

Book of Abstracts

Workshop May 2017, Bielefeld

Graduate School

„Catalysis for Sustainable Synthesis“ (CaSuS)

**Georg-August-Universität Göttingen,
Technische Universität Braunschweig**

together with

Graduate School

„Selectivity in Chemo- and Biocatalysis“ (SeleCa)

RWTH Aachen

	Timetable				title / comment	chair	
	from	until	duration				
29.05.	Arrivel and check-in		12:00				
	Lunch buffet		12:00	- 13:00	1:00		
	Welcoming by Franc Meyer		13:15	- 13:30	0:15		
	Andreea Enachi	13:30	- 13:55	0:25	<i>Development of Ni and Co catalysts for the (co-)polymerization of olefins and polar monomers and hydrofunctionalization of olefins</i>	Mike Schütze	
	Marius Peters	13:55	- 14:20	0:25	<i>From NHC-phosphinidene- to NHC-phosphinidyne complexes</i>		
	Patricia Liebhäuser	14:20	- 14:45	0:25	<i>Hydroxylation Catalysis with a Peroxide Dicopper(II) Complex</i>		
	Break		14:45	- 15:00	0:15		
	Tobias Schindler	15:00	- 15:25	0:25	<i>Decomposition of a Tungsten Propylidyne Complex Featuring a cis-Coordinated Formate Ligand</i>	Óscar Arias	
	Hassan Osseili	15:25	- 15:50	0:25	<i>Alkali Metal Hydridotriphenylborates [(Me₆TREN)M][HBPh₃] (M = Li, Na, K): Synthesis, Structure and Reactivity</i>		
	Coffee break, hang up Posters		15:50	- 16:30	0:40		
	Christoph Schiwiek	16:30	- 16:55	0:25	<i>Unexpected Reactivity in N-methylated Iridium Pincer Complexes for Oxygen Reduction</i>	Elena Bothe	
	Marten Seeba	16:55	- 17:20	0:25	<i>Bioinspired Dinuclear Copper Complexes for Catalytic Phenol Oxidation using Aerial Dioxide</i>		
	Poster Session		17:20	- open-end			
BBQ		18:00	- 19:30				
30.05.	Breakfast		7:00	- 8:15	1:15	Check-out done	
	Sonja Herres-Pawlis	8:15	- 9:15	1:00	<i>Resonanz-Raman-Spektroskopie in der bioanorganischen Chemie</i>	Katharina Rode	
	Konrad Koszinowski	9:15	- 10:15	1:00	<i>ESI Mass Spectrometry and Gas-Phase Methods for the Identification and Characterization of Catalytic Intermediates</i>		
	Coffee break		10:15	- 10:45	0:30		
	Sabrina Tröndle	10:45	- 11:10	0:25	<i>Phosphane-Substituted Trolicenes – Transition Metal Complexes and Catalysis</i>	Jannik Wagner	
	Michael Tauchert	11:10	- 11:35	0:25	<i>Development of Ambiphilic Diphosphinoboron and Diphosphinometal Ligands</i>		
	Alexander Paesch	11:35	- 12:00	0:25	<i>Synthesis of Novel N-heterocyclic Silylenes and their Transition Metal Complexes</i>		
	Lunch buffet		12:00	- 13:00	1:00		
	Daniel Sauer	13:00	- 13:25	0:25	<i>Nitrobindin: Evolution of a Protein-Host for Biohybrid Catalysts</i>	Lena Ebert	
	Lu Lu	13:25	- 13:50	0:25	<i>Ruthenium Catalyzed Hydroboration of Terminal Alkynes to Z-Vinylboronates</i>		
Closing words by Franc Meyer		13:50	- 14:00	0:10			
Social activity (Sparrenburg/Dr. Ötker) or Depature					Departure Aachen 15:00		

Oral Presentations

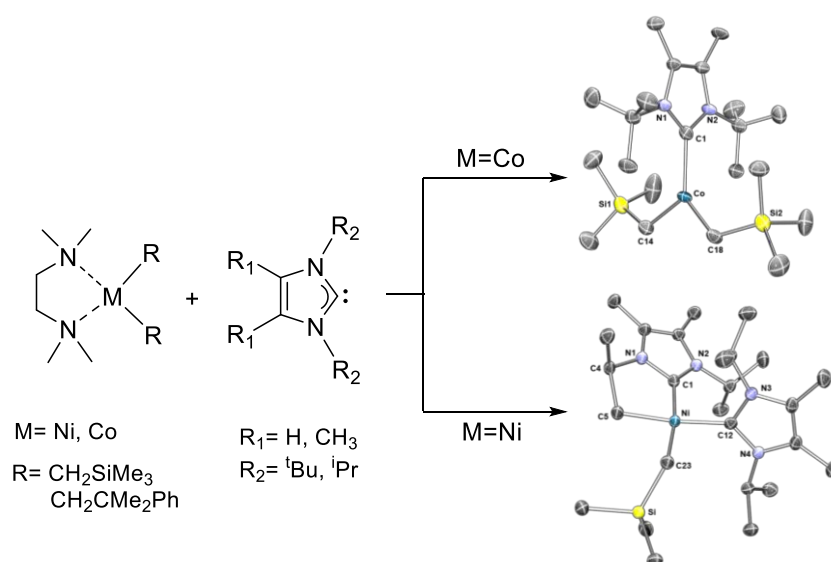
Development of Ni and Co catalysts for the (co-)polymerization of olefins and polar monomers and hydrofunctionalization of olefins

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Transition metal alkyl complexes are among the most reactive species in organometallic chemistry, therefore preparing and isolating them can be a challenge.^[1] However, we were able to synthesize dialkyl metal complexes in a good yield using [(tmeda)M(acac)₂] (M=Ni, Co) as a M²⁺ source and [(tmeda)MgR₂] (R= CH₂SiMe₃, CH₂CMe₂Ph) as the alkyl transfer reagent. Furthermore, the tmeda ligand can be readily displaced by tunable bidentate phosphines and *N*-heterocyclic carbenes (NHCs) which are good sigma donors and 'spectator' ligands and confer good stability to transition metal complexes. The lower oxophilicity and presumed greater functional-group tolerance of late transition metals relative to early metals make them promising targets for the development of catalysts suitable for the preparation of ethylene and polar vinyl monomer copolymers which are currently industrially prepared by radical polymerization.^[2] This and further applications in the hydrofunctionalization of olefins and functionalized olefins will be reported.



Scheme 1. Preparation of *N*-heterocyclic carbene Ni²⁺ and Co²⁺ dialkyl compounds.

[1] D. Zhu, F.F.B.J. Janssen, P.H.M. Budzelaar, *Organometallics* **2010**, 29, 1897.

[2] a) L.K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* **1996**, 118, 267; b) S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, 120, 888.

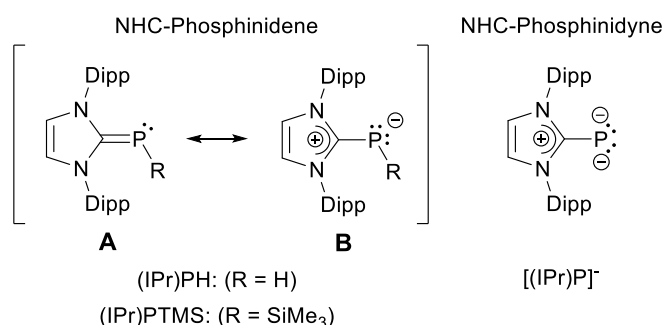
From NHC-phosphinidene to NHC-phosphinidyne complexes

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Over the past ten years the coordination and main-group chemistry of imidazoline-2-iminato and imidazoline-2-imine ligands has been studied intensively^[1], whereas the coordination chemistry of NHC-phosphinidenes gained interest in the last years.^[2]



We report about the reactivity of the parent NHC-phosphinidene (IPr)PH and synthetic, spectroscopic and structural details of several NHC-phosphinidene complexes.^[3] Our group also developed the synthesis of a P-silylated carbene-phosphinidene (IPr)PTMS which was used as starting material for NHC-phosphinidyne complexes.^[4]

- [1] X. Wu, M. Tamm, *Coord. Chem. Rev.* **2014**, *260*, 116-138; T. Ochiai, D. Franz, S. Inoue, *Chem. Soc. Rev.* **2016**, *45*, 6327-6344.
- [2] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. B., *Angew. Chem. Int. Ed.* **2013**, *52*, 2939-2943; T. G. Larocque, G. G. Lavoie, *New J. Chem.* **2014**, *38*, 499-502; V. A. K. Adiraju, M. Yousuffuddin, H. V. R. Dias, *Dalton Trans.* **2015**, *44*, 4449-4454; L. Liu, D. A. Ruiz, F. Dahcheg, G. Bertrand, *Chem. Commun.* **2015**, *51*, 12732-12735; A. Doddi, D. Bockfeld, A. Nasr, T. Bannenberg, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2015**, *21*, 16178-16189; M. Bispinghoff, A. M. Tondreau, H. Grützmacher, C. A. Faradji, P. G. Pringle, *Dalton Trans.* **2016**, *45*, 5999-6003; M. Bispinghoff, H. Grützmacher, *Chimia* **2016**, 279-283; D. Bockfeld, A. Doddi, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2016**, 3704-3712.
- [3] M. Peters, A. Doddi, M. Freytag, D. Bockfeld, P. G. Jones, M. Tamm, *manuscript in preparation*.
- [4] A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2014**, *53*, 13567-13572.

Hydroxylation Catalysis with a Peroxide Dicopper(II) Complex

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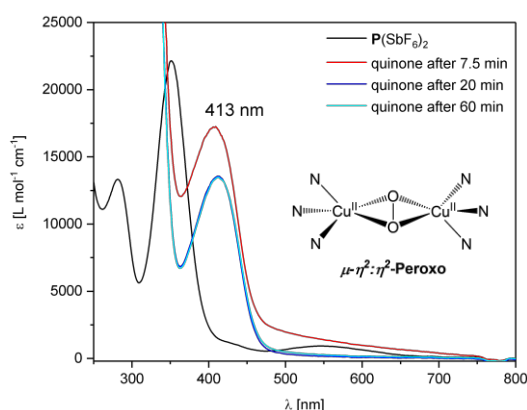


Fig. 1. UV/Vis spectra of the side-on-peroxo species and the hydroxylation of 8-hydroxyquinoline.

In nature, the amino acid tyrosine is selectively oxidised by tyrosinase to the *ortho*-catechol L-DOPA and furthermore to L-dopaquinone. This *ortho*-selectivity derives from the protein structure, especially its catalytic centre. It consists of two copper ions each coordinated by three histidine residues. The incorporation of one oxygen molecule results in a $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ dicopper(II) complex (Fig. 1). So far, different model systems for the active site of tyrosinase were developed, but only few show the catalytic hydroxylation of phenolic substrates^[1] as bis(pyrazolyl)methane copper complexes do.^[2] Peroxo complexes can be monitored via UV/Vis spectroscopy because of their characteristic absorptions (Fig. 1). Successful hydroxylation catalysis is obtained with phenolic substrates and furthermore with the sophisticated substrate 8-hydroxyquinoline (Fig. 1).

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Decomposition of a Tungsten Propylidyne Complex Featuring a *cis*-Coordinated Formate Ligand

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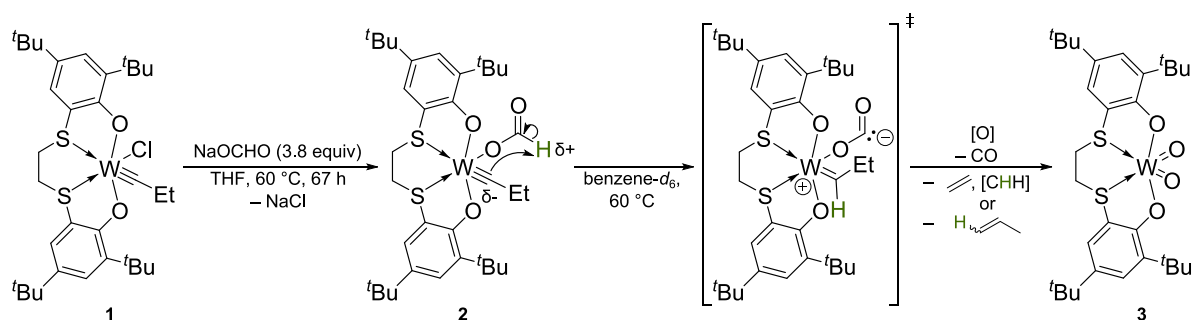


Fig. 1. Decomposition of complex **2** to produce **3**.

The acidity of the formate proton and the basicity of the alkylidyne carbyne are well documented, but little is known about any interaction between these two ligands.^[1-3] Metalation and deprotonation of the formate ligand produces a dimetalloxycarbene which has been proposed as an intermediate in carbon-carbon-coupling reactions.^[1] Interconversion reactions between alkylidyne, alkylidene and vinylidene complexes have been utilized to produce the targeted compounds, relying on reactions at the negatively polarized carbyne $M(\delta^+) \equiv C(\delta^-)$.^[4]

We report the synthesis and characterization of a tungsten propylidyne complex featuring a *cis*-coordinated formate ligand stabilized by an OSSO-type backbone. We prepared the (OSSO)W(CEt)(OCHO), **2**, complex through salt metathesis between (OSSO)W(CEt)Cl^[4], **1**, and NaOCHO. Investigations on the basicity of the propylidyne ligand revealed an intramolecular deprotonation of the formate, producing the decomposition product (OSSO)WO₂, **3**. Studies with isotopic labelled formate complexes enabled the elaboration of a decomposition mechanism.

- [1] A. Paparo, J. S. Sivilia, C. E. Kefalidis, T. P. Spaniol, L. Maron, J. Okuda, C. C. Cummins, *Angew. Chem. Int. Ed.* **2015**, *54*, 9115-9119.
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 [4] H. Nishiyama, K. Yamamoto, A. Sauer, H. Ikeda, T. P. Spaniol, H. Tsurugi, K. Mashima, J. Okuda, *Organometallics* **2016**, *35*, 932-935.

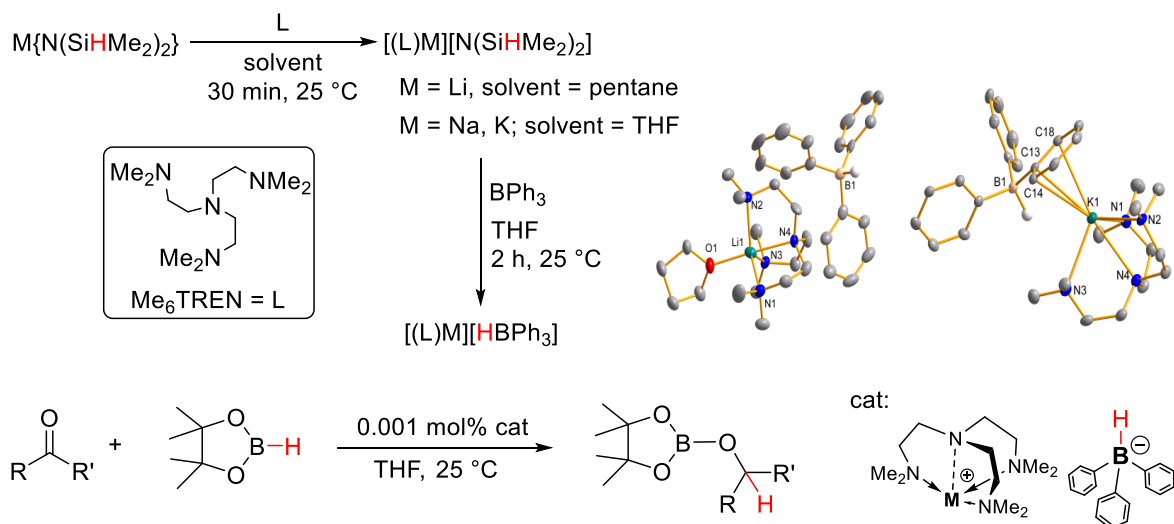
Alkali Metal Hydridotriphenylborates [(Me₆TREN)M][HBPh₃] (M = Li, Na, K): Synthesis, Structure and Reactivity

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Hydridoborates [HBR₃]⁻ are ubiquitous stoichiometric reducing agents in organic synthesis.^[1] The nature of the metal and the boron substituents influence their selectivity.^[2-5] We have synthesized a series of Me₆TREN-coordinated alkali metal hydridotriphenylborates [(Me₆TREN)M][HBPh₃] (M = Li, Na, K) following β-SiH abstraction from the corresponding tetramethyldisilazides [(Me₆TREN)M][N(SiHMe₂)₂]. Among them, the lithium derivative shows remarkable efficiency in chemoselectivity toward catalytic hydroboration of carbonyls.^[6,7] All three metals activate CO₂ and also catalyze its hydroboration to selectively provide formylborane HCO₂Bpin without any over-reduction.



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- [4] N. M. Yoon, K. E. Kim, J. Kang, *J. Org. Chem.* **1986**, 51, 226.
- [5] G. Wittig, G. Keicher, A. Rückert, P. Raff, *Justus Liebigs Ann. Chem.* **1949**, 563, 110.
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- [7] H. Osseili, D. Mukherjee, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2017**, in press.

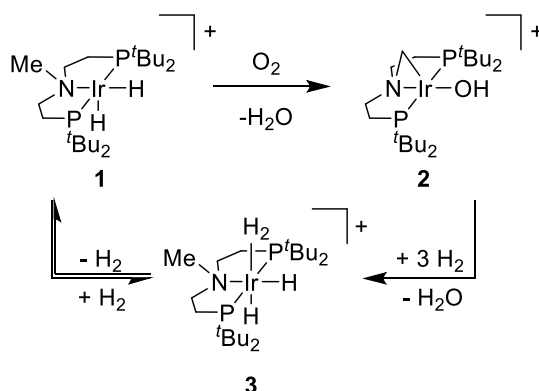
Unexpected Reactivity in N-methylated Iridium Pincer Complexes for Oxygen Reduction

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The oxygen reduction reaction (ORR) requires the delivery of four electrons, which is often accomplished by utilizing multiple redox active metal centers and/or non-innocent ligands.^[1-3] Earlier we presented an iridium dihydrido complex capable of completing the ORR in a synthetic cycle, in which all four electrons are stored in covalent metal-hydride bonds on a single metal center.^[4] Based on kinetic studies, isotope labeling and computations a mechanism, which is first order in the dihydride as well as O_2 , was proposed. However, questions regarding the influence of water on the selectivity and the exact nature of the cooperativity of the secondary amino ligand remained.

In an attempt to study this cooperativity complex $[\text{Ir}^{\text{III}}(\text{H})_2\{\text{CH}_3\text{N}(\text{CH}_2\text{CH}_2\text{P}^t\text{Bu}_2)_2\}]\text{OTf}$ **1** was synthesized, in which the acidic secondary amine has been blocked via N-methylation. However, unexpected formal deprotonation of this methyl group lead to formation of hydroxo complex $[\text{Ir}^{\text{III}}(\text{OH})\{\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{P}^t\text{Bu}_2)_2\}]\text{OTf}$ **2**. Under dihydrogen **2** very slowly forms dihydrogen adduct **3** as well as starting compound **1**. In light of our results the assumption that N-methylation prevents metal-ligand cooperativity should be questioned.

- [1] L. Que, W. B. Tolman, *Nature* **2008**, 455, 333.
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[3] Z. M. Heiden, T. B. Rauchfuss, *J. Am. Chem. Soc.*, **2007**, 129, 14303.
[4] C. Schiwek, J. Meiners, M. Förster, C. Würtele, M. Diefenbach, M. C. Holthausen, S. Schneider, *Angew. Chem. Int. Ed.* **2015**, 54, 15271.

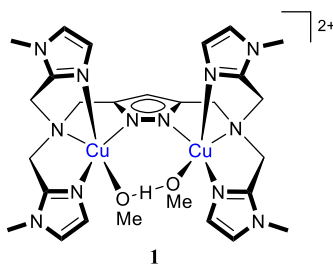
Bioinspired Dinuclear Copper Complexes for Catalytic Phenol Oxidation using Aerial Dioxygen

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Inspired by tyrosinase and related polyphenol oxidases (PPOs), all type-III copper proteins, that are capable of oxygenating and oxidizing phenolic substrates using aerial dioxygen as the oxidant^[1], complex **1** was synthesized based on a compartmental pyrazolate based dinucleating scaffold^[2].



1 was shown to be able to catalyze C—C coupling reactions with substituted phenols such as 2,4,6-trimethyl phenol (TMP) and is furthermore capable of generating different functionalization's of the 4-methyl group of TMP^[3]. Hereby aerial dioxygen is used as the oxidant.

During the reaction the initial Cu^{II}Cu^{II} complex **1** undergoes either partial reduction to a valence localized Cu^ICu^{II} species in case of C—C coupling, or reduction to a Cu^ICu^I species. Both species are reoxidized to their initial state by aerial dioxygen. Catalytic applications and mechanistic insight will be presented.

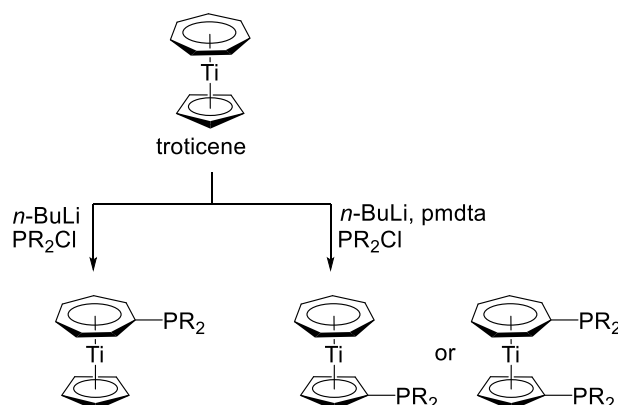
- [1] a) T. Klabunde, C. Eicken, J. C. Sacchettini, B. Krebs, *Nat. Struct. Biol.* **1998**, *5*, 1084; b) Y. Matoba, T. Kumagai, A. Yamamoto, H. Yoshitsu, M. J. Sugiyama, *Biol. Chem.* **2006**, *31*, 8981; c) W. T. Ismaya, H. J. Rozeboom, A. Weijn, J. J. Mes, F. Fusetti, H. J. Wichers, B. W. Dijkstra, *Biochemistry* **2011**, *50*, 5477; d) C. Molitor, S. G. Mauracher, A. Rompel, *PNAS* **2016**, *113*, E1806.
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Phosphane-Substituted Troiticenes – Transition Metal Complexes and Catalysis

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Recent results by us demonstrate the selective modification of troiticene by varying the reaction conditions. Mono-functionalization of troiticene can either occur selectively at the five- or the seven-membered ring according to the reaction conditions.^[1] Also the synthesis of di-functionalized troiticene containing phosphanes is feasible.^[1,2]

Using these different phosphane-substituted troiticenes as ligands we were able to synthesize and fully characterize a large variety of transition metal complexes e.g. with palladium, platinum, gold, iridium and rhodium.^[1,3] Remarkably, in some cases the cycloheptatrienyl moiety acts as a reducing agent.^[4]

The performance of palladium-catalyzed cross coupling reactions strongly depends on the nature of the phosphane ligand and the incorporation of troiticene as non-innocent scaffold offers novel aspects as recently reported.^[4] Suzuki-Miyaura coupling reactions were performed with the monophosphane-functionalized troiticenes and its pentamethyl derivatives indicating the reducing properties of these ligands.

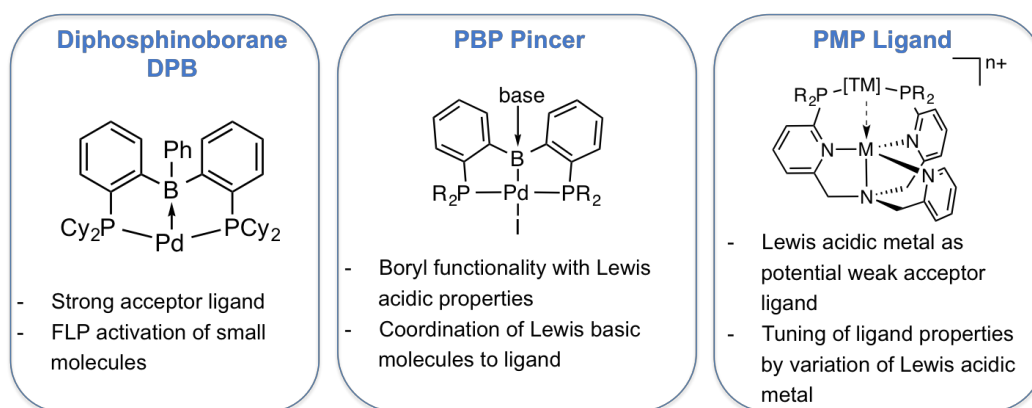
- [1] S. K. Mohapatra, S. Büschel, C. G. Daniliuc, P. G. Jones, M. Tamm, *J. Am. Chem. Soc.* **2009**, *131*, 17014-17023.
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Development of Ambiphilic Diphosphinoboron and Diphosphinometal Ligands

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The combination of Lewis basic and Lewis acidic functional groups in so called ambiphilic ligands provides interesting perspectives for homogeneous transition metal catalysis.^[1] The borane functionality in diphosphinoborane (DPB) ligands serves as a strong σ -acceptor ligand to Lewis basic transition metals resulting in complexes with unique electronic and steric properties, which have successfully been utilized in transition metal catalysis.^[1,2] Recently, we and the Ozerov group used DPB complexes to access PBP pincer complexes featuring a boryl functionality permitting the coordination of Lewis bases to the ligand.^[3] Lewis acidic metals are known to form heterobimetallic complexes with Lewis basic transition metals.^[4] We developed a ligand framework stabilizing such metal only Lewis pairs. These complexes are designed for homogeneous transition metal catalysis with a Lewis acidic metal serving as a weak acceptor functionality in a PMP ligand.

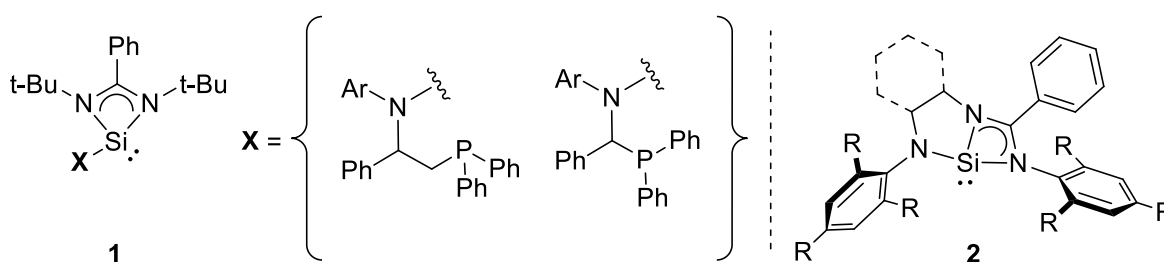
- [1] a) G. Bouhadir, D. Bourissou, *Chem. Soc. Rev.* **2016**, *45*, 1065; b) G. R. Owen, *Chem. Commun.* **2016**, *52*, 10712.
- [2] a) T. Schindler, M. Lux, M. Peters, L. T. Scharf, H. Osseili, L. Maron, M. E. Tauchert, *Organometallics* **2015**, *34*, 1978; b) P. Steinhoff, M. E. Tauchert, *Beilstein J. Org. Chem.* **2016**, *12*, 1573.
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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.

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 metals (Cu, Ag and Au) on the basis of the 4-membered *N*-heterocyclic silylene **1** (**Scheme 1**). There are just a few group 11 NHSi complexes known so far but the various catalytic 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. Ongoing research will also investigate the synthesis of sterically demanding silylenes (**2**) with a very similar binding motif to **1** by providing an intern donor-function.

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Nitrobindin: Evolution of a Protein-Host for Biohybrid Catalysts

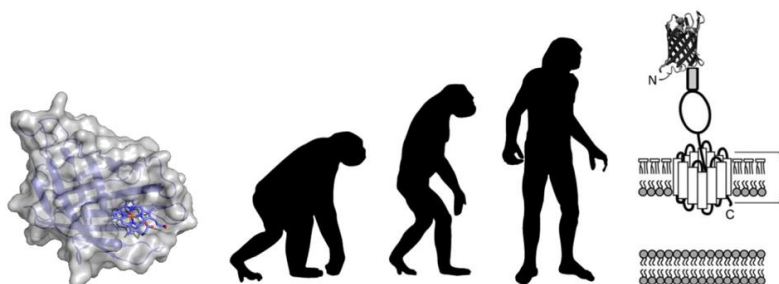
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The heme-containing protein nitrobindin was discovered in 2010.¹ Two years later, the heme-moiety was reconstituted with artificial metal cofactors to perform *cis*-selective polymerization of phenylacetylene^{2,3} and to evolve hydrogen.⁴ Furthermore, incorporation of a Grubbs-Hoveyda type complex to construct an artificial metathesis resulted in an unexpected highly active catalyst for the ring-opening metathesis polymerization (ROMP).⁵ This activity shows relation to the hydrophobic cavity structure that is provided by the protein nitrobindin.

In the recent work, we applied new strategies on the protein scaffold to generate a versatile platform for biohybrid catalyst design, either in solution or as diffusion-barrier free whole-cell systems.

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Ruthenium Catalyzed Hydroboration of Terminal Alkynes to Z-Vinylboronates

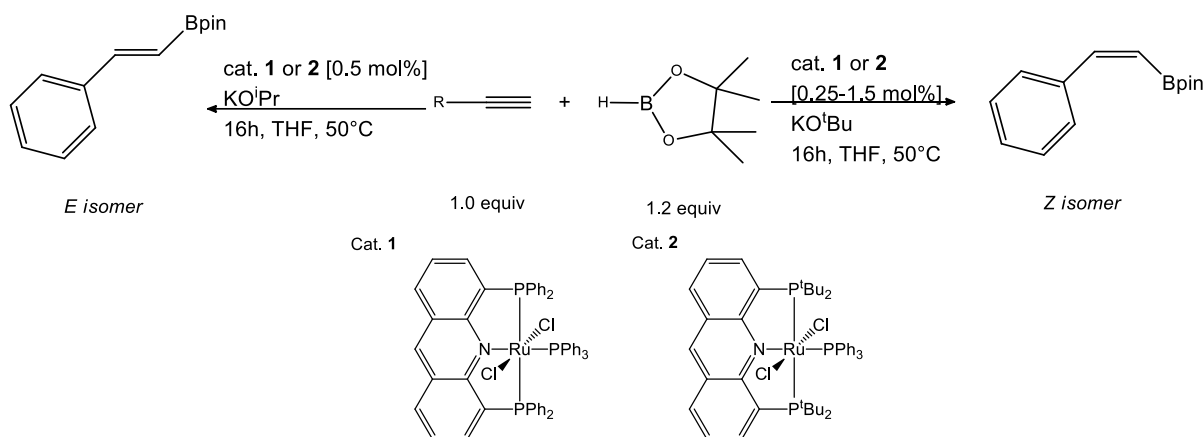
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Vinylboronate esters are versatile reagents in organic synthesis of organic compounds owing to their use as nucleophilic partners in C-C bond forming reactions.^{1,2} Hydroboration of terminal alkynes is a straightforward and atom economical method for the preparation of vinylboronate esters and commonly yields products with E stereochemistry via anti-Markovnikov and syn addition of the boron reagents.^{3,4}

We report the synthesis of Z-vinylboronates via a chemo- region- and stereoselective borylation of terminal alkynes with pinacolborane catalyzed by the ruthenium acriphos complex 1 (Scheme 1), which is active with base KOtBu. This selective hydroboration reaction proceeds for a broad scope of substrates under mild conditions. In addition, the regioselectivity of terminal alkyne hydroborations can be inverted from Z selectivity to E selectivity by changing the activator of catalysts 1 and 2 from KOtBu to KOiPr (Scheme 1).



Scheme 1. Ruthenium Catalyzed Hydroboration of Terminal Alkynes with Pinacolborane Using Catalyst 1 and 2.

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Poster Presentations

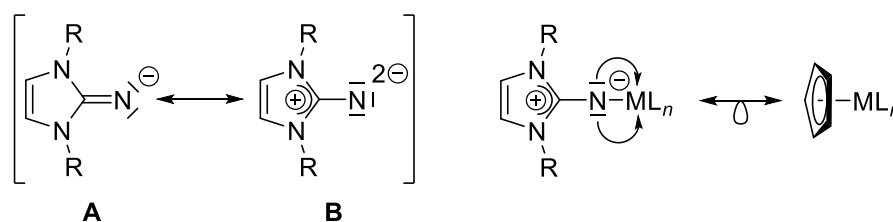
Pogo-Stick Complexes of Ruthenium

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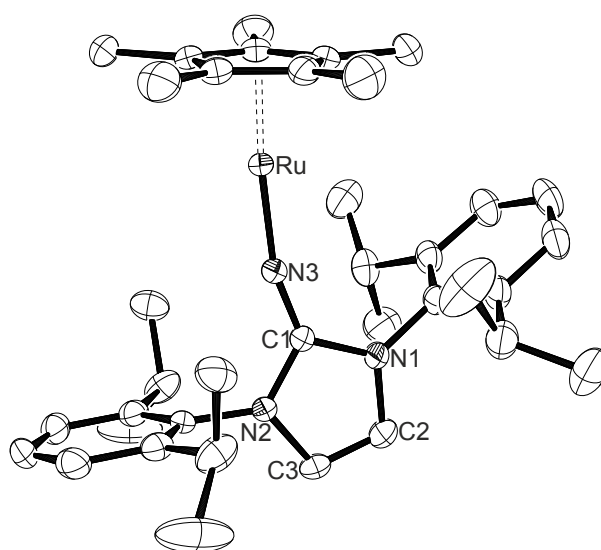
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Over the past ten years the coordination and main-group chemistry of imidazoline-2-iminato and imidazoline-2-imine ligands has been studied intensively.^[1] In these ligands the carbene moiety is capable to stabilize a positive charge, leading to highly basic ligands that can act as $2\sigma,4\pi$ -electron donors. They can be related to phosphoraneiminato ligands and therefore also be seen as monodentate analogues of the widely-used cyclopentadienyl ligand.



In this contribution, we report our latest results with these types of ligands in ruthenium chemistry leading to a rare class of metal complexes as well as other metal complexes exhibiting one-legged piano stool geometries around the metal center.



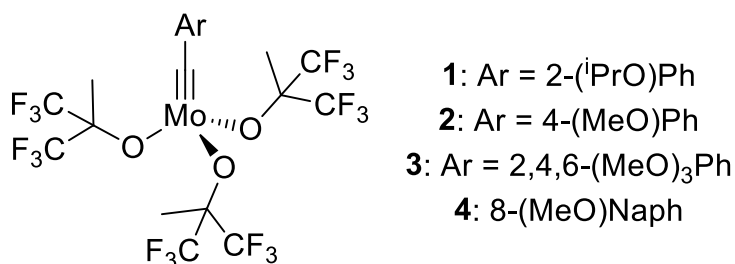
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Ether-functionalized Alkyne Metathesis Catalysts

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Alkyne metathesis – the catalytic formation and breaking of C–C triple bonds – has increasingly found applications in organic, polymer and supramolecular chemistry in the past decades.^[1,2] Although several alkydine complexes of Mo and W have been established as highly active catalysts for this reaction,^[1–3] the functional group tolerance and substrate scope differ from one catalyst to another. For example, terminal alkynes are particularly challenging substrates, but our group recently reported a catalyst that is able to promote terminal alkyne metathesis.^[4] On the other side, most of the catalysts are air-sensitive, which may be inconvenient regarding some applications.

Catalyst design is crucial in order to improve the robustness of the alkydine complexes. Our idea was to functionalise the alkydine moiety in order to favour inter- or intramolecular interactions, which potentially results in air-stable complexes. In this contribution, the introduction of an ether group at different positions of the aryl ring as in complexes **1–4** (see Scheme) will be discussed.

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Towards Supramolecular 10-Heterocorroles

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Supramolecular coordination cages bear new opportunities to influence catalytic processes by tailor-made and well-positioned functional elements within confined spaces. Such cage compounds have been proposed in the past as enzyme mimetics, and several examples for a successful implementation of supramolecular catalysts have been reported.^[1]

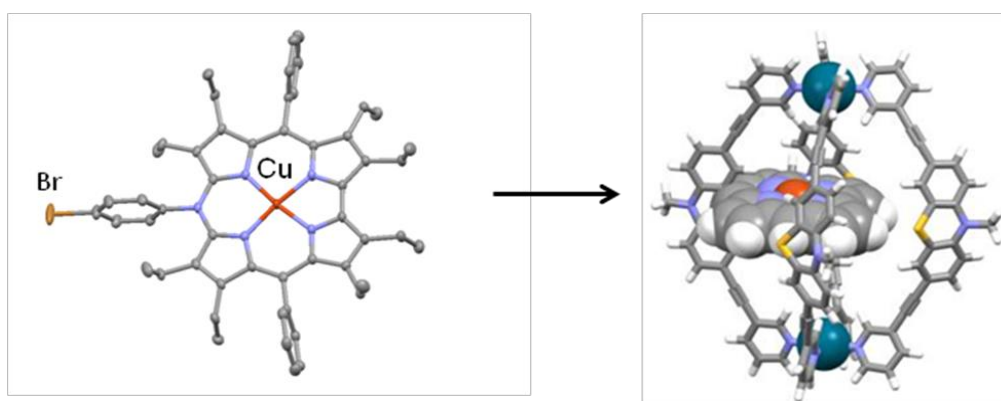


Fig.1. Coordination cage with metal corrole center, and strategic 10-azacorrole precursor.

In this project we aim towards encapsulated porphyrinoids as heme enzyme catalysts, in particular for oxygenation reactions.^[2] As part of a modular approach towards such functional porphyrinoid cages we have investigated the synthesis and coordination chemistry of 10-heterocorroles with and without an active periphery (Fig. 1). The poster will give an overview of the compounds that could be obtained so far along this path.

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Lewis-Acid Catalyzed Ring-Opening of Donor-Acceptor Cyclobutanes with Electron-Rich Arenes

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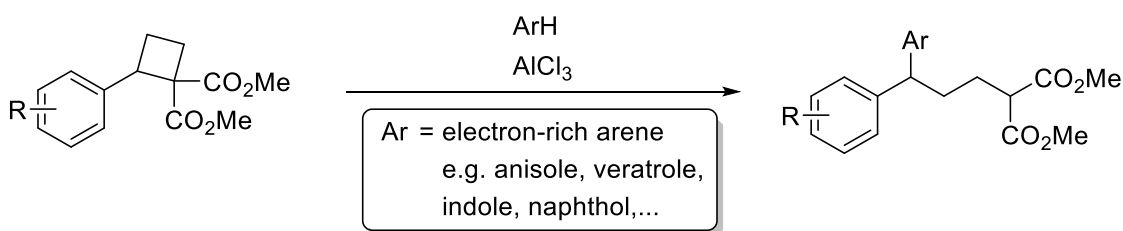


Fig. 1. Reaction of D-A cyclobutanes with electron-rich arenes.

Highly strained carbocycles have become an important tool for the effective construction of complex molecular scaffolds. In the last decade, donor-acceptor (D-A) cyclopropanes have turned into valuable building blocks in organic synthesis, whereas only limited examples for the corresponding reactions with analogous D-A cyclobutanes have been reported. The ring strain of these four-membered rings ($\sim 110 \text{ kJ}\cdot\text{mol}^{-1}$) is comparable to those of cyclopropanes ($\sim 115 \text{ kJ}\cdot\text{mol}^{-1}$), but is distributed among four carbon centers. Due to their substitution pattern D-A cyclobutanes have a strongly polarized C-C bond and are able to react with respect to their formal 1,4-zwitterionic character with various dipoles to generate (hetero)cyclic compounds.^[1,2]

In this study, we present a novel protocol for the nucleophilic ring opening of D-A cyclobutanes. The Lewis-acid catalyzed reaction of these highly strained four-membered rings with electron-rich arenes produces aryl-functionalized butane diesters under formation of a new C-C bond in good yields.^[3]

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Synthesis of Polypeptides with Phosphonate Side-chains using Transition Metal Complexes

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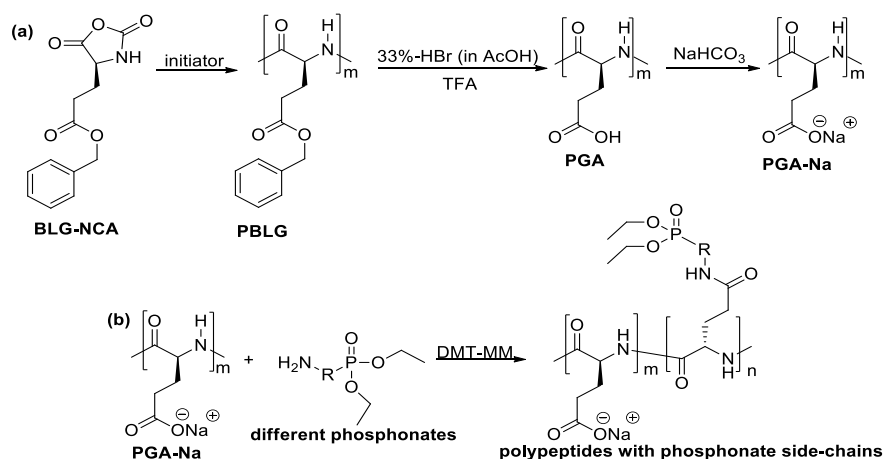


Fig. 1. (a) ring-opening polymerization of BLG-NCA and (b) amide coupling of different phosphonates to PGA-Na.

Phosphoproteins mediate different processes like protein-protein interactions, protein activation and inhibition as well as biomineralization.^[1] The synthesis of phosphoproteins is very complex; therefore artificial analogs such as polypeptides are an interesting approach to mimic the features of phosphor-proteins (e.g. secondary structures). Phosphonate-containing polypeptides can also be used as e.g. dental adhesives or adhesion promoters.^[2] Different catalytic systems are used for the synthesis of polypeptides e.g. amine initiators or transition metal complexes.^[3] The efficiency of these different initiators is compared for the living polymerization of benzyl-L-glutamic-N-carboxy anhydride (BLG-NCA). After deprotection, the resulting poly-L-glutamic acids can be modified with different phosphonate containing side chains via amide coupling with DMT-MM.^[4] (**Fig. 1**) In this way well defined phosphonate containing polypeptides with adjustable degree of polymerization and phosphonate group density are obtained. Polypeptides with different side-chains and phosphonate densities are characterized by CD-spectroscopy to determine changes in the secondary structure. Furthermore, polypeptides are coated on titanium substrates creating monolayer polymer films.

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A New Tyrosinase Model Complex: Activation of Dioxygen and Hydroxylation of Phenols

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Tyrosinase is important for melanin biosynthesis because the enzyme catalyses the oxygenation of L-tyrosine to L-DOPA and afterwards the subsequent dehydrogenation to L-dopaquinone. The catalytically active species is a $\mu\text{-}\eta^2\text{:}\eta^2\text{-dicopper(II)}$ core. Till now just a few catalytically active models are known.^[1,2] Bis(pyrazolyl)methane copper complexes mimic the catalytic active site of tyrosinase structurally and functionally.^[3-5] By adding oxygen the formation of the side-on bonded peroxy core can be monitored via UV/Vis spectroscopy (**Fig. 1**).

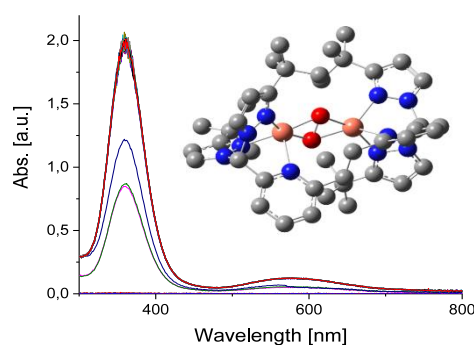


Fig. 1. UV/Vis spectra of the peroxy complex.

The designed peroxodicopper(II) complex with an ethylene bridged bis(pyrazolyl)(pyridinyl)-methane ligand shows catalytic activity towards phenolic substrates and is stable for several days at room temperature. We have also characterised this complex by ESI spectrometry.

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Triaminoguanidinium Based Ligands: Versatile Building Blocks in Supramolecular Chemistry

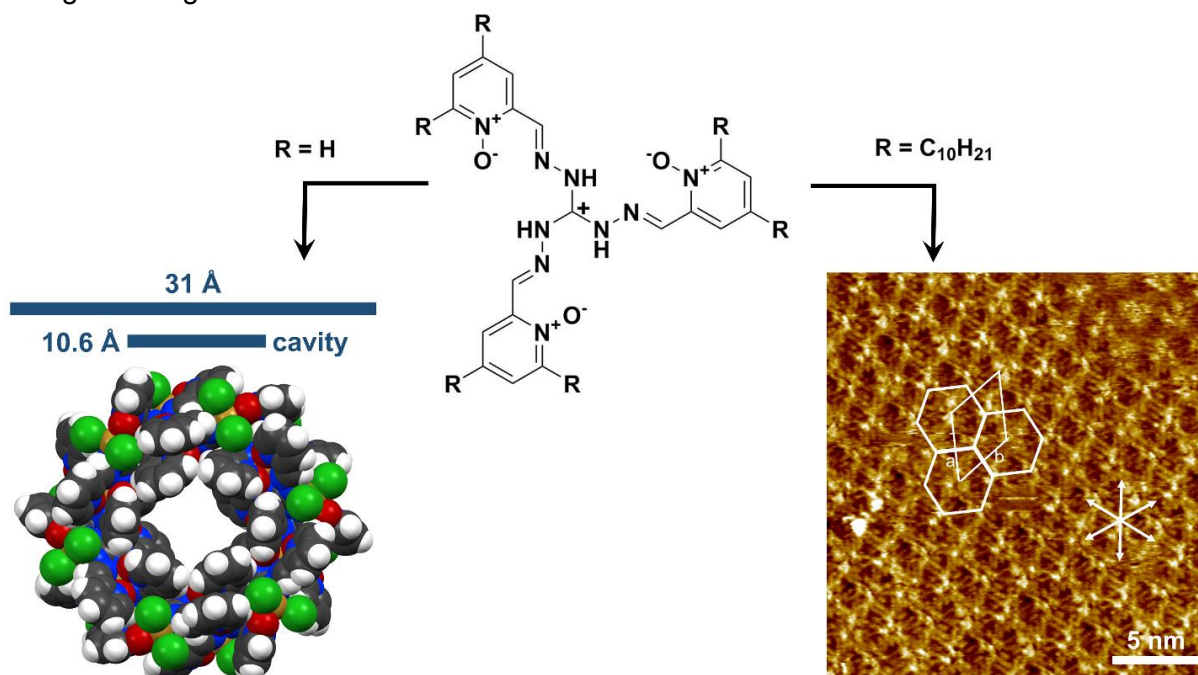
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C₃-symmetric triaminoguanidinium based ligands are able to coordinate soft metal ions like Zn(II), Cd(II) or Eu(III) as well as hard metal ions like Ti(IV) or Zr(IV) in their tridentate chelating binding pockets. As the combination of ligands and metal ions provide flexible coordination environments, a variety of different discrete supramolecular coordination cages, such as tetrahedra, octahedra and trigonal bipyramids, are accessible.^[1] Some of these compounds showed activity in ring opening polymerization of lactide. Two donut shaped coordination oligomers with a diameter of 31 Å will be presented. They exhibit spherical cavities of about 10.6 Å and could be utilized as selective reaction chambers or to crystallize small molecules. Attachment of long alkyl chains to the ligand leads to self-assembly in a positively charged hexagonal structure at the octanoic acid/HOPG interface.^{[2],[3]}



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Alkaline Earth Metal Complexes of Bis(Heterocyclo)-methanides for Small Molecule Activation

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Due to the easily modified electronic and steric properties of the NacNac ligand by simply varying the substituents at the imine moieties so far a bulk of differently substituted derivatives could be synthesized.^[1] In this context especially the Dipp (diisopropylphenyl) substituted NacNac derivative developed to one of the most studied ligand systems.^[2] The phenyl groups within this system display a nearly perpendicular orientation with respect to the residual imine ligand backbone offering a unique shielding towards a coordinated metal ion, thus avoiding oligomerization or electrophilic attacks.^[3] This rising interest has also initiated the research for other promising ligand platforms mimicking the chelating ability of the ubiquitous NacNac ligand. Examples of this development are the bis(2-pyridyl)methane ligand system and its N, P and As bridged derivatives bearing benzo-fused imine moieties.^[4] Our group was able to show that bis(benzoxazol-2-yl)- and bis(benzothiazol-2-yl)methanides work as versatile platforms for Group 1 and 13 metal complexes.^[5] This Chemistry could also be extended to the corresponding N bridged derivatives^[6] and most recently to benzimidazol- and asymmetric substituted bis(heterocyclo)methane species.^[7] This Chemistry is now also extended to bulkier methanide ligand systems and to the s-Block elements.

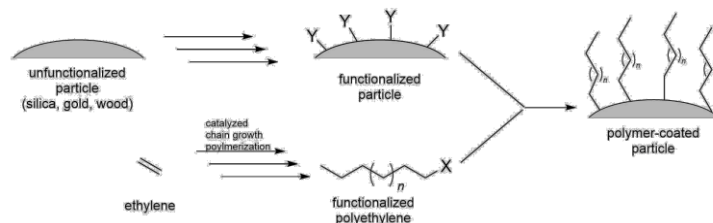
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Tuning Catalyzed Chain Growth Polymerization: Polyethylene Hybrid Materials and End-group Variability

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Scheme 2. Simplified synthetic route for particle functionalization in an arm-first approach.

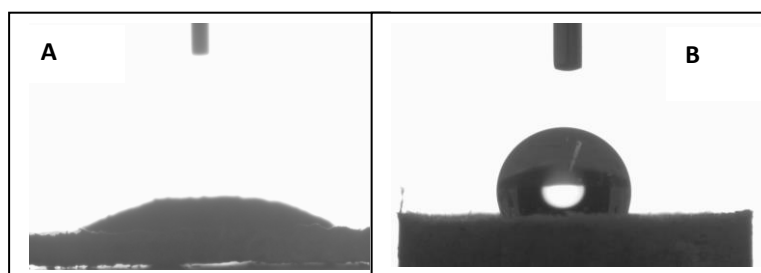


Fig. 1. Water contact angle measurement (degree of the surface-polarity) of **A:** unfunctionalized wood and **B:** polyethylene-coated wood.

Controlled polymerization techniques revolutionized modern polymer chemistry and offer many advantages compared to conventional polymerization systems. These techniques give access to properties as low dispersities, variable end-group functionalities, synthesis of block copolymers and defined macromolecular architectures with predictable and adjustable properties. One controlled polymerization technique suitable for the synthesis of polyethylene is catalyzed chain growth (CCG). CCG is based on a degenerative chain transfer polymerization mechanism including a main group organyl (organomagnesium compound) as a chain transfer agent and a transition metal catalyst ([Nd]).^[1,2] Within this work different types of (nano)particles (wood, gold, silica) were coated with functionalized polyethylene via diverse synthetic approaches. These hybrid materials were fully characterized with a multitude of methods (e.g. DLS, TEM, IR, NMR, TGA, contact angle). Additionally, the efficient functionalization of polyethylene with a charged end-group was performed. This gives an easy access to the characterization of polyethylene via mass spectrometry.

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Polymerisation and Co-polymerisation of Olefins Using Chromium and Titanium Phenoxy-Pyridine-type Catalysts

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Functionalised polymers obtained by co-polymerisation of polar monomers and olefins display excellent polymeric materials with different properties. Studies have shown that polar groups, such as methyl methacrylate, acrylates and vinyl acetate, play a crucial role in the copolymer and have influence on the polymer properties for example on the toughness, the adhesion, the surface properties and the solvent resistance. In recent years, catalysts for functionalized polyolefins have been studied intensively.^[1] Developments in this area have led to the design of catalysts with mostly late transition metals as metal centre since they are less oxophilic and more functional group tolerant than early transition metals. Several nickel catalysts show high activities in the co-polymerisation of methyl methacrylate and ethylene^{[2],[3],[4]} and only few examples use titanium metal ions with tridentate ligand systems.^{[5],[6]}

These results prompted us to develop tridentate ligand systems with an N,N,O-donor set bearing a phenoxy- or an anisole-, a pyridinyl- and a imidazolyl-unit. The ligands were utilised to synthesise the respective chromium and titanium complexes, which were then investigated upon their activity in ethylene and methyl methacrylate polymerisation and co-polymerisation.

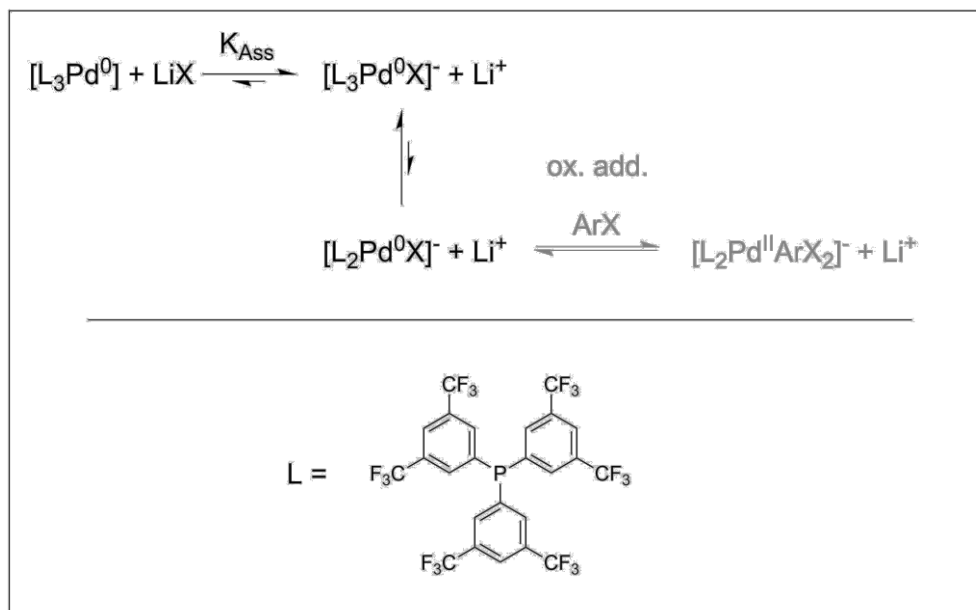
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Formation and Reactivity of Pd⁰ Ate Complexes

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Anionic palladium(0) complexes are often suggested to be important intermediates in palladium-catalyzed transformations, but have up to now been only scarcely characterized at the molecular level.^[1–3] Herein, we have examined the formation of anionic palladium(0) complexes from the electron-poor palladium catalyst $[L_3Pd]$ ($L = \text{tris}[3,5\text{-bis}(\text{trifluoromethyl})\text{-phenyl}]\text{phosphine}$) and a lithium salt LiX ($X = \text{Br}, \text{I}, \text{OAc}$) with a variety of analytical techniques, including electrospray-ionization mass spectrometry, electrical conductivity measurements, and ^{31}P NMR studies. It was shown that $[L_3Pd]$ readily reacts with the lithium salt to form $[L_3PdX]^-Li^+$, whereas more electron-rich ligands do not tend to be incorporated in anionic Pd^0 complexes. Furthermore, the addition of an aryl iodide ArI to the palladate complex resulted in the formation of $[L_2Pd(Ar)X]^-$ *via* oxidative addition.

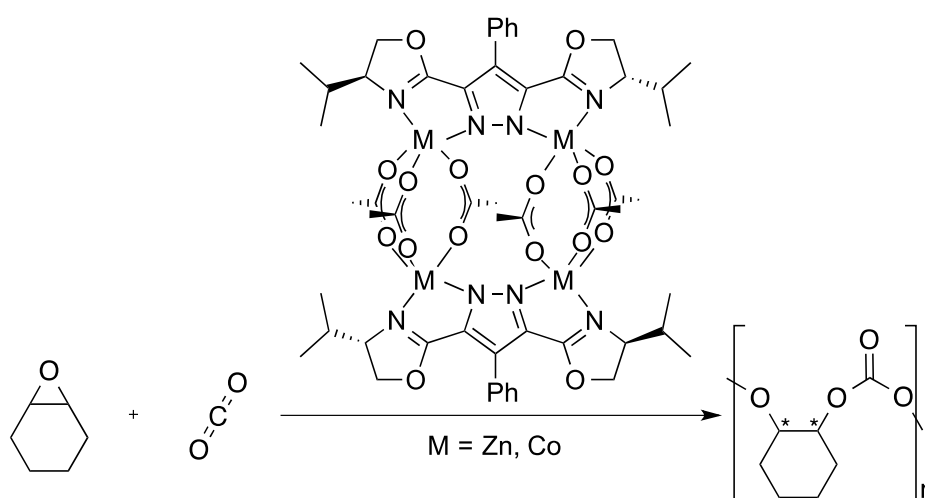
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Catalytic Cooperative Copolymerization of Epoxides with CO₂

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The necessity for sustainable polymers increases as the end of the fossil fuel feedstock approaches. Polycarbonates, prepared from epoxides with CO₂, provide 100% atom economics and qualify as Green Polymers, allowing the use of the industrial waste product CO₂ as a C1 feedstock. In the poly (cyclohexane carbonate) (PCHC) depicted above, 31% of the weight is contributed by CO₂.^[1]

The C₂-symmetric pyrazolate-bridged bis(oxazoline) complexes here presented copolymerize cyclohexene oxide with CO₂. Moreover, the complexes address the important correlation of microstructure and material properties by transferring their stereochemical information to the polymer. Thus, up to 66% of *m*-centered tetrads can be observed in the formed PCHC.^[2]

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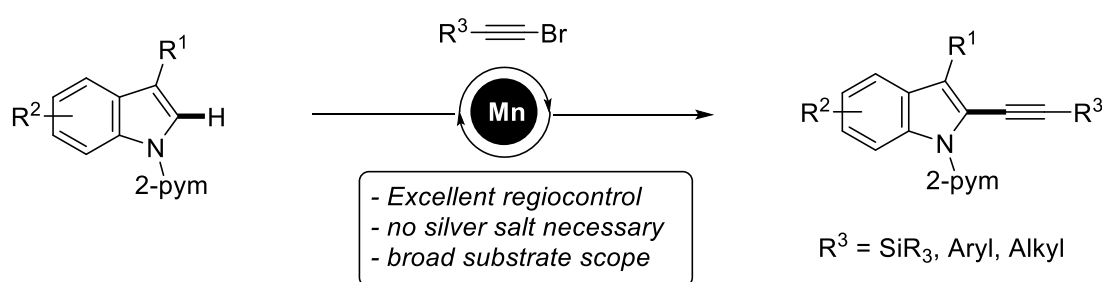
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Direct Alkynylation of Heteroarenes by Base-Metal Catalyzed C–H Activation

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Base metal-catalyzed C–H activation represents a powerful alternative to the use of precious and rare 4d and 5d transition metals in the synthesis of biologically relevant compounds.^[1] In recent years, cobalt,^[2] manganese^[3] and iron^[4] catalysts emerged, among others, as versatile alternatives to noble metal catalysts. Indoles and pyrroles are among the most abundant structural motifs in bioactive molecules and represent key scaffolds in crop protection and pharmaceutical chemistry.^[5]

Herein, we report on two distinct protocols for cobalt-^[6] and manganese-catalyzed^[7] C–H alkynylations of heteroarenes. Notable features of the cobalt-catalyzed reaction are (i) exceedingly mild reaction conditions, (ii) excellent regioselectivity and (iii) good functional group tolerance. The manganese-catalyzed reaction provides two outstanding advantages, On the one hand no costly silver salts are necessary, on the other the addition of Lewis-acidic BPh₃ as a cocatalyst enabled the utilization of aryl and alkyl substituted.

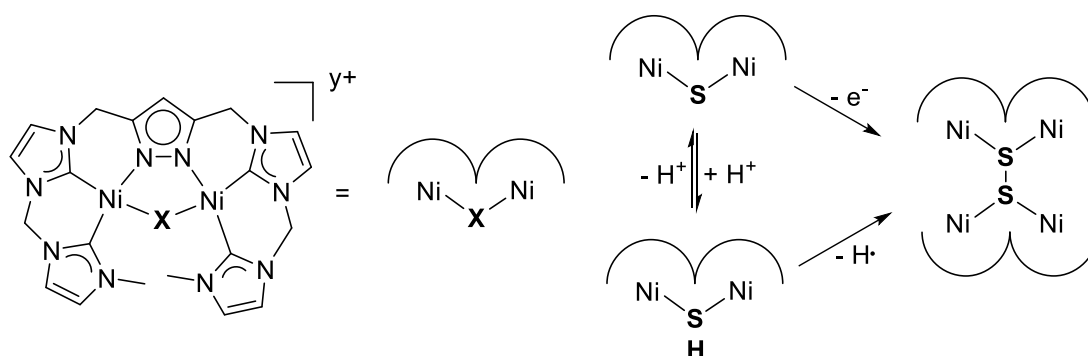
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Hydrosulfido, Sulfido and Persulfido Interconversions at a Preorganized Dinickel Site

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Cooperative effects in di- and multinuclear metal systems play a key role in many enzymatic reactions.^[1] Such cooperative effects can lead to more efficient and selective transformations, conformational control of substrates, higher local reagent concentration at the metal centers and stabilization of reactive species and complex intermediates.^[2] The combination of nickel and S-based ligands is of particular current interest, due to its relevance in various biological systems.^[3]

We have been working on the development of highly preorganized dinuclear metal complexes of metal···metal-bridging compartmental pyrazolate ligands, many of which mediate the bioinspired transformation of small substrates.^[4,5] Here we present a series of hydrosulfido, sulfido and persulfido nickel(II) complexes based on a new compartmental pyrazolate/NHC hybrid ligand.

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