur or nitrogen atom in 10-position have been known for a long time.[1] More recently, renewed interest into such macrocycles has arosen from new synthetic options.[2,3] In this contribution, we present our current efforts in preparing 10-Aminocorroles and some selected protonation studies of metalated macrocycles (Fig. 1).
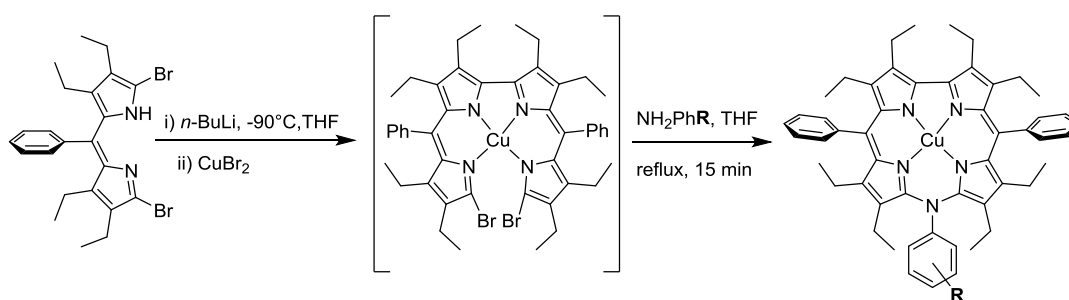
Fig. 1: Synthetic pathway of metalated 10-azacorroles.

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Catalysis with Carbene Complexes Based on Mesoionic Compounds

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The mesoionic compound **1a** was first published by ALCALDE in 1991 and it was studied in terms of its reactivity toward electrophiles (methyl iodide) and dipolarophiles (dimethyl acetylenedicarboxylate).[1]

We have been investigating the commercially available mesoionic compound *Nitron* (**2**) in terms of its carbenic tautomer **2'**.[2] Indeed, **2** is a cryptocarbene and it belongs to the class of conjugated mesomeric betaines (CMBs).[3] Related work on other five-membered CMBs has been reported by CÉSAR and LAVIGNE, DANOPOULOS and BRAUNSTEIN and by SCHMIDT.[4]

In this context we have started to examine the cryptocarbenic properties and coordination ability of compounds **1a** and **1b** and their deprotonated forms **3a** and **3b**,[5] respectively. We were able to prove the cryptocarbenic behavior of **1a** and **1b** by synthesizing seleno- and thiourea derivates **4a** and **4b**.

The compounds of type **1** and type **3** exhibit multiple coordination sites, which we were able to explore by obtaining mono- (**5**, **7a**, **8b**) and heterodinuclear metal complexes (**6a**) selectively. Depending on the substituents, normal and abnormal *N*-heterocyclic carbene ruthenium complexes (**7a**, **8b**) are selectively accessible.[6]

Furthermore, nickel complexes of type **5** turn out to be excellently suited for KUMADA-TAMAO-CORRIU cross-coupling reactions.[7]
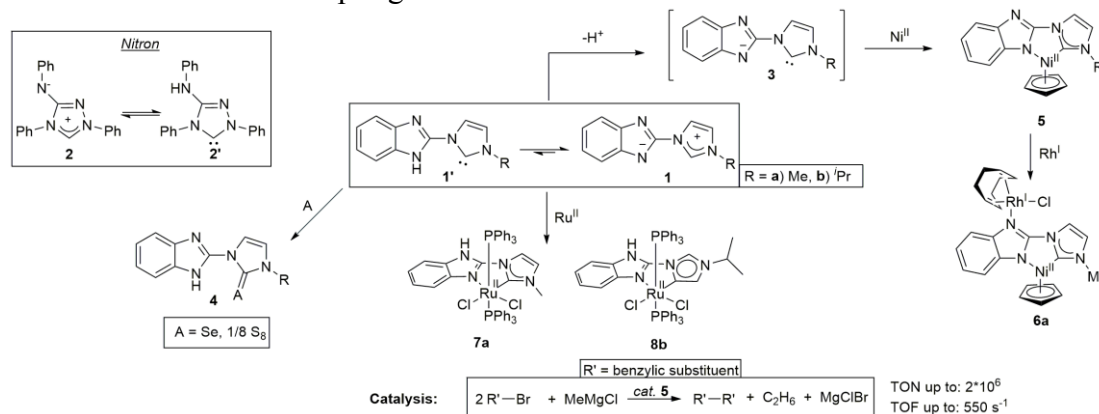
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Catalytic Silylation of Dinitrogen by Dinuclear Cobalt Complexes Based on the Two-in-one Pincer Ligand

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Based on a pyrazolate-bridged two-in-one pincer ligand, a series of dicobalt complexes have been synthesized, including three dicobalt dinitrogen complexes. By employing these cobalt complexes as catalysts, the catalytic silylation of dinitrogen into tris(trimethylsilyl)amine (using KC_8 and Me_3SiCl) has been explored. Therein, the dicobalt dinitrogen complex can catalyse dinitrogen to $N(SiMe_3)_3$ (201 equiv) .

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Mechanistic Studies of a Highly Active Molecular Diruthenium Water Oxidation Catalyst

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Water oxidation catalysis constitutes the bottleneck in exploiting the sun's energy for generating solar fuels. Consequently, in the past decades significant efforts have been devoted to the development of efficient water oxidation catalysts (WOCs), both heterogeneous and homogenous. Molecular complexes are particularly useful due to their convenient tunability and the possibility of obtaining detailed mechanistic insight.

Following this approach, our groups established a series of rugged dinuclear ruthenium complexes for water oxidation based on highly organized pyrazolate-based ligand scaffolds, such as **1-**.[1,2] For further elaboration of these dinuclear ruthenium WOCs, anionic carboxylate groups were incorporated in the ligand framework in order to significantly lower the redox potentials. This resulted in complex **2+**, which exhibits an exceedingly high water oxidation activity.[3]

Herein we present the new complexes **33-** and **43-**, which are derivatives of **2+** with improved water solubility. Both complexes were thoroughly characterized and investigated in regard to their chemical water oxidation activity.

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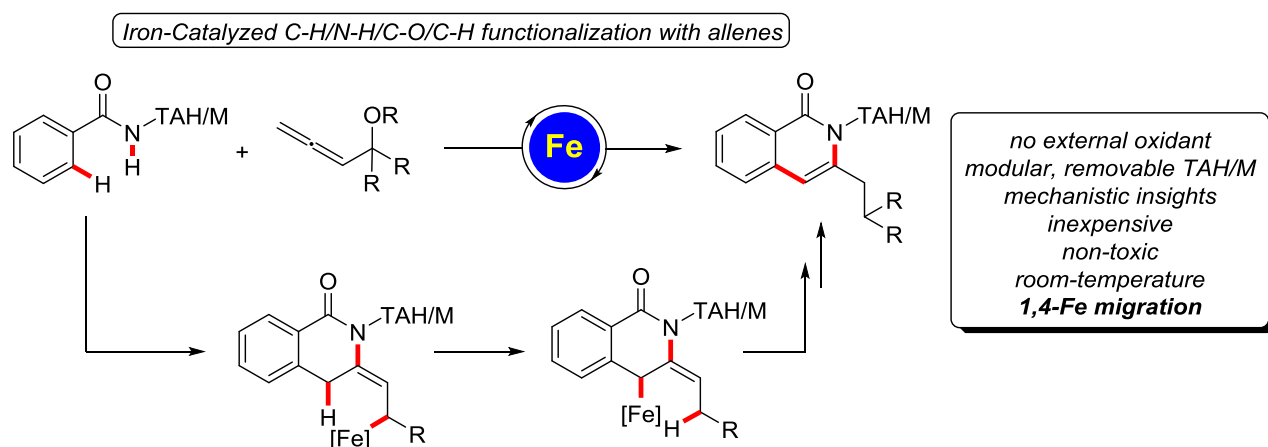
1,4-Iron Migration for Expedient Allene Annulations through Iron-Catalyzed C–H/N–H/C–O/C–H Functionalizations

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The direct functionalization of otherwise inert C–H bonds has been recognized as a transformative tool,[1] enabling sustainable molecular syntheses in a step- and atom-economical manner. While significant progress was realized with the aid of precious, rather toxic 4d and 5d transition metals, 3d metals, especially iron catalysts, are highly attractive due to their beneficial features in terms of earth-abundance, cost-effectiveness and low toxicities.[2]

In stark contrast to alkyne and alkene transformations, applications of allene chemistry in C–H activation strategies, using less expensive 3d base-metal catalysts continue to be scarce. Within our program on sustainable iron catalysis for C–H activation,[3] we developed versatile allene annulations through a unique C–H/N–H/C–O/C–H functionalization sequence.[4] The iron catalysis occurred under external-oxidant-free conditions even at room temperature. Notably, detailed mechanistic studies revealed an unprecedented 1,4-iron migration to be key to success for the C–H activation manifold.

Iron-Catalyzed C-H/N-H/C-O/C-H functionalization with allenes

no external oxidant
modular, removable TAH/M
mechanistic insights
inexpensive
non-toxic
room-temperature
1,4-Fe migration

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A Palladium Terminal Imido Complex

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Terminal oxo and imido complexes of the late transition metals promise new reactivity for applications in homogeneous as well as heterogeneous oxidation catalysis. However, isolated examples for the group 10 elements are exceedingly rare due to their excessive reactivity.[1] We reported recently computational investigations on how to tame elusive palladium terminal oxo and imido complexes through the choice of appropriate ancillary carbene ligands.[2]

Following these computational predictions, we present herein on the synthesis and characterization of a room-temperature stable palladium complex with a terminal imido group.[3] The electronic structure of the compound involves an antibonding highest-molecular orbital (HOMO) and can be understood as a vicinal frustrated Lewis-pair. The complex is therefore highly reactive and activates small molecules such as arenes, acetylenes, carbon monoxide, phosphines, water, and dihydrogen even at room temperature.

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Synthesis of Novel *N*-Heterocyclic Silylenes

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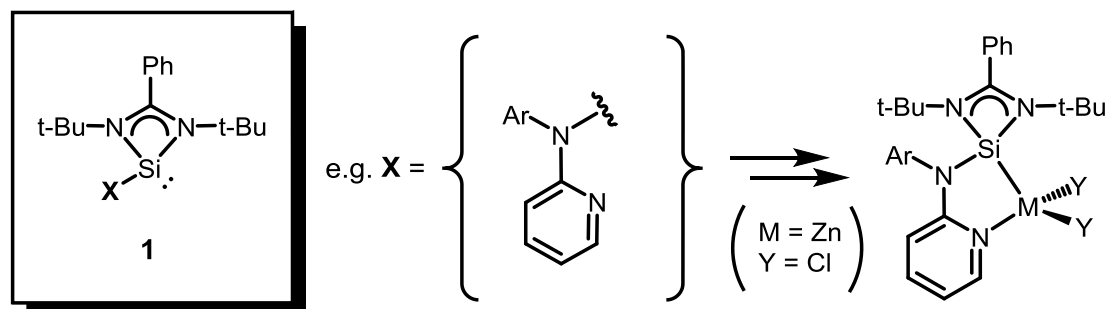
Scheme 1: Examples of the synthesis of novel 4-membered *N*-heterocyclic silylenes and their transition metal complexes.

Since *West* and *Denk* reported the first isolable *N*-heterocyclic silylene (NHSi) in 1994 transition metal complexes now enjoy an enormous attention. But in comparison to the ubiquitous reports of *N*-heterocyclic carbene (NHC) complexes, NHSi complexes are still comparatively rare.[1] Nevertheless they can perform interesting stoichiometric transformations. Since 2012 publications of catalytically active NHSi transition metal complexes are remarkably increasing with a broad range of applications (e.g. C-H bond borylation of arenes, cycloaddition reactions, etc.).[2-4]

The main target is to synthesize and isolate suitable stable *N*-heterocyclic silylene ligands for the complexation of group 11 and 12 metals (e.g. Cu, Au, Zn) on the basis of the 4-membered *N*-heterocyclic silylene **1** (Scheme 1). There are just a few group 11 and 12 NHSi complexes known so far but the various catalytically applications of their NHC analogues illustrate the huge potential of such compounds.[5-6] Therefore the first step is to provide new silylenes containing additional donor-sites for enhanced coordination of transition metal centres. Since the traditional routes of functionalizing silylene **1** did not show to be that straight forward when it comes to pyridine-based donor-sites new routes had to be established to gain the appropriate TM-complexes.

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Cationic NHC-Phosphinidene Ir(I) complexes and their application in Hydrogen Isotope Exchange Reaction

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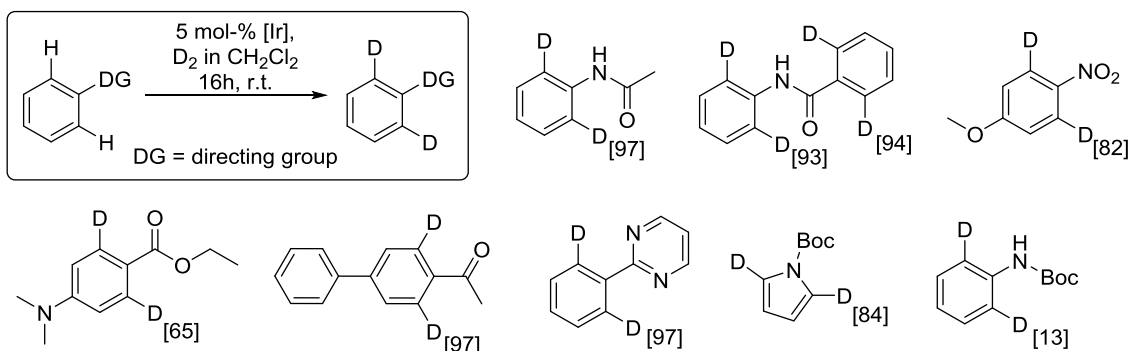
Hydrogen isotope exchange (HIE) has been studied extensively in the last decade, since it is a valuable method for mechanistic studies of biosynthetic pathways or catalytic reactions, as well as for preparation of deuterium labelled analytical tool compounds or tritium labelled radiotracers for pharmaceutical research.[1] The two most prominent catalysts for HIE are, among others, Crabtree's catalysts, as well as the NHC-iridium complexes by Kerr.[2] Both of them catalyse HIE-reactions for a broad range of aromatic substrates.

Herein, we report about the synthesis of new cationic NHC-phosphinidene Ir(I) complexes. NHC-phosphinidene complexes have been of considerable interest recently.[3-5] and the complexes presented herein show a remarkable reactivity in HIE reactions for a wide range of substrates, such as amides, ketones, heterocycles and nitroarenes. More demanding substrates, like benzamides and Boc-protected amines are also well tolerated.

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Sulfide redox and protonation interconversions at a preorganized dinickel site and HAT reactions of a nickel-bound thiyl radical with organic substrates

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Thiyl radicals play an important role in nature. Protein-derived radicals are essential in metabolism, DNA biosynthesis, prostaglandin biosynthesis or acetyl-coenzyme A production.[1–3] They are also used in stoichiometric and catalytic reactions as well as in near-infrared chromophores in dyes.[4–6] The monitoring of most thiyl radicals is challenging due to their temperature instability and their tendency towards dimerization. The reactivity and characteristics of thiyl radicals bridged between two metal centers is mainly unexplored. Here the first pyrazolate-bridged dinickel complex which bears a thiyl radical between the two nickel centers is presented. The location of the electron in the singly occupied S(pz) orbital is supported by EPR spectroscopy and DFT calculations, and HAT processes of this complex with organic substrates have been studied, based on the BDFE(solv.) values of the reaction partners.

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Utilization of Aerial Oxygen as an Abundant Oxidation Agent in Selenium-π-Acid and Photoredox Catalysis

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The direct and controlled oxidative transformation of simple olefins into functionalized compounds still represents a challenge in the area of organic synthesis.[1] To this day, catalytic alkene oxidations are mostly conducted *via* metal-based protocols.[2] However, in the recent past there has been considerable progress in the development of procedures that solely rely on non-metallic catalyst systems.[3] A crucial criterion is the nature of the terminal oxidant used in these systems. Most typically, oxidants such as peroxide derivatives, hypervalent iodine compounds, and (inter)halogen species are used.[4] However, there can be various disadvantages when applying these reagents. Particularly critical aspects are the poor atom economy, cost intensity, and sensitivity toward external conditions (e.g., moisture, heat, or light). Therefore, the utilization of alternative oxidants, such as neat oxygen or ambient air, appears highly desirable, as these reagents are environmentally compatible and abundantly available.[5] From that perspective, our group recently developed a new dual catalytic concept for the use of molecular oxygen (neat or aerial) as the terminal oxidant in the intermolecular allylic esterification of alkenes.[6] On the basis of these results, we now elaborated a highly practical and useful aerobic lactonization protocol, allowing for the cyclization of a broad panoply of alkenoic acids. The title reaction is enabled by the synergistic interplay of (PhSe)$_2$ as precursor to a selenium-π-acid [(PhSe)$_n^{m+}$] and a photoredox catalyst **3** under an atmosphere of ambient air as a gratuitous oxidant and visible light (465 nm) as an inexpensive energy source (Scheme 1).[7]
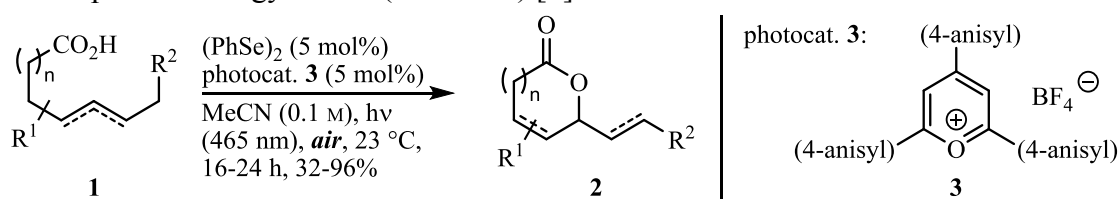
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CO₂-Catalyzed Oxidation of Benzylic and Allylic Alcohols with DMSO

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We have demonstrated the first transition metal-free CO_2-promoted highly chemoselective oxidation of alcohols to the corresponding carbonyl compounds. Earlier, a plethora of methodologies has been explored for alcohol oxidations based on transition metal catalysts. However, owing to the cheaper price, easy separation and non-toxicity, transition metal-free systems are far ahead compared to transition metal catalysts in pharmaceutical industry.[1–4]
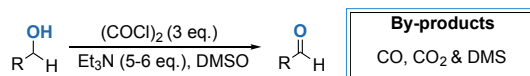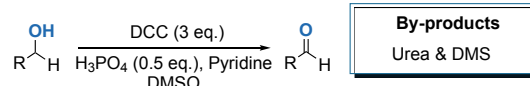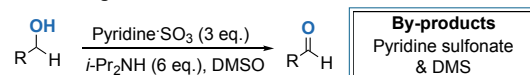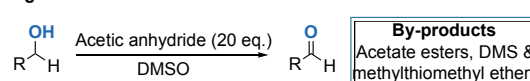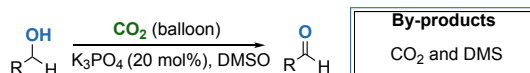
Various primary and secondary alcohols have been selectively oxidized to the corresponding carbonyl compounds in presence of different well tolerated functional groups such as nitrile, nitro, aldehyde, ester, halide, ether, etc. Additionally, we have shown wide application of our catalytic system for the transition metal-free synthesis of valuable natural products and pharmaceuticals as well. [5–8] Finally, detailed mechanistic studies clearly demonstrated the role of CO_2 in the reaction and the mechanism was proposed on an experimental basis. We believe this methodology could find interest in the synthesis of highly functionalized molecules, in the synthesis of natural products and pharmaceuticals.
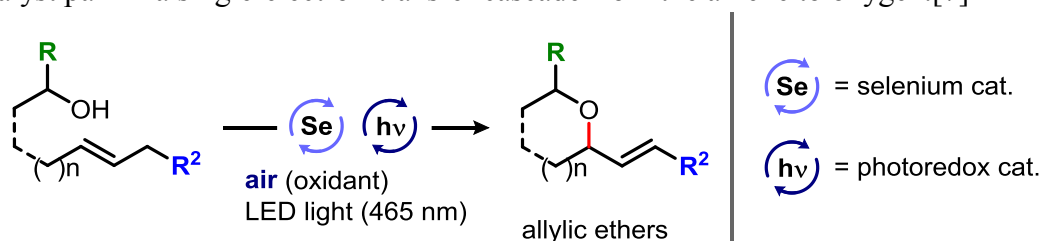
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Aerobic Allylation of simple Alcohols via Dual Organocatalysis

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In various chemical, biological and industrial settings, ethers play a significant role. In nature, they can be found as biologically highly active substances such as polyether-antibiotics[1] or as structural elements in plants (e.g., lignins).[2] In the context of technical, medical and pharmaceutical applications, ethers, especially polyethers, are used in excipients, cosmetics and binders for the production of ceramics.[3] Traditional procedures for the synthesis of simple, non-epoxidic ethers rely on redox-neutral reactions of alcohols or alkoxides with different electrophiles, for instance alkyl- or aryl halides[4] as well as catalytically activated alcohols or alkenes.[5] However, oxidative procedures, especially those that are predicated on the use of ambient air as the terminal oxidant, are scarce, although the environmentally and economically benign profiles of air as the terminal oxidant are in favour of it.[6] In order to apply ambient air as the terminal oxidant in the synthesis of ethers, a novel metal-free catalytic method for the formation of ethers from simple alcohols and alkenes was developed. The title reaction procedes under very mild conditions and relies on a diselenide and a pyrylium ion as a catalyst pair in a single-electron-transfer cascade from the alkene to oxygen.[7]

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Mechanistic Investigation of Olefin Hydrogenation Catalyzed by Cobalt(II) Pincer Complexes

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The cobalt(II) complex $[Co(CH_2SiMe_3)(^{Cy}PNP)]$ ($^RPNP = (R_2PCH_2CH_2)_2N$) was reported by Hanson and Zhang as highly efficient pre-catalyst for the hydrogenation of olefins and carbonyl compounds after activation with Brookhardt's acid.[1] Purely based on computational analysis, mononuclear cobalt(II) hydrides were proposed as active catalyst species.[2] However, well-defined cobalt(II) hydrides are scarce and structural analysis is hampered by the paramagnetism.

Herein we report the spectroscopic characterization of cobalt hydrides relevant to this chemistry. Synthesis and full characterization of the cobalt(II) hydride $[CoH(^{tBu}PNP)]$ (**3**, Figure 1) is presented. However, this compound is catalytically inactive. In contrast, the analogous $[CoH(^{Cy}PNP)]$ (**4**) is thermally unstable and forms dinuclear **5** upon rapid loss of H_2 at room temperature. Compound **5** is an active pre-catalyst for the hydrogenation of styrene. Experimental mechanistic examinations suggest a mono-/dinuclear catalytic cycle, which will be discussed.
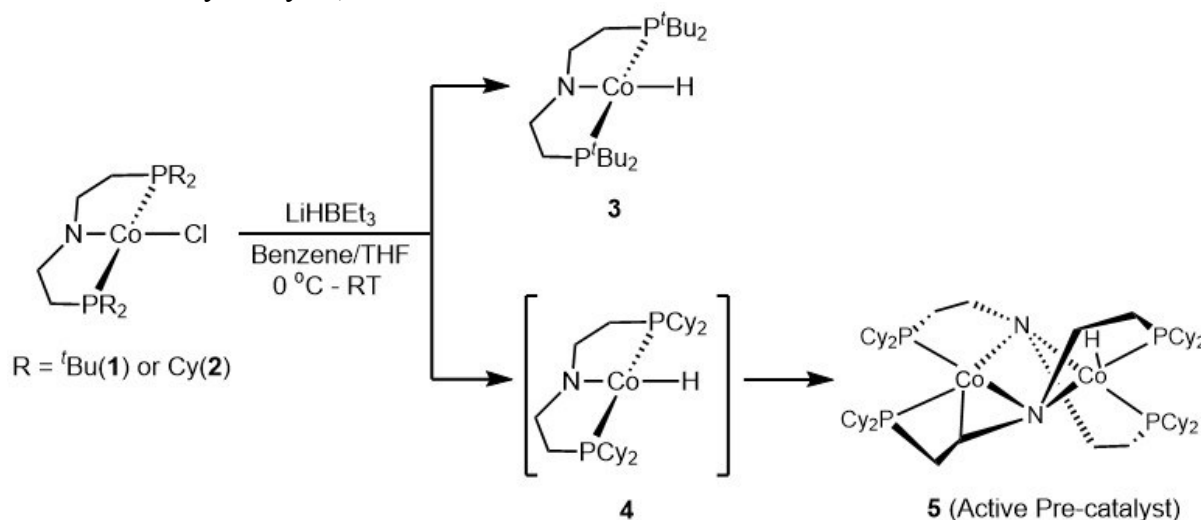

**Figure 1**. Synthesis of cobalt pincer hydride complexes.

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Base Metal-Catalyzed C–H Alkynylation

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Base metal-catalyzed C–H activation represents a powerful synthetic alternative to costly and rare 4d and 5d transition metals in C–H activation chemistry.[1]   In recent years, tremendous progress has been achieved, especially with cost effective and less toxic iron,[2] manganese,[3] cobalt[4] and nickel[5] catalysis for C–H activation. Herein, we present two complementary protocols for the alkynylation of heterocycles using either cobalt(III)-[6] or manganese(I)-catalysis.[7]
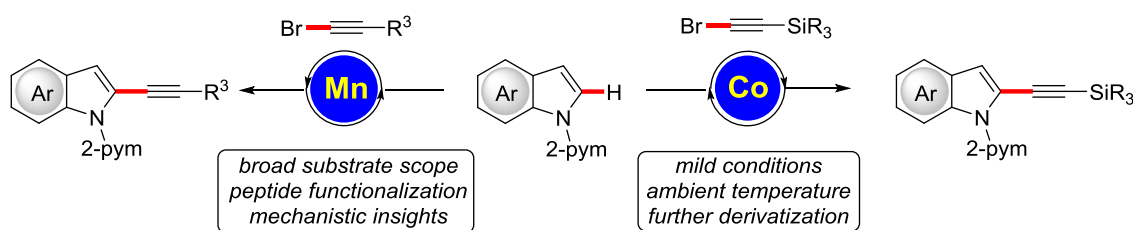
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The Reactivity of Terminal Nitrido Iridium- and Rhodium Complexes

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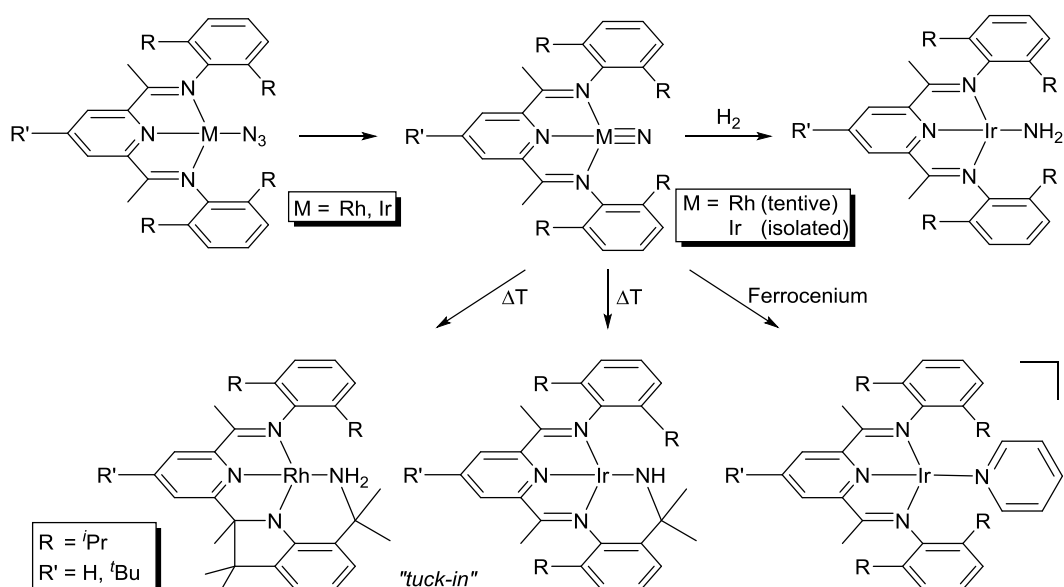
In our group we investigate the activation of small molecules with group 9 transition metal systems. Over the last years, we developed access to terminal nitrido pyridinediimine (PDI) complexes which, allow to activate H-H, Si-H, C-H, and even C-C bonds.[1]

Due to the reactivity of the nitrido complexes, intramolecular ligand C-H activation is an undesired side process for both the iridium and the tentative rhodium system and only the "tuck-in" complex could be hence isolated for Rh. We had previously turned to more stable ligands with 2,6-dichlorophenyl substituents of the ketimine functionality[2]. Further studies were thwarted by the low solubility of the corresponding complexes, however. To increase both the solubility and stability, we recently switched to CF_3-groups in the 2,6-positions of the imine aryl substituents.

In this poster we present, the gram scale synthesis of the PDI-ligand and first results of the synthesis and reactivity this new metal-ligand system.

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Metal-Free Catalyst for Visible-Light-Induced Oxidation of Unactivated Alcohols

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9-Fluorenone acts as a metal-free and additive-free photocatalyst for the selective oxidation of primary and secondary alcohols under visible light. With this photocatalyst, a plethora of alcohols such as aliphatic, heteroaromatic, aromatic, alicyclic, and steroid compounds has been converted to the corresponding carbonyl compounds using air/oxygen as oxidant.[1] The oxidation could be applied to unactivated alcohols as well, which gives this system an advantage over previously reported systems.[2-4]
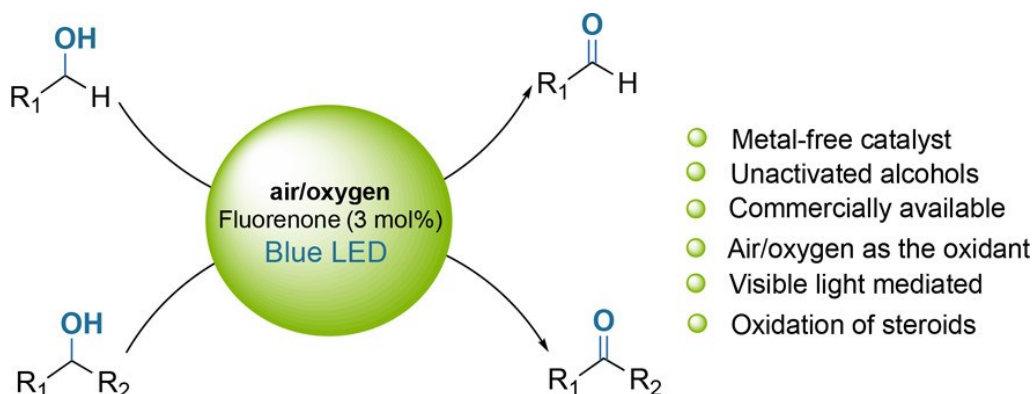
The system can be used for new synthetic strategies for pharmaceuticals and natural products, as it performs excellently under mild conditions. Additionally, the solvent, fluorenone and the formed by-product $DMSO_2$ are known drugs and food additives, which is beneficial for the pharmaceutical industry. Detailed mechanistic studies for this reaction system showed the role of the photocatalysts and oxygen.

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Experimental confirmation of a new intermediate for the reductive disproportionation of CO₂

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In general, the reaction of transition metal hydrides with CO_2 results in a so called normal insertion, generating formate without prior M-C bond formation.[1] In rare examples an abnormal insertion occurs, which forms the hydroxycarbonyl isomer as reaction product. Detailed mechanistic investigations however revealed reductive elimination of the hydride and a coordinating nitrogen atom, resulting in an umpolung, followed by coordination of CO_2 and protonation.[2] Again, no intermediate with the structural motive $MH(CO_2)$ is formed.

Direct coordination of CO_2 to transition metal hydrides has never been observed. Earlier reports[3] of such species were revealed to be formato or carbonato complexes, or contain no CO_2-derived motives at all.[1c, 4] A single example bearing the structural motive $TaH(CO_2)$ could be isolated via oxygen atom transfer to a tantalum hydride carbonyl complex.[5]
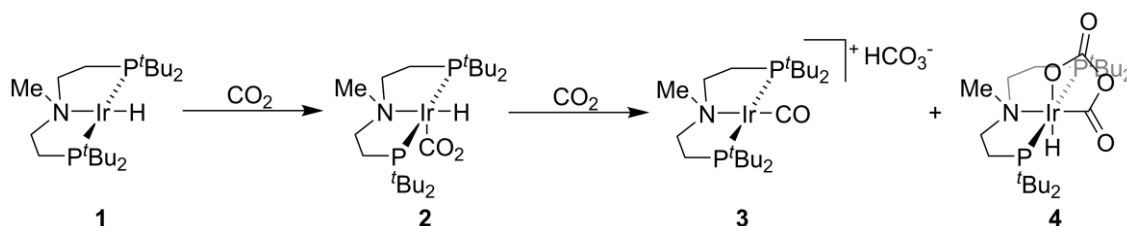
Nonetheless, an intermediate $L_nMH(CO_2)$ has been proposed for the reverse water gas shift reaction or reductive disproportionation of CO_2.[6] Here, we present the first experimental confirmation of such an intermediate in the form of $[Ir(P^{Me}NP)H(CO_2)]$ (**2**; $P^{Me}NP = CH_3N(CH_2CH_2P^tBu_2)_2$). This intermediate reacts further to either the carbonyl bicarbonate $[Ir(P^{Me}NP)(CO)] HCO_3$ (**3**) or a metallacycle (**4**).

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Transition Metal Complexes and Heterogeneous Catalysis Employing Phosphane-Substituted Troticenes

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Thorough investigations show the selective functionalisation of troticene by varying reaction conditions. Substitution of troticene can either occur selectively at the seven- or the five-membered ring. Also isolation of difunctionalised troticenes containing phosphanes is feasible.[1]
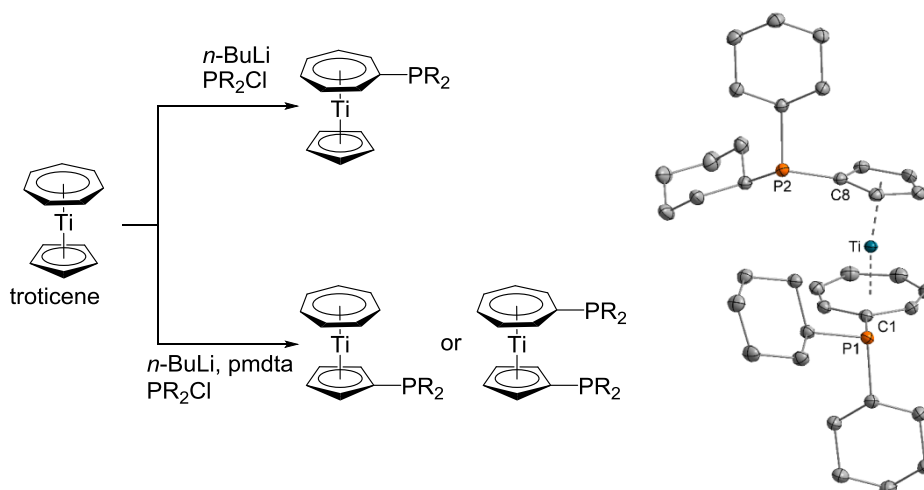
Using these different phosphane-substituted troticenes as ligands we were able to synthesise and fully characterise a large variety of transition metal complexes e.g. with palladium, platinum, nickel, iridium and rhodium.

Suzuki-Miyaura as well as Buchwald-Hartwig coupling reactions were performed with the monophosphane-functionalised troticenes and its pentamethyl derivatives indicating the reducing properties of these ligands in some cases. The performance of these palladium-catalysed cross coupling reactions strongly depends on the nature of the phosphane ligand and the incorporation of troticene as a non-innocent scaffold offers novel approaches as lately reported.[2,3]

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Highly Selective Directed Iridium-Catalyzed

Hydrogen Isotope Exchange Reactions of Aliphatic Amides

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Hydrogen isotope exchange (HIE) allows the direct substitution of hydrogen by its isotopes (deuterium and tritium) at the target molecule itself and thus circumvents the need for additional chemical synthesis steps (e.g. precursor synthesis or a stepwise preparation from isotopically enriched starting materials). While direct HIE reactions on aromatic compounds have been heavily studied there is still a lack of useful protocols for selective aliphatic sp3-labelling.[1,2] This is especially important for drug compounds lacking a reactive aromatic moiety. We present our results of 2H/3H-labelling of DM4, a cytotoxic drug presently being developed in antibody-drug conjugates (ADCs). Using the newly developed protocol a reaction sequence of five radioactive steps could be substituted with a single HIE reaction.
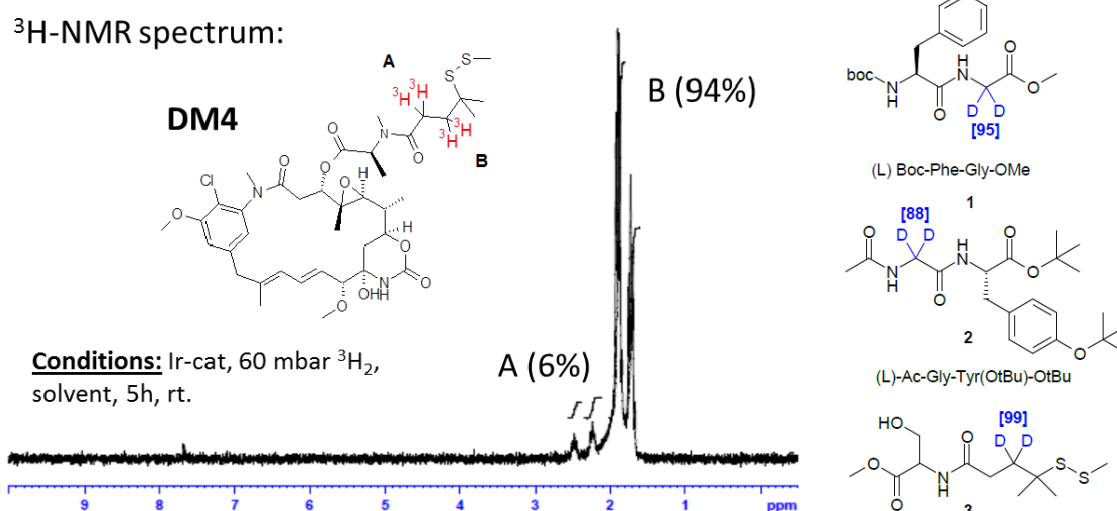
We have discovered that this method can be applied much more broadly, and we have investigated its effectiveness on aliphatic amides like peptides, conjugates and drug precursors.[3] To our great delight we found good deuterium incorporation and regioselectivities especially for glycine derivatives (**1,2**) and linker side chains of type **3**. We are convinced this method will increase the possibilities for isotope chemists to label more complex aliphatic molecules in the future.

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Mechanism of (electro)Chemical N₂ Splitting by a Rhenium Pincer Complex

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Synthetic N₂ fixation at low pressures and temperatures remains as one of the most challenging problems in catalysis.[1] In recent years, several model systems were established that enable catalytic ammonia production using alkali metal (KC₈, NaHg) or organometallic (CoCp₂*) reductants. Ultimately, electrochemical approaches provide an appealing alternative.[2] However, electrocatalytic N₂ fixation is scarcely examined and in general, experimental information regarding key intermediates that activate N₂ remain highly limited. We report a synthetic and mechanistic study on (electro)chemical N₂ splitting from the Re-pincer complexes **1** (Figure 1), that we previously established for N₂ cleavage into **2** and transfer.[3,4], via intermediate **3**. The here proposed complete mechanism for N₂-reduction on **1**, provides valuable information for the design of future electrocatalysts.[5]
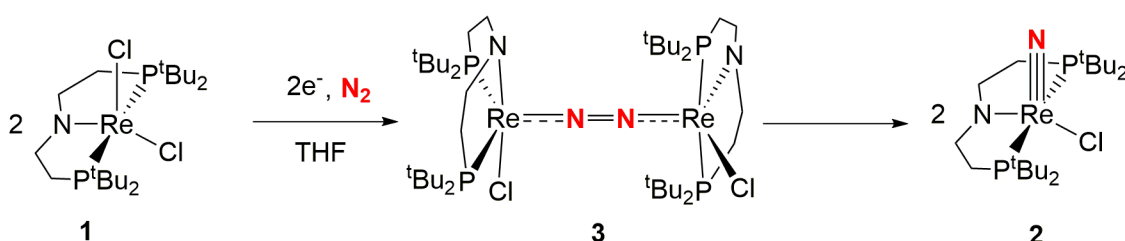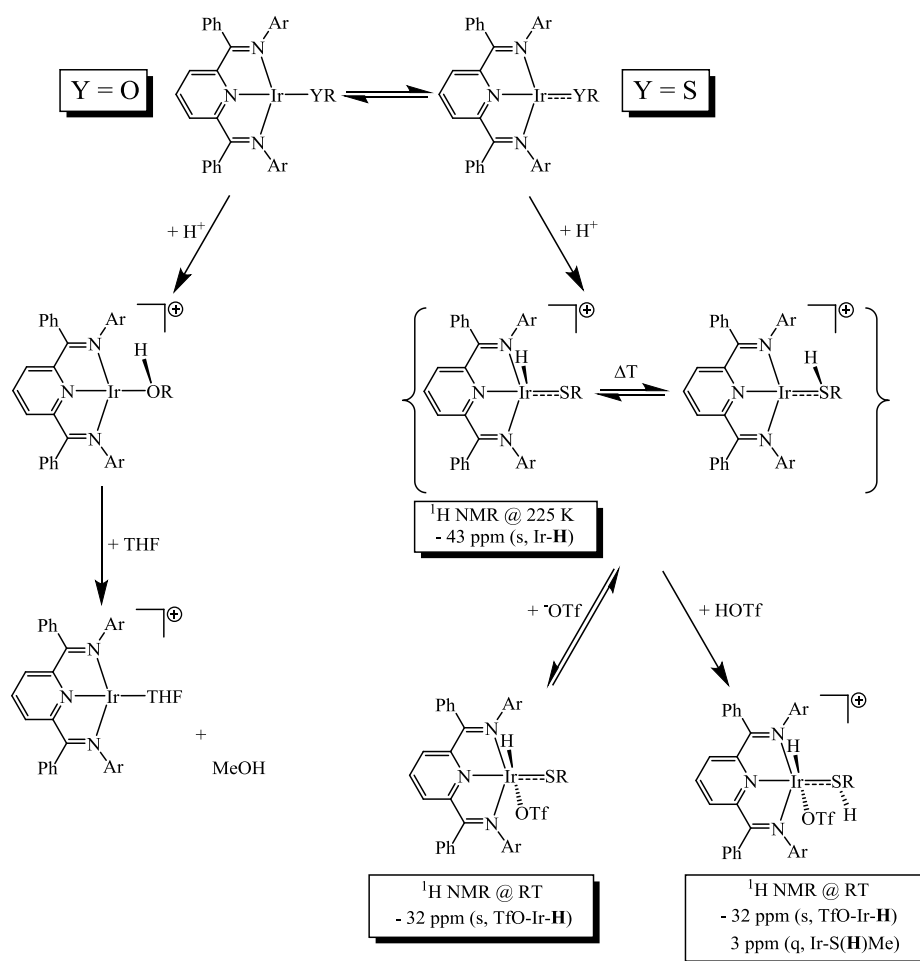
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Metal vs. Ligand Protonation

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Cationic square-planar pyridine-diimine (PDI) iridium complexes are important starting materials for our research. They are typically accessed via protolytic cleavage of the fourth ligand, YR, where YR is preferably a methoxide (Scheme 1).[1] Recently, we switched to sulphido ligands (Y = S) and noted a strikingly different reactivity. Rather than cleavage of the chalcogenido ligand, we observed a delicate balance between protonation at the metal and at the sulfur center giving rise to an equilibrium. The equilibrium position and preference with regard to the substituent of the thiolato ligand were studied in detail and will be presented.

Scheme 2. Protonation studies of PDI iridium complexes with chalcogenido ligands
Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, R = Me, H.

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Catalyzed Chain Growth Polymerization: A Versatile Tool for End-group Functionalization and Surface Modification

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Polyethylene (PE) is one of the most widely used thermoplastics due to its low cost as well as its favoured mechanical and thermal properties. However, the functionalization of the very hydrophobic polyethylene - such as the incorporation of polar moieties - is still challenging. For this purpose, catalyzed chain growth (CCG), a controlled polymerization technique, gives access towards well defined PE with high end-group functionality. CCG is based on a degenerative chain transfer polymerization mechanism including a diorganomagnesium compound as a chain transfer agent and a transition metal catalyst ([Nd]). [1,2]

In one part of this study, we demonstrate an efficient synthesis of thiol/trithiocarbonate end-functionalized polyethylene which is able to self-assemble onto both gold and silver nanoparticles yielding metal-core–PE-shell nanostructures. The advantage of this approach is based on the PE shell which is strongly anchored to the surface of the nanoparticles. Therefore, these modified nanoparticles can be fully dispersed into a PE matrix and possess a reversible temperature dependent dispersibility in solution. [3] The CCG method provides a very variable choice of end-group functionalization which allows further surface modification (e.g. of wood, silica) in a similar grafting approach. In addition to surface modification, by introducing a permanently charged end-group into hydrophobic PE, an easy access to characterization via mass spectrometry is provided. This permanently charged PE can also be applied e.g. as a recoverable phase transfer catalyst.
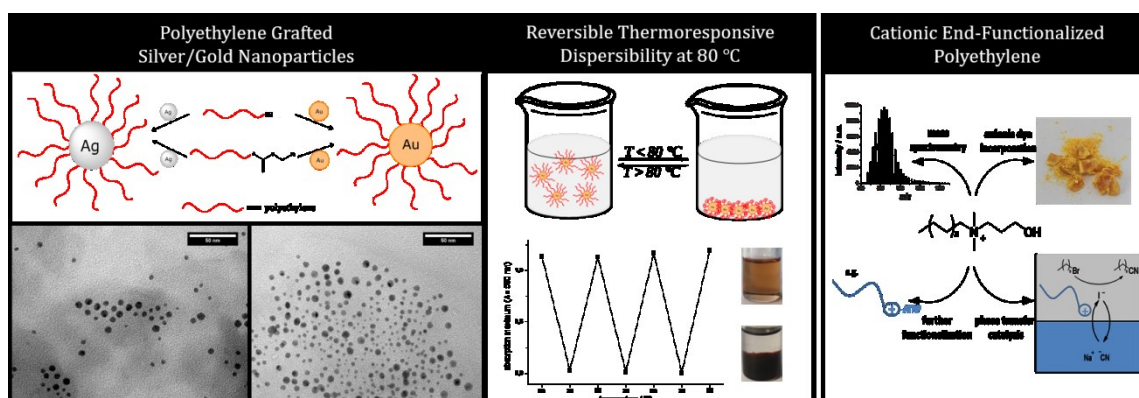
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Dibenzothiophenium Salts as Alkynyl-transfer reagents

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Chemical Umpolung of functional groups using transfer reagents is a powerful synthetical tool for introducing typical nucleophilic moieties like trifluoromethyl, azide or alkynyl-groups into organic molecules, which normally also act as nucleophile. This was shown by the pioneering works from Zhandkin [1], Togni [2] or Waser [3]. The possibility to use this method for the late step functionalisation of pharmaceutical and agrochemical products make it a valuable tool in organic synthesis.

Until these days this field was mainly dominated by hypervalent Iodine compounds. However, their high reactivity sometimes results in the loss of selectivity. Moreover, hypervalent I(III) compounds display exploding character, requiring special knowledge to handle them. One of the few alternatives available are the thiourea-compounds developed by our group. [4]

In order to address these limitations, our group has developed a selective and safe alternative to hypervalent iodine based compounds utilizing a dibenzothiophene-backbone [5]. Dibenzothio-phenium-salts could be synthesized in an easy procedure, starting from cheap, commercial available compounds. It could be shown that these salts could be used to transfer alkynyl-groups to a variety of different nucleophiles like sulfonamides, thiols, activated carbon-based nucleophiles and even phosphorous compounds.

Furthermore, it could be shown that these compounds have the potential to alkynylate complex molecules in a more selective way than the known TIPS-EBX. Finally, straightforward labelling experiments were performed leading to first insights into the mechanism of the transfer reaction.
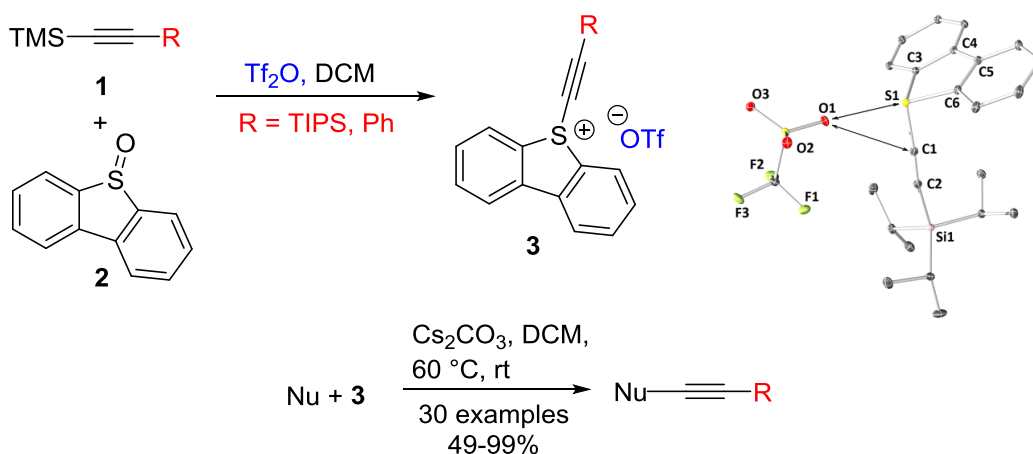
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5th Lower Saxony Catalysis Symposium

September 19th-20th, 2018, Göttingen, Germany

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Wednesday, September 19th		
from 12:00		Arrival and Registration
13:00 – 13:15	F. Meyer	Welcome/Introduction

Session 1		Chair: M. Morganti
13:15 – 14:00	M. Abu-Omar	Chemical Synthons and Recyclable Materials from Lignin
14:00 – 14:45	M. Costas	Selective Oxidations Inspired in Non Heme Iron Dependent Oxygenases
14:45 – 15:00		Photo
15:00 – 15:30		Coffee Break

Session 2		Chair: M. Kolter
15:30 – 16:15	P. Chen	Carbene Complexes in Metathesis and Cyclopropanation
16:15 – 17:00	L. Gonsalvi	Carbon Dioxide Catalytic Conversion to Chemicals and Fuels with Non-noble Metal Complexes
17:00 – 17:20	M. Schütze	The Transformation of CO_2 into Polymeric Materials
17:30 – 19:30		Poster Session with Snacks and Drinks

Thursday, September 20th		
Session 3		Chair: N. Sauermann
8:45 – 9:30	I. Larossa	Transition Metal Catalyzed C-H Activation: Reactivity, Selectivity Control and Late-Stage Functionalization
9:30 – 10:15	V. Derdau	C-H-Functionalization for Hydrogen Isotope Exchange and Modern Application for Life Science
10:15 – 10:45		Coffee Break

Session 4		Chair: J.-P. Du
10:45 – 11:05	C. Kornhaaß	Process Development at Merck - From Laboratory to Large Scale
11:05 – 11:25	A. Wolpers	Controlled Radical Polymerization of Ethylene
11:25 – 12:10	E. Anxolabéhère-Mallart	Electrochemistry and Bioinspired Metallic Complexes for Reductive O_2 Activation
12:10 – 13:15		Lunch break

Session 5		Chair: C. Schiwek
13:15 – 14:00	B. Plietker	Breathing In and Out - Fe-NO-Complexes in Catalysis
14:00 – 14:45	A. Dey	Managing Protons and Electrons in Small Molecule Activation
14:45 – 15:00	F. Meyer	Poster Awards & Farewells
15:00		Departure