Catalysis for Sustainable Synthesis

Technische Universität Braunschweig

CASUS

4. Niedersächsisches

Katalyse-Symposium

(Lower Saxonian Catalysis Symposium)

**TU Braunschweig
September 19-20, 2016**

NIKAS
2016

Supporters

The 4. Niedersächsisches Katalyse-Symposium would not be possible without the generous support of the following companies and organizations. We are grateful to:

Organizing Committee

Òscar Àrias

Marius Peters

Elena Bothe

Vitali Kuhn

Alexander Kreft

Andreea Enachi

Sabrina Tröndle

Dr. Thomas Bannenberg

Prof. Dr. Matthias Tamm

Preface

Dear Participants,

I warmly welcome you to the *4. Niedersächsisches Katalyse-Symposium* (NiKaS) at the Technische Universität Carolo-Wilhelmina zu Braunschweig, the oldest university of technology in Germany.

This symposium is part of the international Ph.D. program *Catalysis for Sustainable Synthesis* (CaSuS), which originally started in October 2009 at the University of Göttingen and was funded until September 2013 by the Ministry for Science and Culture of the federal state Lower Saxony. A second funding period now involving nine research groups from the University of Göttingen and six research groups from the Technische Universität Braunschweig was approved in October 2014.

In continuation of a series of three successful meetings between 2010 and 2014, the *4th Lower Saxonian Catalysis Symposium* has brought together 11 renowned international experts in various fields of catalysis, who will share their latest scientific results with an audience of primarily young scientist – Ph.D. students, postdoctoral fellows and young faculty members. The scholars of the CaSuS program together with other Ph.D. students from Braunschweig, Göttingen and abroad will present their own scientific results during a poster session, which will be organized at the conference banquet in the Old City Hall, one of the most representative locations the city has to offer.

As dean of the Faculty of Life Science, it is my pleasure to declare the *4th Lower Saxonian Catalysis Symposium 2016* open, and I wish us all two days full of inspiring lectures, exciting posters and valuable discussions!

Matthias Tamm

Previous Meetings

1st **Niedersächsisches Katalyse-Symposium**

Georg-August-Universität Göttingen
Faculty of Chemistry
21st and 22nd October 2010

2nd **Niedersächsisches Katalyse-Symposium**

Georg-August-Universität Göttingen
Faculty of Chemistry
18th and 19th October 2012

3rd **Niedersächsisches Katalyse-Symposium**

Georg-August-Universität Göttingen
Faculty of Chemistry
16th and 17th October 2014

Scientific Program

Monday, September 19

11:00–13:00	**Arrival and Reception**
13:00–13:15	**Welcome/Introduction (Prof. Dr. Matthias Tamm)**

<div align="right">Session 1
Chair: Elena Bothe</div>

13:15–14:00	**Prof. Dr. Suzanne A. Blum** (University of California, Irvine, USA) *"Microscopy for Synthetic Chemists"*	**I1**
14:00–14:45	**Prof. Dr. Burkhard König** (University of Regensburg, Germany) *"Making and Breaking Chemical Bonds with Visible Light Photocatalysis"*	**I2**

14:45	**Foto**
15:00–15:30	**Coffee Break**

<div align="right">Session 2
Chair: Andreea Enachi</div>

15:30–16:15	**Prof. Dr. Pedro J. Pérez** (University of Huelva, Spain) *"Development of Catalysts for Methane Functionalization"*	**I3**
16:15–17:00	**Prof. Dr. Regina Palkovits** (RWTH Aachen University, Germany) *"Biorefineries – a Challenge for Catalyst and Process Design"*	**I4**
17:00–17:45	**Prof.Dr. Kálmán J. Szabó** (Stockholm University, Sweden) *"Catalytic Fluorination Methods with New Reagents"*	**I5**
19:00	**Poster Session** **Old City Hall (Dornse) – Conference Dinner**

Tuesday, September 20

|		
	Session 3 **Chair: Sabrina Tröndle**	
08:45–09:30	**Dr. Thomas Schaub** (University of Heidelberg & BASF SE, Germany) *"Innovation in Homogeneous Catalyzed Processes"*	I6
09:30–10:15	**Prof. Dr. Sylviane Sabo-Etienne** (University of Toulouse, France) *"Mechanistic Studies on Polyhydride-Catalyzed Transformations"*	I7
10:15–10:45	**Coffee Break**	
	Session 4 **Chair: Marius Peters**	
10:45–11:30	**Prof. Dr. Moris S. Eisen** (Technion-Israel Institute of Technology, Israel) *"Designing Group 4 Complexes for the Polymerization and Copolymerization of Olefins"*	I8
11:30–12:15	**Prof. Dr. Lutz Gade** (University of Heidelberg, Germany) *"Enantioselective Catalysis with 3d Transition Metal Complexes: Chiral Pincers as Stereodirecting Ligands"*	I9
12:15–13:15	**Lunch**	
	Session 5 **Chair: Alexander Kreft**	
13:15–14:00	**Prof. Dr. Shigeki Matsunaga** (Hokkaido University, Japan) (GDCh lecture) *"Cationic Cp*Co(III) Catalysis for C-H Bond Functionalization"*	I10
14:00–14:45	**Prof.Dr. Michael L. Neidig** (University of Rochester, USA) *"Structure, Bonding and Mechanism in Iron-Catalyzed Cross-Coupling"*	I11
14:45	**Closing Remarks**	
15:00	**Departure**	

Invited Speakers

Notes

Microscopy for Synthetic Chemists

<u>Suzanne A. Blum</u>*

University of California, Irvine, Department of Chemistry, Irvine CA, 92697-2025, USA

email: <u>blums@uci.edu</u>
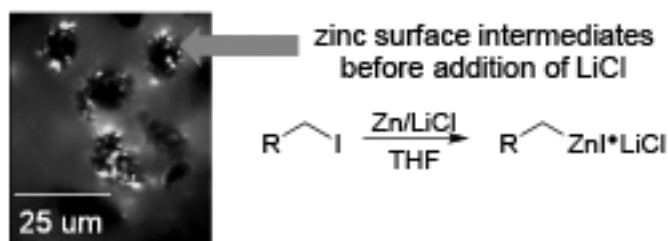
The sensitivity provided by fluorescence microscopy enabled the observation of surface intermediates in the synthesis of soluble organozinc reagents by direct insertion of alkyl iodides to commercial zinc powder. This technique was employed to determine the role of lithium chloride in generating soluble organozinc reagents. Five hypotheses for the mechanistic role of lithium chloride in enabling this direct insertion were examined. We herein describe fluorescence microscopy experiments with sensitivity as high as up to single-molecules that rule out some mechanistic possibilities and rationalize why the synthetic system optimized to LiCl rather than a different salt. It is anticipated that this improved understanding of the mechanistic basis for the effect will facilitate the future development of currently unknown organometallic reagents by direct insertion into presently recalcitrant metals. The data is consistent with lithium chloride solubilizing organozinc reagents from the surface of the zinc after direct insertion. These studies bring mechanistic understanding to an area of chemistry that is currently progressing empirically.
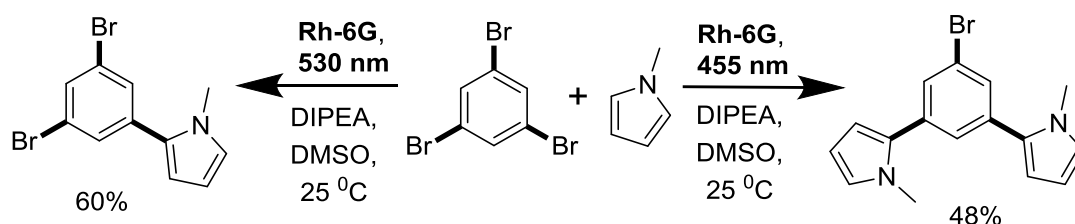
Notes

Making and Breaking Chemical Bonds with Visible Light Photocatalysis

Burkhard König*

University of Regensburg, Faculty of Chemistry and Pharmacy, Universitätsstrasse 31, 93053 Regensburg, Germany

email: burkhard.koenig@ur.de

Light is a fascinating reagent for chemistry as it provides energy to drive reactions, but leaves no trace. In visible light photoredox catalysis[1] colored redox active dyes, such as ruthenium(trisbipyridine),[2] eosin Y[3] or rhodamine 6G,[4] convert the absorbed light into redox energy allowing photo-induced electron transfer reactions. We discuss recent examples using the method for metal free cross-coupling reactions[5,6] in organic synthesis and the late stage functionalization of complex molecules.[7]

[1]   B. König, B., *Chemical Photocatalysis*, De Gruyter, **2013**.
[2]   D. Ravelli, S. Protti, M. Fagnoni, *Chem. Rev.* **2016**,
       DOI: 10.1021/acs.chemrev.5b00662.
[3]   D. P. Hari, B. König, *Chem. Commun.* **2014**, *50*, 6688.
[4]   I. Ghosh, B. König, *Angew. Chem. Int. Ed.* **2016**, *55*, 7676.
[5]   I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* **2014**, *346*, 725.
[6]   I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, *Acc. Chem. Res.* **2016**, *49*, 1566.
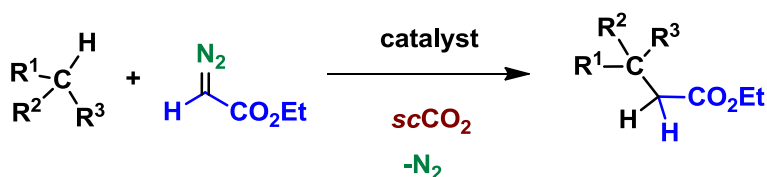[7]   E. Brachet, T. Ghosh, I. Ghosh, B. König, *Chem. Sci.* **2015**, *6*, 987.

Notes

Development of Catalysts for Methane Functionalization

Pedro J. Pérez *

Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21007 Huelva, Spain

email: perez@dqcm.uhu.es

The development of practical catalytic systems that would employ methane as C1-source for synthetic purposes yet constitutes one of the challenges of modern chemistry [1]. Only a few systems have been described with soluble catalyst toward that end, albeit to date none of them find practical application. In the search for novel reaction pathways using methane and other light alkanes as starting materials, we have developed [2] a family of catalysts that promote the functionalization of the C-H bonds of such hydrocarbons by means of a carbene insertion reaction induced by a metal center. Diazo compounds are employed as the carbene source. In this contribution, the development of such catalytic systems along the years until such goal was achieved will be presented.

[1] (a) V. N. Cavaliere, B. F. Wicker, D. J. Mindiola, *Adv. Organomet. Chem.***2012**, *60*, 1−47. (b) A. Caballero, P. J. Pérez, *Chem. Soc. Rev.* **2013**, **42**, 8809-8820.

[2](a) A. Caballero, E.Despagnet-Ayoub, M. M. Díaz-Requejo, A. Díaz-Rodríguez, M. E: González-Núñez, R. Mello, B. K. Muñoz, W. Solo-Ojo, G. Asensio, M. Etienne, P. J. Pérez, *Science***2011**, *332*, 835-838. (b) M. A. Fuentes, A. Olmos, B. K. Muñoz, M. E. González-Núñez, R. Mello, G. Asensio, A. Caballero, M. Etienne, P. J. Pérez, *Chem. Eur. J.* **2014**, *20,* 11013-11018.
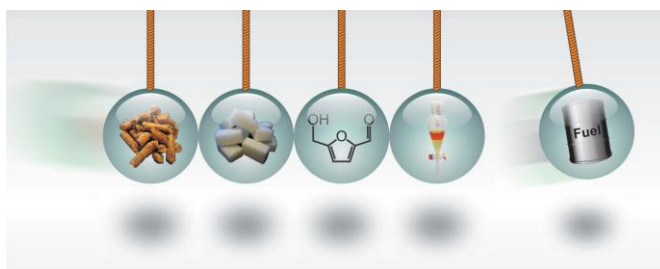
Notes

Biorefineries – a Challenge for Catalyst and Process Design

Regina Palkovits*

RWTH Aachen University, Institut für Technische und Makromolekulare Chemie, Chair of Heterogeneous Catalysis & Chemical Technology, Worringerweg 2, 52074 Aachen, Germany

email: palkovits@itmc.rwth-aachen.de

Reproduced from Ref. 1 with permission from the Royal Society of Chemistry

Lignocellulose presents a sustainable and abundant carbon source for the production of fuels and chemicals. In recent years, research focused on a tailored valorisation of cellulose and hemicellulose – major components of lignocellulose.[1]

Despite intense research, efficient catalytic transformations in aqueous phase as well as a separation of highly polar platform molecules from aqueous phase remain challenging.[2,3] Major challenges comprehend a selective depolymerisation and deoxygenation of the oxygen-rich feedstocks aiming for novel monomers as well as potential biofuel candidates. Herein, research challenges along the value-chain of a potential chemo-catalytic biorefinery will be highlighted based on selected examples including promising platform chemicals such as 5-hydroxymethylfurfural, levulinic and formic acid as well as sorbitol. Aspects of catalyst development for water as solvent, an energy-efficient product separation and the design of suitable reaction pathways for integrated biorefineries will be discussed.

References

[1] I. Delidovich, K. Leonhard, RP, *Energy Environ. Sci.* **2014**, 7, 2803

[2] C. Detoni, C. Gierlich, M. Rose, RP, *ACS Sustain. Chem. Eng.* **2014**, 2, 10, 2407

[3] P. Hausoul, C. Broicher, R. Vegliante, C. Göb, RP, *Angew. Chem. Int. Ed.* 55 (**2016**) 5597
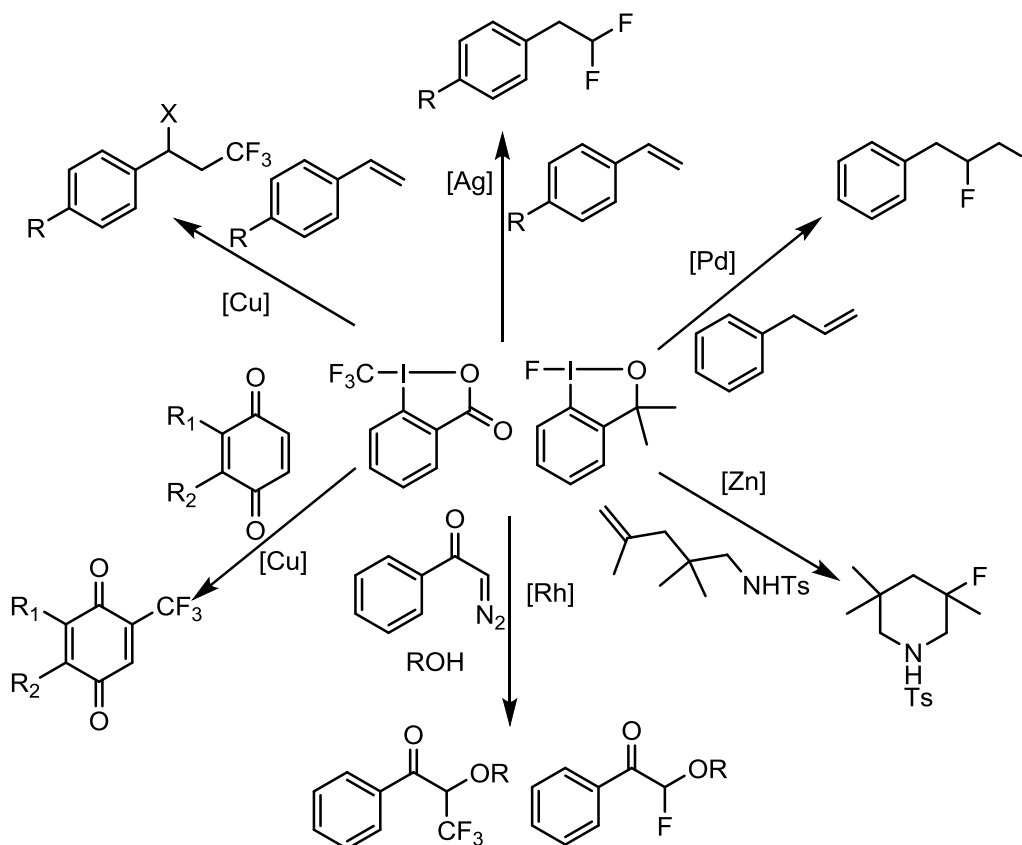
Notes

Catalytic Fluorination Methods with New Reagents

Kálmán J. Szabó*

Department of Organic Chemistry, Stockholm University, Sweden

email: kalman.j.szabo@su.se

Various fluorination and trifluoromethylation reactions were developed using fluoro and trifluoromethyl benziodoxol(on) reagents. The reactions involve, fluorination[1-4] and trifluoromethylation[5-7] based disubstitutions,[1,3-6] cyclization[2] and other[7] reactions. The hypervalent iodine reagents were activated by various metal (Pd, Rh, Zn, Cu, Ag) salts.

[1] N. O. Ilchenko, B. O. A. Tasch, K. J. Szabó, *Angew. Chem. Int. Ed.* **2014**, *53*, 12897.
[2] W. Yuan, K. J. Szabó, *Angew. Chem. Int. Ed.* **2015**, *54*, 8533.
[3] W. Yuan, L. Eriksson, K. J. Szabó, *Angew. Chem. Int. Ed.* **2016**, *55*, 8410.
[4] N. O. Ilchenko, M. A. Cortés, K. J. Szabo, *ACS Catal.* **2016**, *6*, 447.
[5] P. G. Janson, I. Ghoneim, N. O. Ilchenko, K. J. Szabó, *Org. Lett.* **2012**, *14*, 2882.
[6] N. O. Ilchenko, P. G. Janson, K. J. Szabo, *J. Org. Chem.* **2013**, *78*, 11087.
[7] N. O. Ilchenko, P. G. Janson, K. J. Szabó, *Chem. Commun.* **2013**, *49*, 6614.
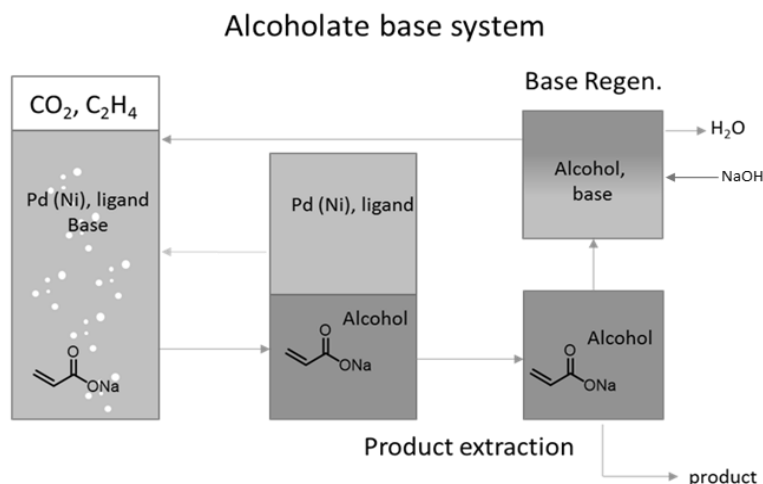
Notes

Innovation in Homogeneous Catalyzed Processes

Thomas Schaub*

Lab Head CaRLa; Catalysis Research Laboratory (CaRLa) Heidelberg & Synthesis and Homogeneous Catalysis (GCS/H), BASF SE, Ludwigshafen, Germany

email: thomas.schaub@basf.com

New Homogenous Catalyzed Process Concept for the Synthesis of Sodium Acrylate from CO_2 and Ethylene

Homogeneous catalysis has a long tradition at BASF and is used in a broad range of applications. Our view of this area will be discussed using the new menthol process and the current research project towards sodium acrylate based on CO_2 as examples. The pipeline from early stage to production, the motivation for projects and the approaches used in process development will be highlighted.

[1] N. Huguet, I. Jevtovikj, A. Gordillo, M. Lejkowski, R. Lindner, M. Bru, A.Y. Khalimon, F. Rominger, S.A. Schunk, P. Hofmann, M. Limbach, *Chem. Eur. J.* **2014**, *20*, 16858-16862.

[2] I. Jevtovikj, S. Manzini, M. Hanauer, F. Rominger, T. Schaub, *Dalton Trans.* **2015**, *44*, 11083-11094

[3] S.C.E. Stieber, N. Huguet, T. Kageyama, I. Jevtovikj, P.I Ariyananda, A. Gordillo, S.A. Schunk, F. Rominger, P. Hofmann, M. Limbach, *Chem. Commun.* **2015**, *51*, 10907-10909.

[4] S. Manzini, N. Huguet, O. Trapp, T. Schaub, *Eur. J. Org. Chem.* **2015**, *32,* 7122-7130.

[5] S. Manzini, N. Huguet, O. Trapp, R. Paciello, T. Schaub, *Catal. Today* **2016**, DOI: 10.1016/j.cattod.2016.03.025

Notes

Mechanistic Studies

on Polyhydride-Catalyzed Transformations

Sylviane Sabo-Etienne*

Laboratoire de Chimie de Coordination du CNRS (LCC-CNRS), University of Toulouse, 205 route de Narbonne, BP 44099, 31077 Toulouse Cedex 4, FRANCE

email: sylviane.sabo@lcc-toulouse.fr

Polyhydride ruthenium complexes, and particularly those incorporating one or two dihydrogen ligands, are attractive species. The dihydrogen ligand is labile or/and prepares the metal center for hydrogen transfer processes.[1] Activation and functionalization of small molecules are highly desirable as broad applications in the fields of catalysis and energy are expected. Selected recent examples from our group will be detailed with a special focus on mechanistic issues dealing with some important catalytic transformations such as hydrogenation/dehydrogenation reactions, isotopic labeling and CO_2 functionalization.

[1] *a)* Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.,* **2007,** *46*, 2578-2592. *b)* Alcaraz, G.; Grellier, M.; Sabo-Etienne, S. *Acc. Chem. Res.* **2009**, *42*, 1640-1649. *c)* Alcaraz, G.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 7170-7179. *d)* Grellier, M.; Sabo-Etienne, S. *Chem. Commun,* **2012,** *48*, 34-42. *b)* Grellier, M.; Sabo-Etienne, S. *Dalton Trans.* **2014**, *43*, 6283-6286.
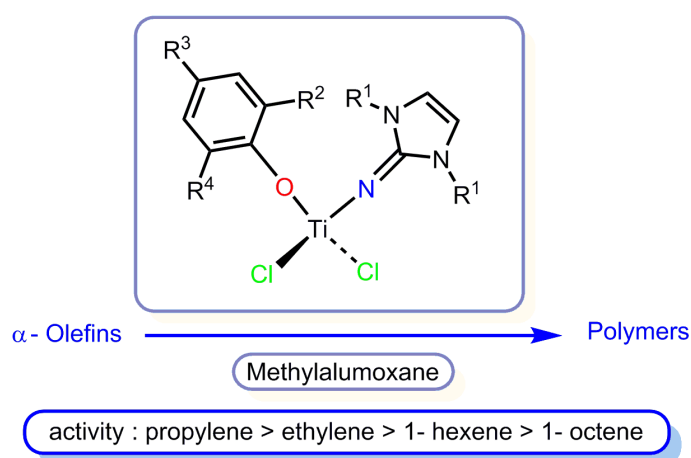
Notes

DESIGNING GROUP 4 COMPLEXES for the POLYMERIZATION and COPOLYMERIZATION of OLEFINS

Moris S. Eisen*

Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Kyriat Hatechnion, Haifa, 32000, Israel

email: chmoris@technion.ac.il

During the last decades an enormous advancement has been made in the design and synthesis of "well-defined' or "single-site" catalysts for the polymerization of olefins. The majority of these catalysts belong to the metallocene ensemble, although some are known that contains one cyclopentadienyl ring and (for example) a pendant amido ligand. Complexes containing many other functionalities including chelating diamido or chelating benzamidinate ancillary ligands have received attention as potential Ziegler-Natta catalysts.

We have investigated the α-olefin polymerization chemistry catalyzed by several group 4 bis(benzamidinate) complexes. We have shown that we are able to tune the stereoregularity of various polymers just by changing the monomer concentration during the polymerization to obtain elastomers. In addition, we will show unique imidazoline-2-iminato complexes allowing to reduce the amount of the cocatalyst (MAO = methylalumoxane) to impressive values. The presentation will also show recent results with new systems. [1]

[1] D. Shoken, L. J. W. Shimon, M. Tamm, M. S. Eisen, *Organometallics* **2016**, *35,* 1125−1131.

Notes

Enantioselective Catalysis with 3d Transition Metal Complexes: Chiral Pincers as Stereodirecting Ligands

Lutz H. Gade*

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg

email: lutz.gade@uni-heidelberg.de

Meridionally coordinating chiral tridentate ligands, frequently referred to as "pincers", provide the structural platform for the construction of efficient stereodirecting molecular environments. Whilst many of the known chiral systems of the "pincer" type perform relatively poorly in enantioselective catalysis due to certain lack of control of substrate orientation, their assembly from rigid heterocyclic units recently has given rise to several highly enantioselective catalysts which have been proven to be efficient in a variety of applications in organic synthesis.

Recently, we developed bis(oxazolinylmethylidene)isoindoline ("Boxmi") ligands which have been used in a variety of enantioselective transformations including alkylations of β-ketoesters and their subsequent cyclization to spirolactones, as well as the trifluoromethylation, trifluoromethylthiolation and azidation of β-ketoesters as well as oxindoles. The proved equally efficient in the enantioselective Ni-catalyzed hydrodehalogenation of prochiral geminal dihalides and their iron(II) complexes match the activity and selectivity of the most efficient noble metal catalysts for the hydrosilylation of ketones.

The focus of the lecture will be the elucidation of the catalytic reaction mechanisms and the identification and characterization of the (frequently) paramagnetic species involved.

Selected references: B. K. Langlotz, H. Wadepohl, L. H. Gade, *Angew. Chem. Int. Ed.* **2008**, *47*, 4670; Q.-H. Deng, H. Wadepohl, Lutz H. Gade, *Chem. Eur. J.* **2011**, *17*, 14922; Q.-H. Deng, H. Wadepohl, L. H. Gade, *J. Am. Chem. Soc.* **2012**, *134*, 2946; Q.-H. Deng, H. Wadepohl, L. H. Gade, *J. Am. Chem. Soc.* **2012**, *134*, 10769; Q.-H. Deng, T. Bleith, H. Wadepohl, L. H. Gade, *J. Am. Chem. Soc.* **2013**, *135*, 5356; C. Rettenmeier, H. Wadepohl, L. H. Gade, *Chem. Eur. J.* **2014**, *20*, 9657; C. A. Rettenmeier, H. Wadepohl, L. H. Gade, *Angew. Chem. Int. Ed.* **2015**, *54*, 4880; T. Bleith, H. Wadepohl, L. H. Gade, *J. Am. Chem. Soc.* **2015**, *137*, 2456; C. A. Rettenmeier, H. Wadepohl, L. H. Gade, *Chem. Sci.* **2016,** *7,* 3533; T. Bleith, L. H. Gade, *J. Am. Chem. Soc.* **2016,** 138, 4972; T. Bleith, Q.-H. Deng, H. Wadepohl, L. H. Gade, *Angew. Chem. Int. Ed.* **2016**, *55*, 7852.
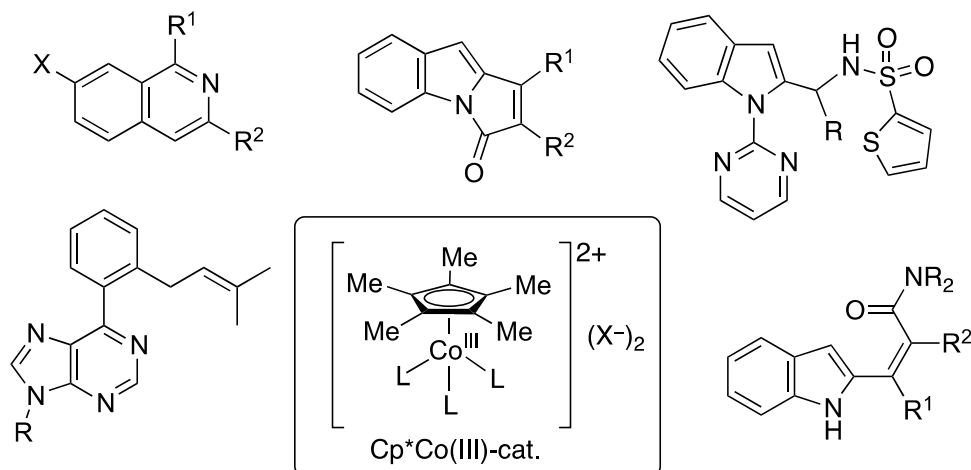
Notes

Cationic Cp*Co(III)-Catalysis
for C-H Bond Functionalization

Shigeki Matsunaga*

Hokkaido University, Faculty of Pharmaceutical Sciences, Sapporo, Japan

email: smatsuna@pharm.hokuda.ac.jp

Our group is interested in the development of atom-efficient catalytic organic transformation. Towards this goal, we have developed several bifunctional asymmetric catalysts, which promoted variety of carbon-carbon bond forming reactions via simple proton transfer process.[1] To further broaden our research concept onto C-H activation chemistry, we recently initiated a new research program on cationic high valentCp*Co(III) catalysis,[2] which are now actively studied by many chemists in the world.[3]In this lecture, the unique catalytic activity of Cp*Co(III) in comparison with related Cp*Rh(III) will be presented in detail. High nucleophilicity of organo-Co(III) species was important in one-pot pyrroloindolone synthesis,[4a] while highly oxophilic property of Co(III) center played a key role in dehydrative C-H allylation using free allylic alcohols.[4b,d] Highly site selective C-H bond functionalization was also achieved based on the small ionic size of Co(III) in comparison with Rh(III).[4c]

[1] Account: S. Matsunaga, M. Shibasaki, *Chem. Commun.***2014**, *50*, 1044.
[2] T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, M. *Angew.Chem. Int. Ed.***2013**, *52*, 2207.
[3] Review: M. Moselage, J. Li, L. Ackermann, *ACSCatal.***2016**, *6,* 498.
[4] a) H. Ikemoto, T. Yoshino, K. Sakata, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.***2014**, *136*, 5424. b)Y. Suzuki, B. Sun, K. Sakata, T. Yoshino, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.***2015**, *54*, 9944. c) B. Sun, T. Yoshino, M. Kanai, S. Matsunaga, *Angew. Chem. Int. Ed.***2015**, *54*, 12968. d) Y. Bunno, N. Murakami, Y. Suzuki, M. Kanai, T. Yoshino, S. Matsunaga, *Org. Lett.***2016**, *18*, 2216.
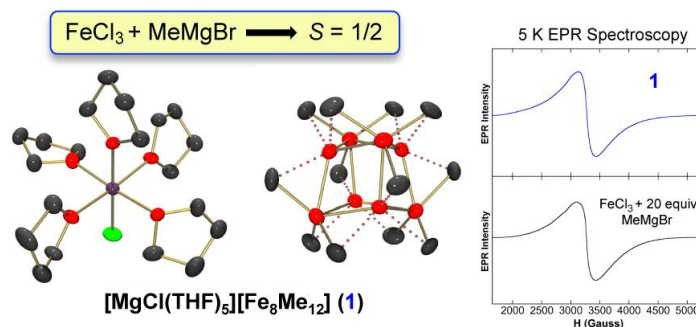
Notes

Structure, Bonding and Mechanism in Iron-Catalyzed Cross-Coupling

Michael L. Neidig*

University of Rochester, Department of Chemistry, Rochester, New York, USA

email: neidig@chem.rochester.edu

$FeCl_3 + MeMgBr \longrightarrow S = 1/2$

$[MgCl(THF)_5][Fe_8Me_{12}]$ (1)

5 K EPR Spectroscopy

$FeCl_3$ + 20 equiv MeMgBr

Despite the success of iron-based catalysts for cross-coupling, a detailed molecular level understanding of these systems has remained elusive. This limitation is in stark contrast to palladium chemistry, where detailed studies of active catalyst structure and mechanism have provided the foundation for the continued design and development of catalysts with novel and/or improved catalytic performance. The use of an experimental approach combining advanced inorganic spectroscopies (Mössbauer, magnetic circular dichroism, electron paramagnetic resonance), density functional theory studies, synthesis and kinetic analyses enables the direct evaluation of the active iron species and insight into the mechanisms of catalysis in iron cross-coupling. Previous studies from our group using this approach have established the active iron species in iron-bisphosphine catalysed cross-coupling of mesityl Grignard and primary alkyl halides[1] as well as phenyl nucleophiles and secondary alkyl halides.[2] Of particular interest are iron-catalyzed cross-couplings with simple ferric salts where we have previously reported the isolation and characterization of $[MgCl(THF)_5][FeMe_4]$, an intermediate in the reduction pathway of simple ferric salts with methylmagnesium bromide.[3] This presentation focuses on recent results from our group on the isolation, characterization and reactivity of iron-ate species of relevance to cross-coupling.

[1] S. L. Daifuku, M. H. Al-Afyouni, B. E. R. Snyder, J. L. Kneebone, M. L. Neidig, *J. Am. Chem. Soc.* **2014**, *136*, 9132-9143.

[2] S. L. Daifuku, J. L. Kneebone, B. E. R. Snyder, M. L. Neidig *J. Am. Chem. Soc.* **2015**, *137*, 11432-11444.

[3] M. H. Al-Afyouni, K. L. Fillman, W. W. Brennessel, M. L. Neidig, *J. Am. Chem. Soc.* **2014**, *136*, 15457-15460.
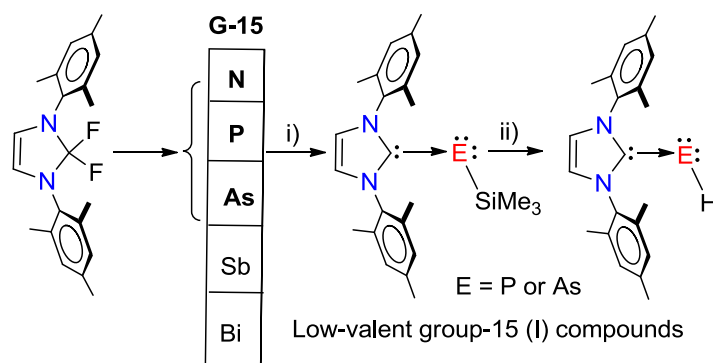
Poster Presentations

Applications of NHC-Pnictinidenes in the Stabilization of Reactive Organometallic Fragments

Adinarayana Doddi and Matthias Tamm*

Technical University Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

email: adinarayana.doddi@tu-bs.de

Scheme 1: Synthesis of NHC-Pnictinidenes; i) M= $E(SiMe_3)_3$, and ii) CH_3OH.

Recently, our group has developed a novel synthetic protocol for the isolation of an *N*-heterocyclic carbene supported new phosphinidene ($IPr·P–SiMe_3$ and $IPr·P–H$) and it was introduced as a synthon for the preparation of various terminal carbene–phosphinidyne transition metal complexes of the type $[(IPr=P)ML_n]$ ($ML_n = (\eta^6$-*p*-cymene)RuCl and (η^5-C_5Me_5)RhCl). The spectroscopic and structural characteristics of these metal complexes showed some similarities with their arylphosphinidene counterparts. The formally mono negative "IPr=P" ligand is also capable of bridging two or three metal atoms as demonstrated by the preparation of bi- and trimetallic complexes.

In order to isolate similar homologues of the type $NHC=E-SiMe_3$, the same synthetic protocol (as reported for the isolation of $IPr·P-SiMe_3$) has been extended to other heavier analogues in the group-15 as shown in scheme 1. In this contribution, synthetic and bonding aspects of the new main-group and transition metal complexes of formally pnictinidene (I) reagents will be discussed in detail.

References

[1] (a) O. Back, M. H. Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed*. **2013**, *52*, 2939-2943. (b) G. Frison, A. Sevin, *J. Organomet. Chem*, **2002**, *643–644*, 105-111.

[2] H. Aktaş, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed*. 2010, 49, 2102-2113.

[3] (a) A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed*. **2014**, *53*, 13568-13572. (b) A. Doddi, D. Bockfeld, A. Nasr, T. Bannenberg, P. J. Jones, M. Tamm, *Chem. Eur. J*. **2015**, *21*, 16178-16189.

An Overlooked Donor: The Cyclopropyl Group in Donor-Acceptor Cyclopropane Chemistry

Alexander Kreft, Daniel B. Werz*

Technische Universität Braunschweig, Institut für Organische Chemie, Hagenring 30, 38106 Braunschweig, Germany

email: a.kreft@tu-bs.de

Donor-Acceptor-substituted (D-A) cyclopropanes are due to their high ring strain ($\sim$115 kJ$\cdot$mol^{-1}) and their polarized C-C-bond a versatile and valuable building block in organic synthesis. 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 functionalized carbon chains or (hetero)cyclic compounds.[1,2]

Although in the past years different combinations of donors and acceptors were computed and experimentally investigated,[1,3] there are only rare examples using alkyl groups as donor.[4,5] In our study, we present reactions with D-A cyclopropanes substituted by a cyclopropyl group showing that this aliphatic cycle is able to act as a donor (Scheme 1).[6]
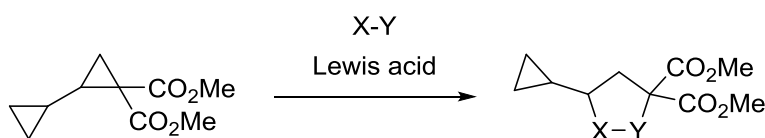
Scheme 1: Cycloaddition reactions of donor-acceptor cyclopropanes bearing a cyclopropyl group as donor.

[1] T. F. Schneider, J. Kaschel, D. B. Werz, *Angew. Chem. Int. Ed.* **2014**, *53*, 5504–5523, *Angew. Chem.* **2014**, *126*, 5608–5628.
[2] H.-U. Reissig, R. Zimmer, *Chem. Rev.* **2003**, *103*, 1151–1196.
[3] T. F. Schneider, D. B. Werz, *Org. Lett.* **2011**, *13*, 1848–1851.
[4] S. Danishefsky, *Acc. Chem. Res.* **1979**, *12*, 66–72.
[5] Z. Zhang, W. Zhang, J. Li, Q. Liu, T. Liu, G. Zhang, *J. Org. Chem.* **2014**, *79*, 11226–11233.
[6] A. Kreft, D. B. Werz, *unpublished results*.

# A Radical Ring-Opening of Donor-Acceptor Cyclopropane

Alexander Lücht, Lukas J. Patalag, Daniel B. Werz*

Technische Universität Braunschweig, Institut für Organische Chemie, Hagenring 30, 38106 Braunschweig, Germany

email: a.luecht@tu-bs.de

In the last years, the synthetic application of donor-acceptor (D-A) cyclopropanes in cycloadditions, ring-openings or rearrangements resulted in different molecular scaffolds. The driving force of these reactions is the high ring strain of cyclopropanes (27.5 kcal/mol). In most cases, mechanisms are explained with the concept of a 1,3-zwitterionic character.[1,2] In addition to that, a few examples of radical ring-opening transformations are known.[3]

Up to now, D-A cyclopropanes have never reacted with radical anions. Herein, we report, that 1,4-naphthoquinone can form a radical anion in presence of $SnCl_2$ and open the cyclopropane (Schema 1). This product is the starting point for interesting follow up chemistry.[4]
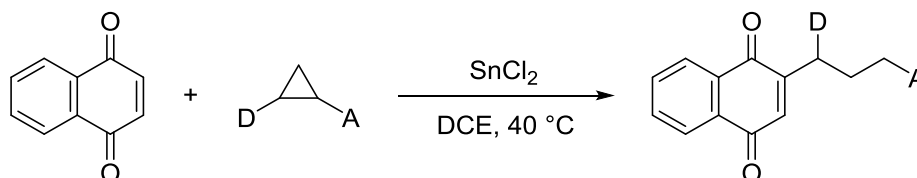
Scheme 1: Radical ring-opening of a D-A cyclopropane with 1,4-naphthoquinone.

[1] T. F. Schneider, J. Kaschel, D. B. Werz, *Angew. Chem. Int. Ed* **2014**, *53*, 5504−5523, *Angew. Chem* **2014**, *126*, 5608−5628.
[2] H.-U. Reissig, R. Zimmer, *Chem. Rev.* **2003**, *103*, 1151–1196.
[3] L. K. B. Garve, P. Barkawitz, P. G. Jones, D. B. Werz, *Org.Lett.* **2014**, *16*, 5804−5807.
[4] A. Lücht, L. J. Patalag, D. B. Werz, *unpublished results*.

N-Heterocyclic Carbenes of Sydnones and Sydnone Imines in Catalysis

Ana-Luiza Lücke[a], Tyll Freese[a], Sascha Wiechmann[a], Martin Nieger[b], and Andreas Schmidt[a]*

[a]: *Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstrasse 6, D-38678 Clausthal-Zellerfeld*
[b]: *Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, (A.I. Virtasenaukio 1), FIN-00014 Helsinki.*

email: ana-luiza.luecke@tu-clausthal.de
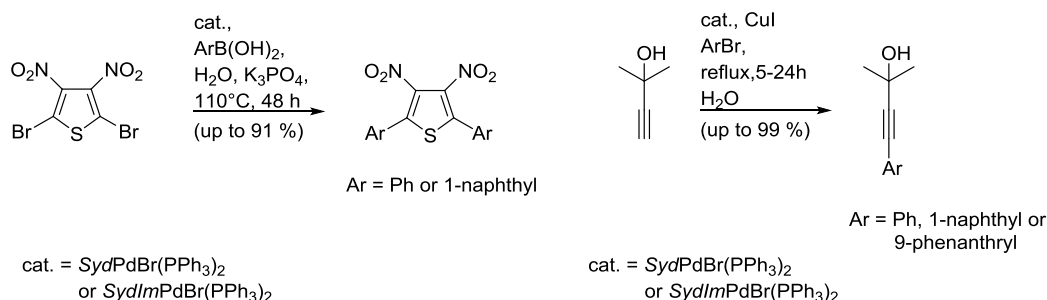
The palladium complexes of the sydnonecarbenes **2** (*Syd*PdBr(PPh$_3$)$_2$) as well as the palladium complexes of the sydnone imine carbenes **4** (*SydIm*PdBr(PPh$_3$)$_2$) proved to be highly efficient catalysts in SONOGASHIRA-HAGIHARA and SUZUKI-MIYAURA reactions.[1,2]

Of all mesoionic compounds sydnones **1** are probably the most prominent. The best single representation which reflects the properties of sydnones appears to be **II**, although **I** is commonly used. We were able to prepare sydnone anions **2** which can be represented as anionic abnormal (**III, IV**) or anionic normal N-heterocyclic carbenes (**V**).[3]
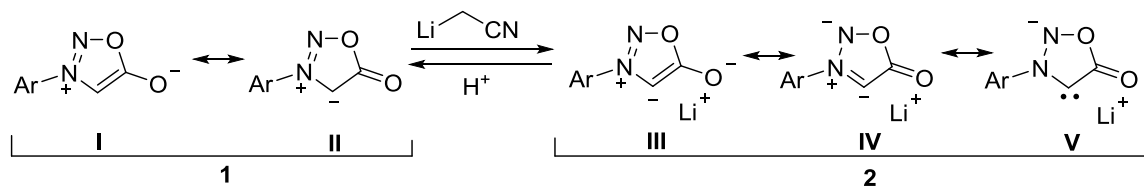
Likewise, we prepared sydnone imine anions **4** which can also be represented as different N-heterocylic carbenes (**VIII-X**).[3]
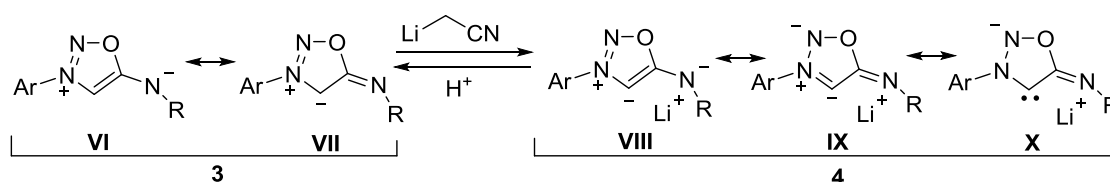
[1] A.-L. Lücke, S. Wiechmann, T. Freese, Z. Guan, A. Schmidt, *Z. Naturforsch.* **2016,** *71 B*, 643.

[2] T. Freese, S. Wiechmann, A.-L. Lücke, M. Nieger, A. Schmidt, unpublishedresults.

[3] S. Wiechmann, T. Freese, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo, M. Nieger, A. Schmidt, *Chem. Commun.* **2014**, *50*, 11822.

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

Andreea Enachi, Matthias Freytag, Peter G. Jones, Marc Walter*

TU Braunschweig, Institute for Inorganic and Analytical Chemistry, Hagenring 30, 38106, Braunschweig, Germany

email: a.enachi@tu-bs.de

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 M^{2+} source and [(tmeda)MgR$_2$] (R= CH$_2$SiMe$_3$, CH$_2$CMe$_2$Ph) 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.
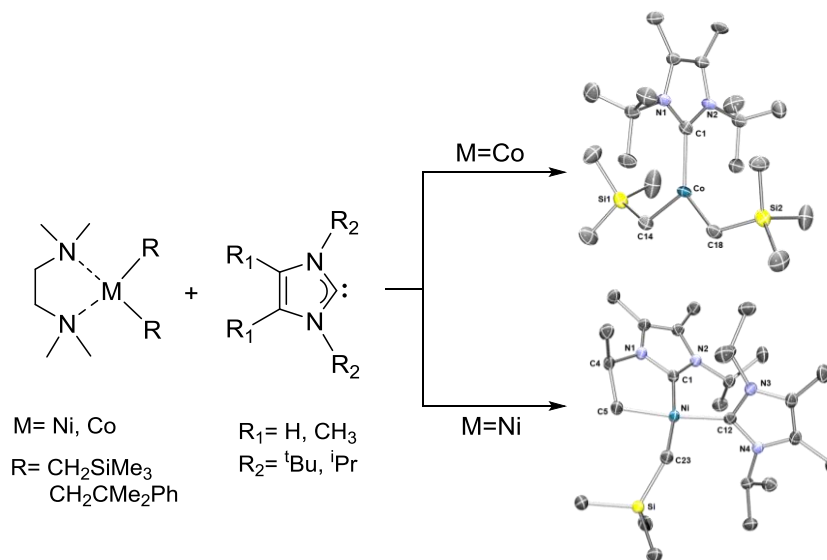
Scheme 1. Preparation of *N*-heterocyclic carbene Ni^{2+} and Co^{2+} dialkyl compounds.

[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.

Synthesis of Pentadentate Tetrapodal Phosphine Ligands and Application to Nitrogen Fixation

Andrei Kindjajev[a], Svea Hinrichsen[a], Jan Krahmer[a], Christian Näther[a] and

Felix Tuczek[a]*

[a:] Christian-Albrechts-Universität Kiel, Institute of Inorganic Chemistry, Max-Eyth-Straße 2, D-24118 Kiel, Germany

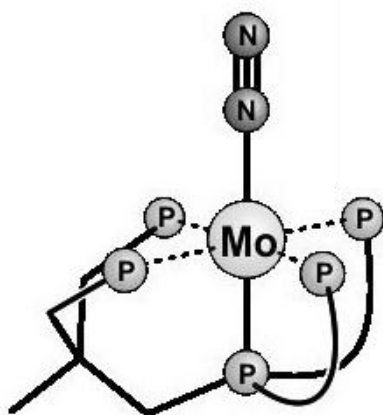*email: akindjajev@ac.uni-kiel.de*

Figure 1. Schematic illustration of the pentaPod.

A molybdenum complex is presented which is supported by a pentadentate tetrapodal (pentaPod) ligand. The synthesis of the pentaPod ligand $P_2^{Me}PP_2^{Ph}$ is described. Reaction of the ligand $P_2^{Me}PP_2^{Ph}$ with $[MoCl_3(thf)_3]$ followed by a sodium amalgam reduction leads to the molybdenum monodinitrogen complex $[MoN_2(P_2^{Me}PP_2^{Ph})]$, which is the first example for a Chatt-like system with a pentadentate phosphine ligand. It shows the highest activation of the N_2 ligand ever found for a molybdenum complex with a pentaphosphine environment ($\tilde{v}_{NN}$ = 1929 cm^{-1}). This complex reacts with trifluoromethanesulfonic acid to the hydrazido complex $[Mo(NNH_2)(P_2^{Me}PP_2^{Ph})](OTf)^2$ under full retention of the phosphine ligation. Due to the special topology of the ligand, the Mo-P bond to the phosphine in trans-position to N_2 is significantly shortened, explaining the very strong activation of the dinitrogen ligand.[1]

[1]   S. Hinrichsen, A. Kindjajev, S. Adomeit, J. Krahmer, C. Näther, F. Tuczek, *Inorg. Chem.* **2016**, *in press.*

# Highly Active Iron Catalyst for Ammonia Borane Dehydrocoupling

Arne Glüer[a], M. Förster[b], V. R. Celinski[c], J. Schmedt auf der Günne[c], M. C. Holthausen[b], S. Schneider[a]*

[a:] Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany
[b:] Institut für Anorganische und Analytische Chemie, Goethe-Universität, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany
[c:] Inorganic Materials Chemistry, University of Siegen, Adolf-Reichwein-Straße 2, 57068 Siegen, Germany

email: arne.glueer@chemie.uni-goettingen.de
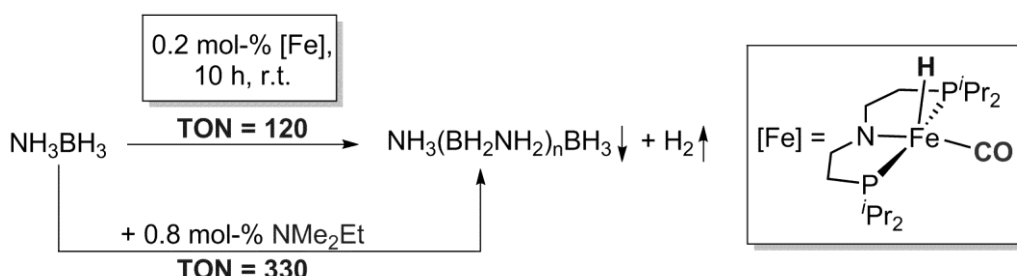
Ammonia borane (NH_3BH_3, AB) is a potential hydrogen storage material due to its high gravimetric H_2 content (19.6 wt-%).[1] The release of H_2 from AB requires elevated temperatures[2] or catalysis. Base metal catalysts generally suffer from low turnover numbers and –frequencies and require high catalyst loading (≈5 mol-%), elevated temperatures (≈60°C) and/or photochemical activation.[3]

Here we describe the use of FeH(CO)(PNP) (PNP = $N(CH_2CH_2PiPr_2)_2$) for AB dehydrocoupling at room temperature to mainly linear polyaminoborane with unprecedented activity for a base metal catalyst. The catalyst deactivation mechanism was examined. Catalyst deactivation to $Fe(BH_4)H(CO)(HPNP)$ can be delayed upon addition of small amounts of an amine (0.8 mol-%) leading to a three times higher TON at the same reaction rate. Kinetic studies afford for a mechanistic model which will be discussed.[4]

[1] a) F. H. Stephens, V. Pons, R. Tom Baker, *Dalton Trans.* **2007**, 2613; b) E. M. Leitao, I. Manners, *Eur. J. Inorg. Chem.* **2015**, 2199.
[2] W. J. Shaw, J. C. Linehan, N. K. Szymczak, D. J. Heldebrant, C. Yonker, D. M. Camaioni, R. T. Baker, T. Autrey, *Angew. Chem. Int. Ed.* **2008**, *47*, 7493.
[3] a) R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott, N. C. Smythe, *J. Am. Chem. Soc.* **2012**, *134*, 5598; b) P. Bhattacharya, J. A. Krause, H. Guan, *J. Am. Chem. Soc.* **2014,** *136*, 11153.
[4] A. Glüer, M. Förster, V. R. Celinski, J. Schmedt auf der Günne, M. C. Holthausen, S. Schneider, *ACS Catal.* **2015**, *5*, 7214.
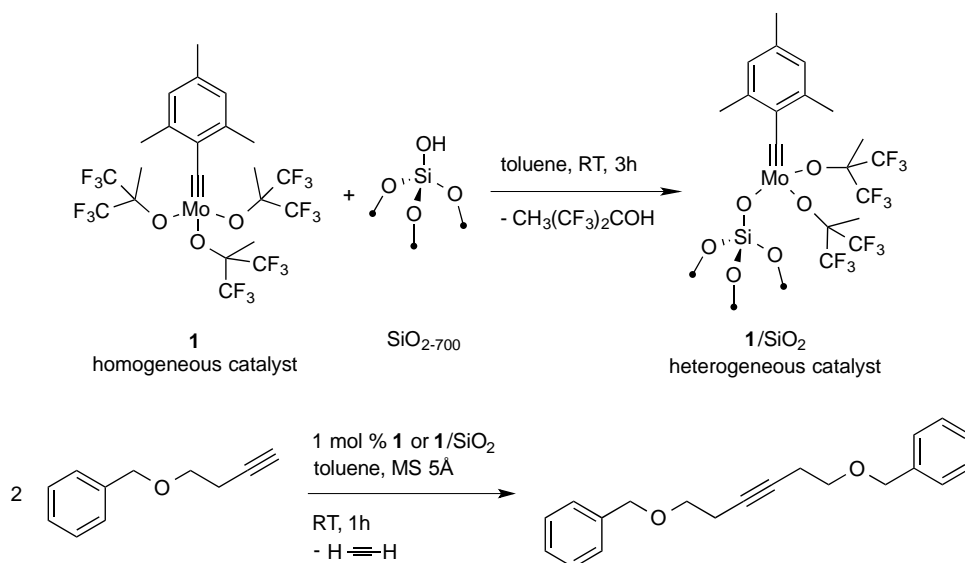
Homogeneous and Heterogeneous Alkyne Metathesis

C. Bittner[a], D. P. Estes[b], M. Casey[b], A. Fedorov[b], C. Coperét[b], M. Tamm[a]*

a: TU Braunschweig, Institut für Anorganische und Analytische Chemie, Hagenring 30, 38106 Braunschweig, Germany
b: ETH Zürich, Department of Chemistry and Applied Biosciences, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

email: c.bittner@tu-bs.de

Over the time, alkyne metathesis became a useful tool for organic and natural product synthesis and numerous catalytic systems have been established.[1] However, the efficient metathesis of terminal alkynes was achieved only lately by Tamm and coworkers using the well-defined molybdenum precatalyst [MesC≡Mo{OCCH$_3$(CF$_3$)$_2$}$_3$] (**1**). It had been shown that terminal alkynes can be metathesized at room temperature with short reaction times and low catalyst loading in high yields.[2] Additionally, the homogeneous system could be transformed into a heterogeneous catalyst by grafting the molecular precursor onto partially dehydrated silica (SiO$_{2\text{-}700}$). This process resulted in a catalytic system **1**/SiO$_2$ which is almost as fast as its homogeneous congener only limited by the enhanced rigidity at the molybdenum centre.[3] Both systems are capable of internal and terminal alkyne metathesis as well as alkyne cross metathesis. A selected reaction is shown in the graphical abstract.

[1]   a) A. Fürstner, *Angew. Chem. Int. Ed.* **2013**, *52* (10), 2794. b) X. Wu, M. Tamm, *Beilstein J. Org. Chem.* **2011**, *7*, 82.
[2]   B. Haberlag, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2012**, *51* (52), 13019.
[3]   D. P. Estes, C. Bittner, Ò. Àrias, M. Casey, A. Fedorov, M. Tamm, C. Copéret, *Angew. Chem. Int. Ed.* **2016**, *accepted* DOI:10.1002/anie.201605129.

Atomic Layer Deposition

A Manifold Tool for Tailored Interfaces.

Christian Volkmann [a], Sven Schneider [a]

[a]: Georg-August-University Göttingen, Inorganic Chemistry, Tammannstr. 4, 37077 Göttingen, Germany
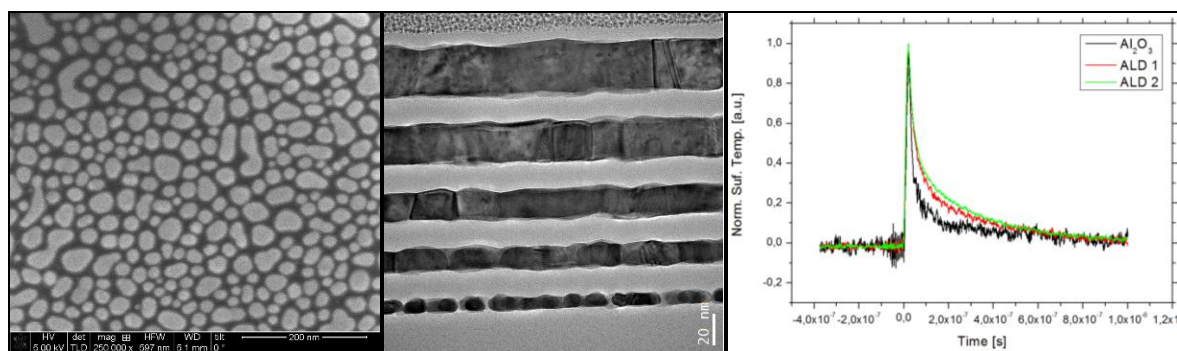
Email: *christian.volkmann@chemie.uni-goettingen.de*

Figure **1**: Scanning electron microscope image of Pt Nanodots on SiO_2(left), transmission electron micrograph of a Pt/Al_2O_3multilayer structure (middle) and transient thermoreflectometry measurements (right).

Nanostructured materials are of interest to examine charge and energy transfer across internal interfaces. For example, widebandgapmetal/semiconductorSchottky contactsare widely usedas photocatalysts[1]and periodic on the nanoscale can be used as thermal bandgap materials to control heat transport.[2]

In this contribution we present the use of atomic layer deposition (ALD) for the production of Pt/Al_2O_3 multilayers out of thin films down to 2 nm (Al_2O_3) and 10 nm (Pt), respectively with high uniformity, low roughnessand minor levels of contamination.Growth conditions and (multi-)film properties are displayed.

These materials were used to study energy transport across the metal/insulator interfaces using thermal reflectivity and molecular beam scattering experiments.[3] These results will be discussed.

[1] D. Ding, K. Liu, S. He, C. Gao, and Y. Yin, *NanoLett.***2014**, *14*, 6731-6736.

[2] M. Maldovan, *Nature Materials***2015**, *14*, 667-674.

[3] O. Buenermann, H. Jiang, Y. Dorenkamp, A. Kandratsenka, S.M. Janke, D.J. Auerbach, and A.M. Wodtke, *Science***2015,** *350*, 1346-1349.

Unsymmetrical Diborane(4) Derivatives: Versatile Tools for the Synthesis of Diaminoboryl Complexes

Corinna Borner[a], Christian Kleeberg[a]*

[a:] Technische Universität Braunschweig, Institut für Anorganische und Analytische Chemie, Hagenring 30, 38106 Braunschweig, Germany

email: corinna.borner@tu-bs.de
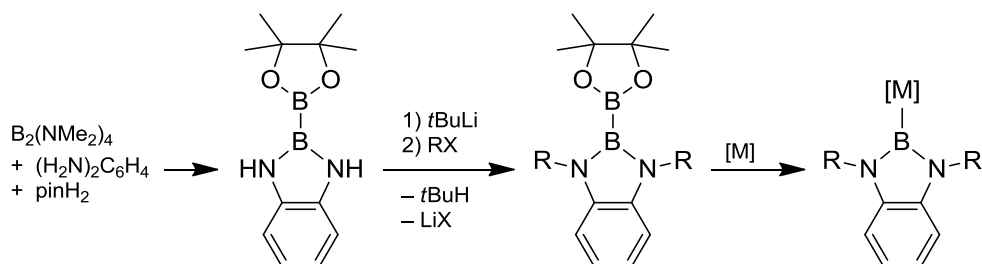
Scheme 2: Synthetic route to diaminoboryl metal complexes via unsymmetrical diboranes.

Transition metal boryl complexes are important intermediates in metal catalyzed borylation reactions.[1] Moreover, boryl and in particular diaminoboryl ligands have received attention due to their interesting coordination chemical properties, e.g. very strong *trans* influence.[2]

A versatile synthetic route to boryl transition metal complexes is the B–B bond cleavage of diboranes by transition metal complexes *via* σ-bond metathesis or oxidative addition.[1] However, tetrakisamino diboranes as precursors of diaminoboryl complexes suffer from low reactivity in such B–B bond activation reactions. Unsymmetrical sp^2-sp^2 diboron compounds of the type $(R_2N)_2B–B(OR')_2$ should overcome this problem and may provide a flexible route to diaminoboryl transition metal complexes.

We have established a flexible synthetic route to unsymmetrical diborane(4) derivatives of the type $pinB–B((NR)_2C_6H_4)$ (R = e.g. Me, Bn, TMS) and explored their use in selective B–B bond activation reactions (**Scheme 1**).[3] The synthesis, structure and reactivity of novel diaminoboryl complexes of platinum, rhodium and copper will be addressed.

[1] G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685-2722; L. Dang, Z. Lin, T. B. Marder, *Chem. Commun.* **2009**, 3987-3995; H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110,* 3924-3957; E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott, T. B. Marder, *Chem. Rev.* **2016**, DOI: 10.1021/acs.chemrev.6b00193 and literature cited therein.
[2]   For an overview see: H. Braunschweig, K.Radacki, K. Uttinger, *Chem. Eur. J.* **2008**, *14*, 7858-7866; Y. Segawa, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 9201-9203; H. Kameo, H. Nakazawa, *Chem. Asian J.* **2013**, *8*, 1720; T. Miyada, M. Yamashita, *Organometallics* **2013**, *32*, 5281-5284; H. Ogawa, M. Yamashita, *Dalton Trans.* **2013**, *42*, 625-629.
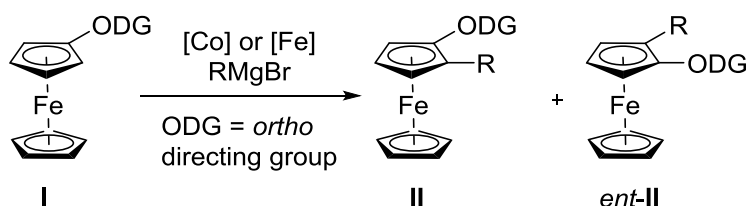[3] C. Borner, C. Kleeberg, *Eur. J. Inorg. Chem.* **2014**, 2486-2489; C. Borner, K. Brandhorst, C. Kleeberg, *Dalton Trans.* **2015***, 44*, 8600-8604.

Cobalt- and Iron-Catalyzed C-H Activation of Ferrocene Derivatives

David Schmiel, Holger Butenschön*

Leibniz Universität Hannover, Institut für Organische Chemie, Schneiderberg 1B, 30167 Hannover, Germany

email: david.schmiel@oci.uni-hannover.de

Planar-chiral 1,2-disubstituted ferrocenes are important chiral ligands for asymmetric catalysis and are generally synthesized by stereoselective stoichiometric *ortho*-lithiation procedures.[1] Another possibility is the kinetic resolution of racemic mixtures.[1] Recently, transition-metal catalyzed enantioselective C-H activation of ferrocene emerges as an powerful alternative and palladium is the most frequently used noble metal in this context.[2] The application of environmentally benign first-row transition metals as catalysts for C-H activation of ferrocene has been scarcely investigated.[3-5] Our first successful results using cobalt and iron as catalysts for C-H activation of ferrocenes bearing various *ortho*-directing groups (ODG) will be presented. Alkylation and arylation reactions were achieved using Grignard reagents as the reactant. The desired products of types **II** and *ent*-**II** were obtained as racemic mixtures.

[1] L.-X. Dai, X.-L. Hou (Eds.), Chiral Ferrocenes in Asymmetric Catalysis, Wiley-VCH, Weinheim, **2010**.
[2] *Recent review:* D.-Y. Zhu, P. Chen, J.-B. Xia, *ChemCatChem* **2016**, *8*, 68 – 73.
[3] S. Siegel, H.-G. Schmalz, *Angew. Chem.* **1997**, *109*, 2569 – 2572; *Angew. Chem. Int. Ed.* **1997**, *36*, 2456 – 2458.
[4] M. Moselage, N. Sauermann, S. C. Richter, L. Ackermann, *Angew. Chem.* **2015**, *127*, 6450 – 6453; *Angew. Chem. Int. Ed.* **2015**, *54*, 6352 – 6355.
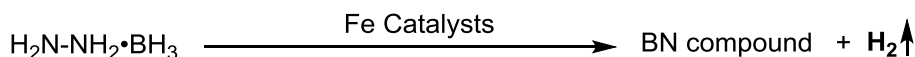[5] G. Cera, T. Haven, L. Ackermann, *Angew. Chem.* **2016**, *128*, 1506 – 1510; *Angew. Chem. Int. Ed.* **2016**, *55*, 1484 – 1488.

IRON-BASEDCOMPLEXESWITH PNP BACKBONE: SELECTIVEANDACTIVECATALYSTSFORDEHYDROGENATION OFHYDROZINEBORANE

Delong Han[a], TorstenBeweries[a]*

[a]: Leibniz-Institut für Katalyse e.V. an der Universität
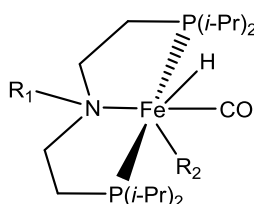
Rostock, Albert-Einstein-Str. 29a, Germany

email: Delong.Han@catalysis.de

Scheme 1. Iron complex catalyzed dehydrogenation of hydrazine borane.

As ecofriendly, recyclable and high energy capacity, dihydrogen is believed as a substitution of traditional fuels. While, taking the properties of hydrogen under consideration, ideal hydrogen store materials are necessary for so-called hydrogen economy.[1]Hydrazine borane (HB),as one of promising hydrogen storage materials,hasoutstanding advantages in terms of high gravimetric hydrogen capacity (15.4 %), easily synthesis, long-term stable *et al.*[2]Thus, it is worth developing efficient methods to release dihydrogen from it. To our best knowledge, various means has been explored to release dihydrogenfrom HB but few transition organometallic complexes which has merits utilized as dehydrogenation catalysts studied and issued.[3]

By now, our group has accomplished the study on dehydrogenating HB using Brookhart's complex and its derivatives[4]as catalysts. Experimental data reveals is that the serial of $R_2POCOPIrHX$(R=COOMe, H, *t*-Bu; X=H, Cl) are selective and efficient catalysts for dehydrogenation of HB. After that, iron-based catalysts ligated with PNP pincer are chosen sinceiron is earth-abundant and no-noble metal and the definded iron pincer catalyst is active catalyst for dehydrogenating amine borane efficiently.[5]So that, we give insight into an array of iron complexes with the same back bone for catalytic dehydrogenation of HB.

[1] T. B. Marder, *Angew. Chem. Int. Ed.* **2007**, *46*, 8116.
[2] R. moury, U. B. Demirci, *Phys. Chem. Chem. Phys*. **2012**, *14*, 1768.
[3] *Selected examples:* (a) J. Hannauer, U. B. Demirci, Qiang Xu,*Energy Environ. Sci.***2011**,*4*, 3355. (b) R. moury, U. B. Demirci, *International Journal of Hydrogen Energy*, **2015**, *40*, 7475. (c) W. B. Aziza,U. B. Demirci,*International Journal of Hydrogen Energy*, **2014**, *39*, 16919.
[4] J. Thomas, M. Klahn, A. Spannenberg, T. Beweries, *Dalton Trans*., **2013**, *42*, 14668.
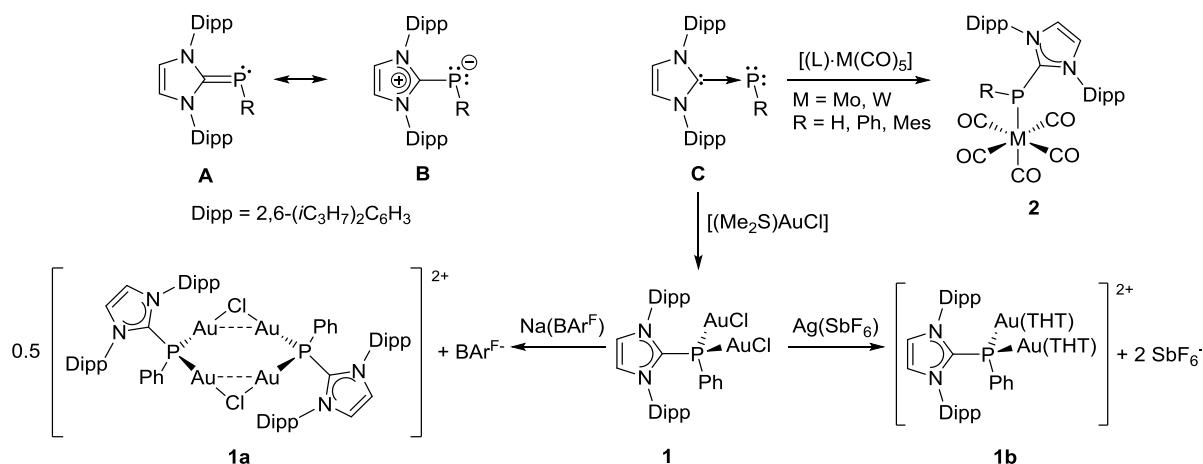[5]   A. Glueer, Sven Schneider, *ACS Catal.***2015**,*5,*7214.

NHC-Phosphinidenes - New Electron Rich Ancillary Ligands in Homogeneous Gold Catalysis

Dirk Bockfeld[a], Adinarayana Doddi[a], Matthias Tamm[a]*

a: Technische Universität Braunschweig, Institut für Anorganische und Analytische Chemie, Hagenring 30, 38106 Braunschweig, Germany

email: d.bockfeld@tu-braunschweig.de

N-heterocyclic carbene-phosphinidene adducts (NHC-PPh) were first reported by Arduengo et al. back in 1997.[1] These compounds can formally be regarded as phosphaalkenes (**A**) as well as carbene stabilized phosphinidenes (**C**). After a series of such adducts with different NHCs was reported by Bertrand et al. in 2013, the first metal complexes using these adducts as ligands were reported.[2] Cationic tetra- and dinuclear coinage metal NHC-phosphinidene complexes (**1a** and **1b**) were studied as catalysts for enyne cyclization and carbene transfer reactions.[3] NHC-phosphinidene transition metal carbonyl complexes (**2**) were employed to study the electron donating properties of NHC-phosphinidenes by infrared-spectroscopy.[4] These studies show that NHC-phosphinidenes are an electron rich addition to the family of P based ligands which can be varied extensively by different NHCs as well as different substituents on the phosphorus atom to adapt to the demands of a specific catalytic process.

[1]   A. J. Arduengo, III, H. V. R. Dias, J. C. Calabrese, *Chem. Lett.* **1997**, 143-144; A. J. Arduengo, III, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem.* **1997**, *36*, 2151-2158.

[2]   O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *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. Yousufuddin, H. V. R. Dias, *Dalton Trans.* **2015**, *44*, 4449-4454.

[3]   A. Doddi, D. Bockfeld, A. Nasr, T. Bannenberg, P. G. Jones, M. Tamm, *Chem. - Eur. J.* **2015**, *21*, 16178-16189.

[4] D. Bockfeld, A. Doddi, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* **2016**, 3704-3712.

Transition metal catalyzed synthesis of polypeptides with phosphonate side-chains

E. Bothe,[1] *H. Menzel*[1],*

1 Institut für Technische Chemie, TU Braunschweig
* e.bothe@tu-bs.de

Phosphoproteins mediate different processes like protein-protein interactions[1], protein activation and inhibition[2] and biomineralization[3]. The synthesis of phosphoproteins is very complex and artificial analogs such as polypeptides are an interesting approach to mimic the features of phosphoproteins (e.g. secondary strucures). Phosphonate-containing polypeptides can be used as e.g. dental adhesives or adhesion promoters[4]. Different catalytic systems are used for the synthesis of polypeptides e.g. amine initiators or transition metal complexes[5]. 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[6] (**Figure 1**). In this way well defined phosphonate containing polypeptides with adjustable degree of polymerization and phosphonate group density are obtained.
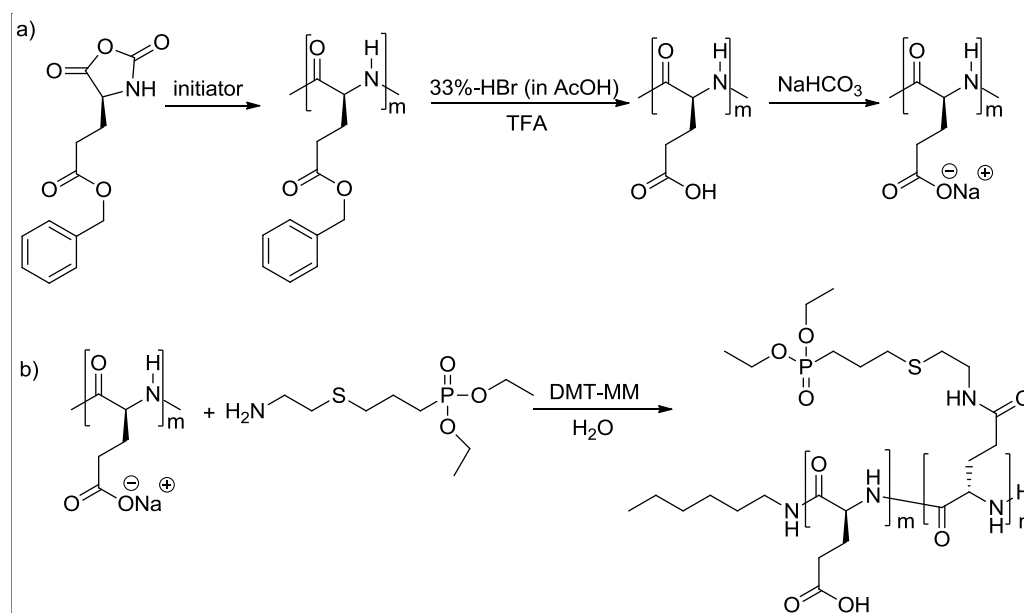
Figure 1. (a) polymerisation of BLG-NCA and (b) amide coupling of diethyl (3-((2-aminoethyl)thio)propyl)phosphonate to PGA-Na .

[1] Yaffe, M. B.; Elia, A. E. H.; *Curr. Opin. Cell Biol.* **2001**, 13, 131 -138.
[2] Zolnierowicz, S. ;*Biochem. Pharmacol.* **2000**, 60, 1225 - 1235.
[3] Bleek, K.; Taubert, A.; *Acta Biomater.* **2013**, 9, 6283 - 6321.
[4] Monge, S.; Canniccioni, B.; Graillot, A.; Robin, J.-J. ;*Biomacromolecules* **2011**, 12, 1973 - 1982.
[5] Deming, T.J.; *Macromolecules* **1999**, 32, 4500 – 4502.
[6] Mildner, R.;Menzel, H.; *J. Polym. Sci. Pol. Chem.* **2013**, 51, 3925-3931.

Catalytic Cyclotrimerization of Halodiynes with Nitriles – Synthesis of 2- and 3-Halopyridines

Eva Bednářová[a,b], Evelina Colacino[b], Frédéric Lamaty[b], Martin Kotora[a]*

a: Charles University in Prague, Faculty of Science, Department of Organic Chemistry, Hlavova 8, 128 43 Prague 2, Czech Republic
b: University of Montpellier, Institut des Biomolécules Max Mousseron, Place Eugène Bataillon, 340 95 Montpellier Cedex 5, France

email: eva.bednarova@natur.cuni.cz
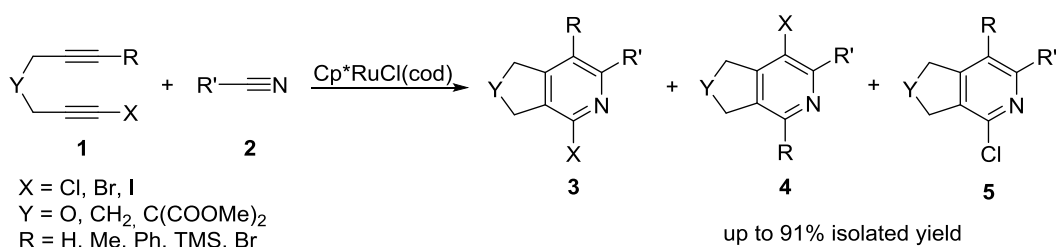
Pyridines and their derivatives, as significant class of hererocyclic compounds, are of a great importance in many fields of chemistry[1]. The simplest method for their preparation is cyclotrimerization of alkynes with nitriles[2]. Cyclotrimerization of 1-haloalkynes with nitriles would give halopyridines that should be readily available for further modification, i.e. by cross-coupling reactions.

In our work we would like to present the first example of a direct synthesis of 2- and 3-halopyridines from halodiynes and nitriles by an efficient transition-metal complex catalyzed [2+2+2] cyclotrimerization[3].

We explored catalytic cyclotrimerization of 1-monohalo and 1,1'-dihalo diynes **1** with nitriles **2** to a mixture of 2- and 3-halopyridines **3** and **4**. We studied regioselectivity of this reaction based on the structure of the starting diynes **1**, the structure of the nitrile **2**, and reaction conditions. Creation of an unexpected third product **5** during the course of the cyclotrimerization revealed a synthetically interesting halogen exchange reaction. The course and the mechanism of the halogen exchange were studied as well.

[1] F. Fache, E. Schulz, M. L., Tommasino and M. Lemaire, *Chem. Rev.* **2000,** *100,* 2159.
[2] M. D. Hill, *Chem. Eur. J.* **2010**, *16*, 12052.
[3] E. Bednarova, E. Colacino, F. Lamaty, M. Kotora, *Adv. Synth. Catal.* **2016**, 358, 1916.

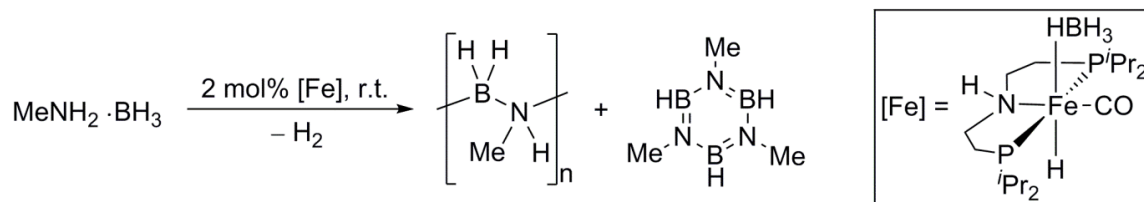# Iron Complex Catalyzed Dehydropolymerization of Methylamine Borane

Felix Anke[a], Marcus Klahn[a], Torsten Beweries[a]*

a: *Leibniz-Institut für Katalyse e.V. an der Universität Rostock,*
Albert-Einstein-Str. 29a, 18059 Rostock, Germany

email: felix.anke@catalysis.de

Catalytic routes for the formation of bonds between main group elements are very important for targeted construction of new molecules and materials. In contrast to the formation of C-C bonds or C-X bonds, main group bond-forming reactions lag behind. For instance catalytic dehydropolymerization reactions of amine borane adducts ($RNH_2 \cdot BH_3$, R = H, Me) provide a clean, atom efficient route to synthesize polyamineboranes, involving the loss of hydrogen. These polymeric BN materials are isoelectronic to technologically versatile polyolefins and are discussed as high performance polymers, as precursor to BN-based ceramics and single-layer hexagonal BN thin films (white graphene).[1] These dehydrocoupling reactions offer significant advantages over previous classical methods such as reductive coupling, high temperature condensation or salt metathesis.[2]

In 2010 Manners demonstrated $MeNH_2 \cdot BH_3$ dehydrocoupling by transition metal complexes to afford linear polyamineborane.[3] In recent years our group focused on the catalytic dehydrogenation of dimethylamine borane using group 4 metallocene complexes.[4]

Scheme 1. Iron complex catalyzed dehydropolymerization of methylamine borane.

Herein we describe the use of a pincer PN*H*P iron complex bearing a η^1-HBH_3 ligand as a highly active catalyst for dehydrocoupling of methylamine borane at room temperature to give mainly linear high molecular weight polyamineborane. The resulting polymeric compound was fully characterized by NMR, IR, ESI-MS and GPC.

[1]   H. C. Johnson, E. M. Leitao, G. R. Whittell, I. Manners, G. C. Lloyd-Jones, A. S. Weller, *J. Am. Chem. Soc.* **2014**, *136*, 9078−9093.
[2]   R. L. Melen, *Chem. Soc. Rev.* **2016**, *45*, 775−788.
[3]   A. Staubitz, M. E. Sloan, A. P. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. S. a. d. Guenne, I. Manners, *J. Am. Chem. Soc.* **2010**, *132*, 13332−13345.
[4]   a) T. Beweries, S. Hansen, M. Kessler, M. Klahn, Uwe Rosenthal, *Dalton Trans.* **2011**, *40*, 7689−7692; b) M. Klahn, D. Hollmann, A. Spannenberg, A. Brückner, T. Beweries, *Dalton Trans.* **2015**, *44*, 12103−12111.

Alkaline Earth Metal Complexes Derived from Chelating Heteroaromates for Small Molecule Activation

Ingo Köhne[a], Dietmar Stalke[a]

a: Göttingen University, Institute of Inorganic Chemistry, Tammannstraße 4, 37077 Göttingen, Germany

email: ikoehne@chemie.uni-goettingen.de

Heteroaromatic nitrogen ligands find extended applications in several important research and technological fields, asymmetric homogeneous and heterogeneous catalysis. Metal hydrides are important because their complexes are considered as potential targets for hydrogen storage. Main group and d-block elements form many metal hydrides. Especially with the well investigated *β*-diketiminate ligand and its derivatives whichcan be used as catalysts in a number of reactions.[1],[2] The chemistry of the Group 2 elements is dominated by the +2 oxidation state. A variety of theoretical investigations of compounds of the type RMMR (M=Be, Mg or Ca; R = alkyl, aryl, amide etc.) have concluded that the strength of their M-M bonds is not insignificant, and that examples that are stable under ambient conditions
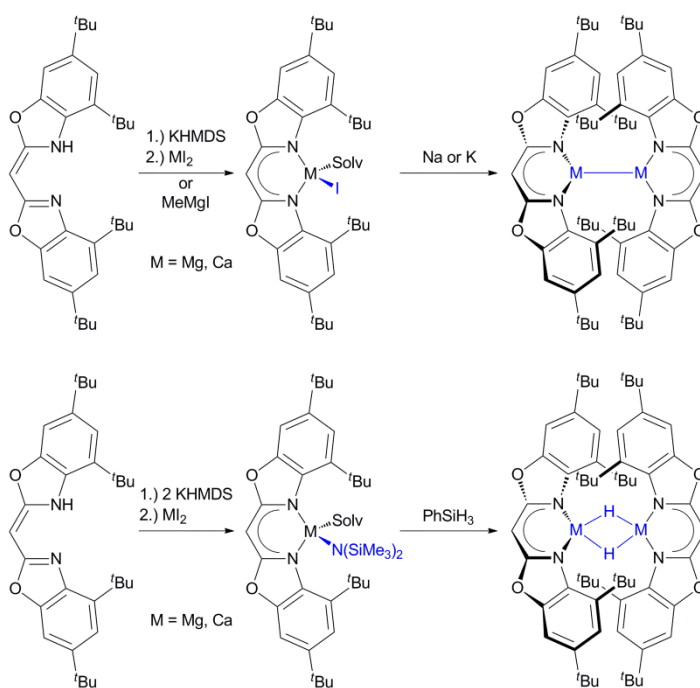
Figure 1: *β*-diketiminate like ligand (left) and intended complex syntheses.

might be accessible if sufficiently bulky ligands (R) are employed.[3] Finally in late 2007, the first "bottleable" magnesium(I) compounds, [LMgMgL] (L = [(ArN)$_2$CN*i*Pr$_2$], priso or[(ArNCMe)$_2$CH], nacnac; Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), were reported.[4]

References

[1] S. P. Sarish, A. Jana, H. W. Roesky, T. Schulz, M. John, D. Stalke, *Inorg. Chem.* **2010**, *49*, 3816-3820.

[2] A. Abbotto, S. Bradamante, A. Facchetti, G. A. Pagani, *J. Org. Chem.* **2002**, *67*, 5753-5772.

[3] S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938-955.

[4] S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna, A. Stasch, *Angew. Chem.* **2009**, *121*, 3017-3021.

Tuning Catalyzed Chain Growth Polymerization: Complex Topologies and High Pressure Performance

Jannik Wagner, Philipp Vana*

Georg-August-University Goettingen, Institute of Physical Chemistry, Tammannstraße 6
37077 Goettingen, Germany

email: *Jannik.wagner@chemie.uni-goettingen.de*
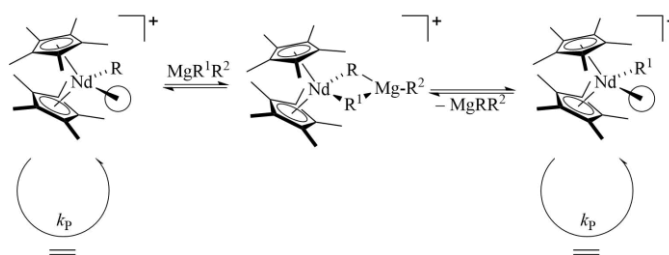
Controlled polymerization techniques revolutionized modern polymer chemistry and offer many advantages compared to conventional polymerization systems. These techniques give access to properties as low dispersities, high end-group functionality, synthesis of block copolymers and defined macromolecular architectures with predictable and adjustable properties. One controlled polymerization technique suitable for monomers like ethylene and propylene 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] Despite these advantages there are still some challenges in CCG.

This work seeks to overcome two main obstacles of CCG. The development of new approaches for the synthesis of telechelic polyethylene and more complex polymer topologies is pursued through the design of novel chain transfer agents and optimization of polymerization conditions. Additionally, the investigation of the systems kinetics at high pressures (up to 3000 bar) is expected to provide an enhanced comprehension of the catalyzed chain growth mechanism. The insight into the detailed mechanism might enable to remove molecular weight limitations.

[1] V. C. Gibson, *Science* **2006**, *312*, 703-704.
[2] T. Chenal, X. Olonde, J.F. Pelletier, K. Bujadoux, A. Mortreux, *Polymer* **2007**, *48*, 1844-1856.

Chromium and Titanium Phenoxy-Pyridine-type Complexes for the Polymerisation and Co-polymersiation of Olefins

Jia-Pei Du[a], Inke Siewert[a]*

a: Georg-August-University Göttingen, Institute of Inorganic Chemistry, Tammannstr. 4,
D-37077 Göttingen, Germany

email: *jia-pei.du@chemie.uni-goettingen.de*

Since the early discovery of the Ziegler-Natta catalysts there has been an increasing academic and industrial interest to develop polymerisation catalysts with enhanced performances and a better control over the molecular weight distribution and the stereochemistry of the resulting polymers.[1] Further development led to the discovery of a new class of polymerisation catalysts, the so-called FI catalysts. In the last decade several metal complexes with phenoxy-imine-type ligands bearing two donor atoms have been established as polymerisation catalysts.[2] Not only polymers resulting from olefin polymerisations are of great use, but also functionalised polyolefins obtained by co-polymerisation of olefins with polar monomers such as methyl methacrylate, acrylates, and vinyl acetate.[3] Developments in this area have led to the design of catalysts with mostly late transition metals as metal centre.[4] However, there are only few examples of titanium-based complexes with tridentate ligand systems which show activity in co-polymerisation.[5]

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

[1] S. D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1204.
[2] R. Furuyama, T. Fujita, F, S, Funaki, T. Nobori, T. Nagata, K. Fujiwara, *Catal. Surv. Asia* **2004**, *8*, 61-71.
[3] L. S. Boffa, B. M. Novak, *Chem. Rev.* **2000**, *100*, 1479-1494.
[4] a) V. C. Gibson, A. Tomov, *Chem. Commun.* **2001**, 1964-1965.; b) X.-F. Li, Y.-G. Li, Y.-S. Li, Y.-X. Chen, N.-H. Hu, *Organometallics* **2005**, *24*, 2502-2510.
[5] a) M.-L. Gao, X.-L. Sun, Y.-F. Gu, X.-L. Yao, C.-F. Li, J.-Y. Bai, C. Wang, Z. Ma, Y. Tang, Z. Xie, S.-Z. Bu, C. Qian, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 2807-2819.; b) X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z. Xie, Y. Tang, *Angew. Chem., Int. Ed.* **2009**, *48*, 8099-8102.;

Oxidative Lactonizations of Alkenoic Acids Actualized by Cooperative Selenium-Oxidase-Catalysis

Rene Rieger[a], Katharina Rode[a], Stefan Ortgies[a], Alexander Breder[a]*

a: Georg-August-Universität Göttingen, Institut für Organische und Biomolekulare Chemie,

Tammannstr. 2, D-37077 Göttingen, Germany

email: katharina.rode@chemie.uni-goettingen.de, abreder@gwdg.de
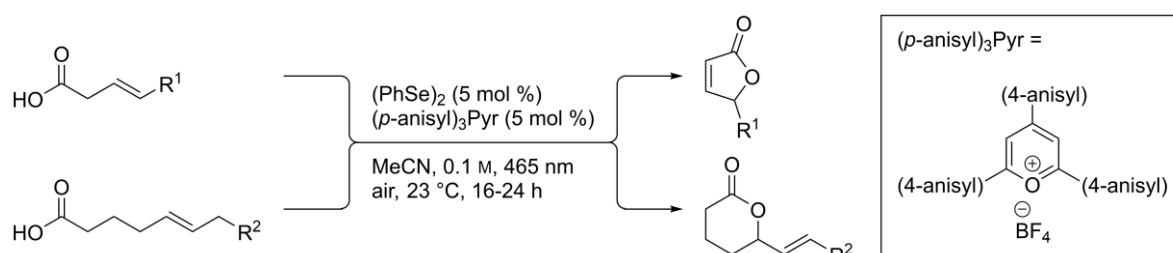
The catalytic oxidative functionalization of alkenes is a topic that has triggered a lot of research activities in the last decades.[1,2] As a result of these efforts, various methods for the selective formation of C-N,[3a] C-O,[3b] or C-C[3c] bonds have been developed. These catalytic systems include *inter alia* transition metals, such as palladium or copper complexes, as well as non-metallic catalysts (e.g. iodine or selenium species).[3] Traditional oxidants, such as λ^3-iodanes, *N*-halo imids and -amides, generally lead to the production of high-molecular waste. Therefore, the search for ecologically more compatible oxidants is a task of great interest. In this context, O_2 has been shown to serve as a non-polluting oxidant in the realm of transition metal catalyzed oxidase reactions.[4] However, cognate examples of artificial oxidase reactions with non-metallic catalysts are very scarce.[5,6]

In our group, we have recently developed a light-driven dual catalysis regime for the oxidative allylic esterification of alkenes, using air as the sole oxidant.[6] The cooperative catalyst system consists of diphenyl diselenide and 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate, which facilitates the formation of the target esters in yields of up to 89%. As an advancement of this novel oxidase catalysis protocol we present herein the lactonization of alkenoic acids as well as further insights into the reaction mechanism.

[1] S. Mann, L. Benhamou, T. Sheppard, *Synthesis* **2015**, *47*, 3079–3117.
[2] R. I. McDonald, G. Liu, S. S. Stahl, *Chem. Rev.* **2011**, *111*, 2981–3019.
[3] a) A. Breder, *Synlett* **2014**, *25*, 899–904; b) S. E. Allen, R. R. Walvoord, R. Padilla-Salinas, M. C. Kozlowski, *Chem. Rev.* **2013**, *113*, 6234–6458; c) C. Liu, J. Yuan, M. Gao, S. Tang, W. Li, R. Shi, A. Lei, *Chem. Rev.* **2015**, *115*, 12138–12204; d) P. Finkbeiner, B. Nachtsheim, *Synthesis* **2013**, *45*, 979–999.
[4] S. S. Stahl, *Angew. Chemie Int. Ed.* **2004**, *43*, 3400–3420.
[5] K. Chen, P. Zhang, Y. Wang, H. Li, *Green Chem.* **2014**, *16*, 2344-2374.
[6] S. Ortgies, C. Depken, A. Breder, *Org. Lett.* **2016**, *18*, 2856–2859.

Reactivity of P,N Ligand Decorated Iridium Catalysts in the Hydrogen Isotopic Exchange Reaction

Kristof Jess[a], Volker Derdau[b], Remo Weck[b], Jens Atzrodt[b], Matthias Freytag[a], Peter G. Jones[a], Matthias Tamm[a]*

[a:] TU Braunschweig, Institute for Inorganic and Analytical Chemistry, Hagenring 30, 38106 Braunschweig, Germany
[b:] Sanofi-Aventis Deutschland GmbH, R&D, Integrated Drug Discovery, Med. Chem., Isotope Chemistry & Metabolite Synthesis, Industriepark Höchst, 65926 Frankfurt, Germany

email: k.jess@tu-bs.de
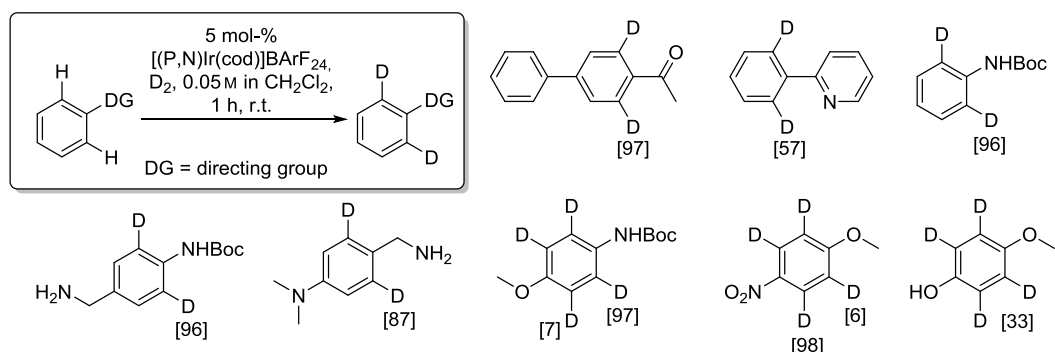
Hydrogen isotopic exchange (HIE) proved to be a valuable method e.g. for mechanistic studies of biosynthetic pathways or catalytic reactions, for preparation of deuterium labelled analytical tool compounds or tritium labelled radiotracers for pharmaceutical research.[1] Among others, particularly Crabtree's catalyst and the NHC-iridium catalysts developed by Kerr[2] were found to catalyse HIE-reactions for a wide range of aromatic substrates. Recently, Muri and Pfaltz[3] used also P,N-chelate iridium catalysts for HIE with a similar substrate scope.

Herein, the synthesis of a series of new iridium complexes, bearing bidentate P,N ligands with electron rich nitrogen donor atoms, is presented. The new bidentate P,N catalysts show remarkable HIE reactivity towards a wide range of functionalities such as Boc-protected anilines, benzyl amines and even weakly coordinating anisole derivatives, which were all out of scope with established catalyst systems so far.

[1]   J. Atzrodt, V. Derdau, T. Fey, J. Zimmermann, *Angew. Chem. Int. Ed.***2007**, *46* (41), 7744–7765.
[2]   J. A. Brown, S. Irvine, A. R. Kennedy, W. J. Kerr, S. Andersson, G. N. Nilsson, *Chem. Commun.***2008** (9), 1115–1117.
[3]   M. Parmentier, T. Hartung, A. Pfaltz, D. Muri, *Chem. Eur. J.***2014**, *20* (36), 11496–11504.

Investigations on Cyclopentadienylalkylphosphide Chelates

Lauren Heinisch[a], Holger Butenschön[a]*

a: Institut für Organische Chemie, Leibniz Universität Hannover, Schneiderberg 1B, 30167 Hannover, Germany

email: lauren.heinisch@oci.uni-hannover.de

1: X = Cl, R = SitBuMe$_2$
2: X = Br, R = SitBuMe$_2$
3: X = Br, R = SiiPr$_3$

4   5   6

7   8   9
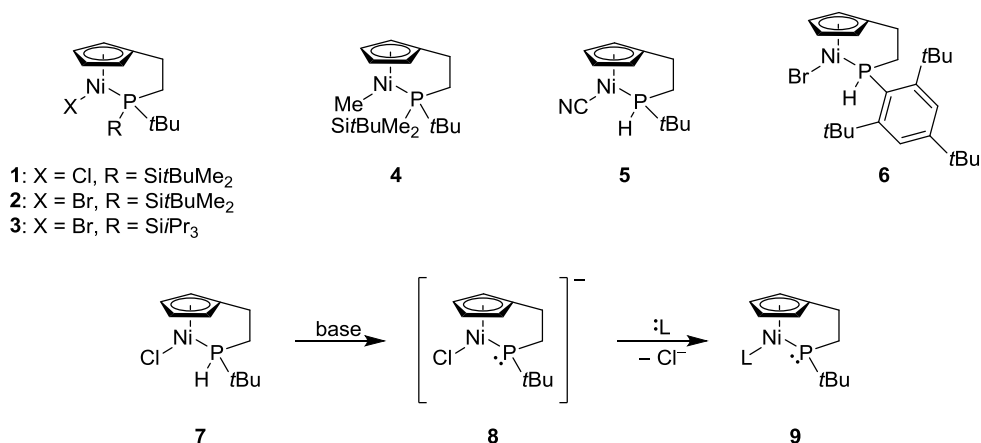
The cyclopentadienyl ligand and its derivatives are one of the most important ligands in organometallic chemistry as they are able to form complexes with nearly all metals in the periodic table.[1] The Cp ligand can be modified by introducing a donor functionalized sidechain leading to more stable complexes and changed chemical properties.[2] In 2014 our group reported on the synthesis of the first cyclopentadienyl nickel complexes **1-4** and **5-6** bearing a silyl group and hydrogen substituted phosphine chelating sidechain, respectively.[3]

Chelates such as **7** should allow for a deprotonation leading to intermediate **8**. Dissociation of chloride and occupying the vacant coordination site by an external ligand should give phosphide chelate **9**. Such phosphide chelates are of interest with respect to potential catalytic applications.

Current work of our group is focused on the synthesis of new cyclopentadienyl nickel complexes, which should undergo a deprotonation.

[1] C. Elschenbroich, *Organometallchemie*, B. G. Teubner Verlag, Wiesbaden, 6. Aufl., **2008**.
[2] C. Müller, D. Vos, P. Jutzi, *J. Organomet. Chem.* **2000**, *600*, 127-143.
[3] I. Werner, H. Butenschön, *Eur. J. Inorg. Chem.* **2014**, *35*, 6051-6060.

Molybdenum Dinitrogen Complexes Coordinated by Tridentate PEP Ligands (E = N or P): Impact of the Central E Donor in *Trans*-Position to N_2

Mareike Pfeil[a], Svea Hinrichsen[a], Ann-Christin Schnoor[a], Katharina Grund[a], Henning Broda[a], Ludger Söncksen[a], Jan Krahmer[a] and Felix Tuczek[a]

a: Christian-Albrechts-Universität zu Kiel, Institute of Inorganic Chemistry, Max-Eyth-Straße 2, 24118 Kiel, Germany
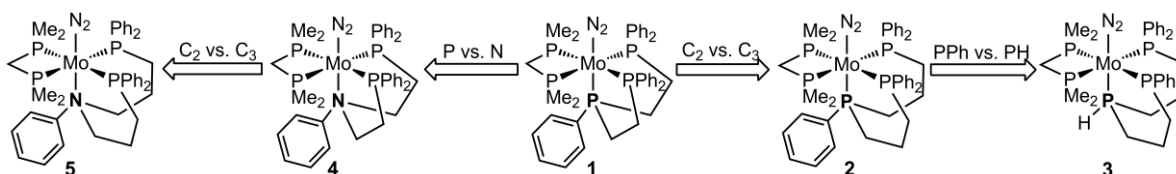
email: mpfeil@ac.uni-kiel.de

Figure 1: Overview of Mo(0) dinitrogen complexes with tridentate PEP ligands which are relevant to the investigation of the influence of the central donor atom E (E = P or N) and the chain length of the alkyl spacers.

The conversion of dinitrogen into bioavailable species like ammonia is one of the most important reactions in nature. In the context of synthetic nitrogen fixation our working group developed Chatt-like systems[1] with a pentaphosphine environment consisting of a bidentate coligand and a tripod or trident ligand which are able to saturate the pivotal position *trans* to N_2 avoiding the formation of a $[Mo(I)N_2XL_4]$ species prone to disproportionation.[2-7] In this context, tridentate PEP (E = N or P) ligands have been applied. The ligand design therefore affords complexes where the *trans* position to the N_2 ligand is occupied by the central donor atom E. We were interested in the impact of E as well as the chain length of the aliphatic linkages particularly with respect to the activation of N_2. Therefore we were investigated the molybdenum(0) dinitrogen complexes **2 - 5** supported by the tridentate ligands prPP(Ph)P, prPPHP, PN(Ph)P and prPN(Ph)P (Figure 1). These systems were compared to $[Mo(N_2)(dpepp)(dmpm)]$ (**1**) prepared by GEORGE *et al.*[8] Whereas the chain length in the alkyl arms was found to be of minor influence, a big increase in activation was observed when P as the trans-donor was replaced by N.

[1] S. Hinrichsen, H. Broda, L. Söncksen, C. Gradert and F. Tuczek, *Annu. Rep. Prog. Chem., Sect. A*, **2012**, *108*, 17-47.

[2] H. Broda, S. Hinrichsen, J. Krahmer, C. Näther and F. Tuczek, *Dalton Trans.*, **2014**, *43*, 2007-2012.

[3] H. Broda, J. Krahmer and F. Tuczek, *European Journal of Inorganic Chemistry*, **2014**, 3564-3571.

[4] J. Krahmer, H. Broda, C. Näther, G. Peters, W. Thimm and F. Tuczek, *European Journal of Inorganic Chemistry*, **2011**, 4377-4386.

[5] L. Söncksen, C. Gradert, J. Krahmer, C. Näther and F. Tuczek, *Inorganic Chemistry*, **2013**, *52*, 6576-6589.

[6] S.Hinrichsen, A. Kindjajev, S. Adomeit, J. Krahmer, C. Näther and F. Tuczek *Inorganic Chemistry* **2016**, *available online DOI:* 10.1021/acs.inorgchem.6b01255

[7] S. Hinrichsen, A.-C. Schnoor, K. Grund, B. Flöser, C. Näther, J. Krahmer and F. Tuczek, *Dalton Trans.* **2016**, *available online DOI:* 10.1039/C6DT02316A

[8] T. A. George and R. C. Tisdale, *Inorg. Chemistry*, **1988**, *27*, 2909-2912

POCOP Fluoride Complexes of Group 10 Metals for Halogen and Hydrogen Bonding

Markus Joksch, Anke Spannenberg, Torsten Beweries*

Leibniz Institute for Catalysis at the University of Rostock (LIKAT), Albert-Einstein-Straße 29a, D-18059 Rostock, Germany

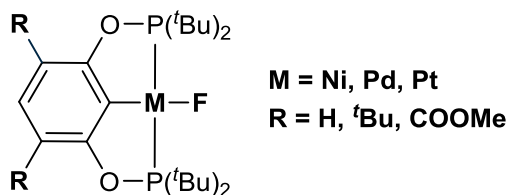*email: markus.joksch@catalysis.de*

Figure 1. General scheme of the metal fluoride complexes.

In the field of noncovalent interactions halogen bonding is of increasing interest.[1] Halogens are common constituents of organic and inorganic molecules. The coordination environment determines whether the compound exhibits Lewis acidic or basic character. This leads to two classes of strong, directional intermolecular interactions, referred to as halogen and hydrogen bonding. Structures of this kind have found various applications including coordination and organometallic chemistry, supramolecular chemistry and crystal engineering as well as biochemistry, molecular recognition, topochemical reactions, molecular conductors, and liquid crystals.[2]

Transition metal halide complexes are known to participate in hydrogen and halogen interactions.[3] Examples for experimental determination of bonding energies and enthalpies were reported, however, no isostructural series of metal fluorides for direct comparison of ligand and metal influence is known to date.[4]

We have synthesized a series of group 10 metal fluoride complexes bearing tridentate POCOP (1,3-*bis*((di-*tert*-butylphosphino)oxy)benzene) ligands (Figure 1). The backbone was functionalized (COOMe, ^{t}Bu) to adjust the electronic properties and investigate the influence on the halogen bonding. All complexes were characterized via NMR, mass spectrometry and X-ray analysis.

[1]   M. H. Kolář, P. Hobza, *Chem. Rev.*, **2016**, *116*, 5155-5187.
[2]   G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.*, **2016**, *116*, 2478-2601.
[3]   Selected recent examples: a) D. A. Smith, T. Beweries, C. Blasius, N. Jasim, R. Nazir, S. Nazir, C. C. Robertson, A. C. Whitwood, C. A. Hunter, L. Brammer, R. N. Perutz, *J. Am. Chem. Soc.*, **2015**, *137*, 11820-11831
[4]   T. Beweries, L. Brammer, N. A. Jasim, J. E. McGrady, R. N. Perutz, A. C. Whitwood, *J. Am. Chem. Soc.*, **2011**, *133*, 14338-14348.

Stability and Unimolecular Reactivity of Organopalladium(II) Ate complexes

Marlene Kolter[a], Konrad Koszinowski[a]*

a: Georg-August-Universität Göttingen, Institut für Organische und Biomolekulare Chemie, Tammannstraße 2, 37077 Göttingen, Germany

email: marlene.kolter@chemie.uni-goettingen.de
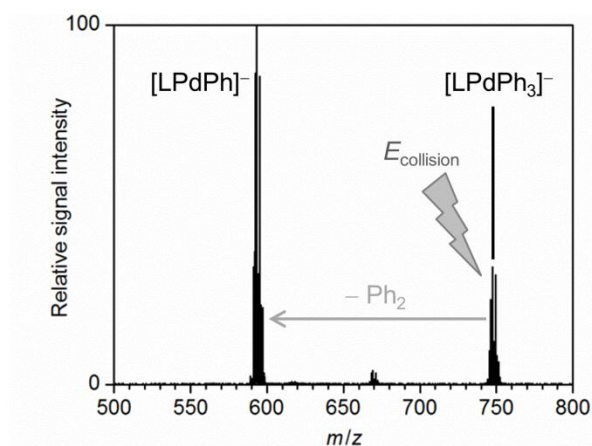
Figure 1. Gas-phase fragmentation of $[LPdPh_3]^-$ yields a Pd^0 complex that resembles the active catalystofmany palladium-catalyzedreactions.

Palladium-mediated reactions are of outstanding importance in modern organic synthesis. In many palladium-catalyzed cross-coupling reactions, the catalytically active Pd^0 species is generated *in situ* by the reduction of a Pd^{II} precursor in the presence ofa phosphine ligand. Besides phosphines,[1] the organometallic reagents used in these transformations can also accomplish this reduction. To investigate the mechanism of the latter reduction pathway, we have treated solutions of $Pd(OAc)_2$ and a phosphine ligand L in tetrahydrofuran with RMgCl (R = Ph, Bn, Bu) as well as other organometallic reagents. These model systems were examined by electrospray-ionization mass spectrometry. The detection of palladium(II) ate complexes of the type $[L_nPdR_3]^-$ (*n* = 0 and 1) suggested a transmetallation reaction. In gas-phase fragmentation experiments, these complexes underwent reductive elimination of R_2 yielding Pd^0 species that closely resemble the active catalyst. Thus, the transmetallation of $Pd(OAc)_2$ with organometallic reagents and subsequent reductive elimination was shown to be a viable mechanism for the precatalyst reduction.

[1] C. Amatore, A. Jutand, M. A. M'Barki, *Organometallics* **1992**, *11*, 3009–3013.

Bioinspired Dinuclear Copper Complexes for Catalytic Phenol Oxidation using Aerial Dioxygen

Marten Seeba; Angelina Prokofieva; Sebastian Dechert; Franc Meyer*

Georg-August-University Göttingen
Institute for Inorganic Chemistry
Tammannstraße 4
D-37077 Göttingen
Germany

marten.seeba@chemie.uni-goettingen.de

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 compartimental pyrazolate based dinucleating scaffold[2].
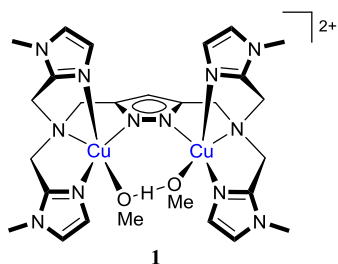
1 was shown to be able to catalyze C—C coupling reactions with substituted phenols such as 2,4,6-trimethyl phenol (TMP) and is futhermore capable of generating different functionalizations oft he 4-methyl group of TMP[3]. Hereby aerial dioxygen is used as the oxidant.

During the reaction the initial $Cu^{II}Cu^{II}$ complex **1** undergoes either partial reduction to a valence localized $Cu^{I}Cu^{II}$ species in case of C—C coupling, or reduction to a $Cu^{I}Cu^{I}$ species. Both species are reoxidzed to their initial state by aerial dioxygen. Catalyic 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.
[2] A. Prokofieva; A.I. Prikhod'ko; E.A. Enyedy; E. Farkas; W. Maringgele; D. Demeshko; S. Dechert; F. Meyer; Inorg.Chem. **2007**, 46, 4298.
[3](a) A. Prokofieva; A.I. Prikhod'ko; S. Dechert; F. Meyer, Chem Comm **2008**, 8, 1005. (b) A. Prokofieva; S. Dechert; C. Große, G.M. Sheldrick; F. Meyer; Chem. Eur. J. **2009**, 15, 4994.

Synthesis and Coordination of Circular P-N-P Containing Ligands

Martha Höhne, Bernd H. Müller, Uwe Rosenthal*

Leibnitz Institute for Catalysis, University of Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany

martha.hoehne@catalysis.de
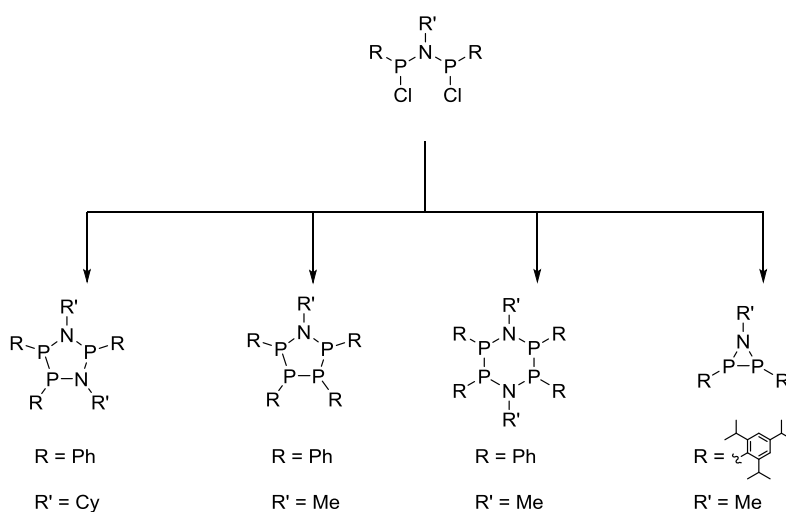
Figure 2. The reduction of dihalogenated P-N-P fragments yields different products in dependence of the substituents R and R', the reducing agent or the solvent.

Established PNP ligands such as diphosphinoamines[1] or PNP Pincertype ligands[2] are well known and investigated. However annular P-N-P containing compounds are less attended and with regard to their catalytic potential as ligands barely examined.

A selective synthesis of annular P-N-P ligands was developed by varying and optimizing the reduction of dihalogenated P-N-P fragments (Figure 1). Consequently the preparation of innovative ring-shaped P-N-P compounds succeeded, which could find application as potential ligands in coordination chemistry and homogeneous catalysis. First attempts of coordinating the circular P-N-P ligands to group (VI) transition metal carbonyls showed surprising and versatile coordination behavior.

[1] M.- S. Balakrishna, V. S. Reddy, S. S. Krishnamurthy, J. F. Nixon, J. Laurent, S. Burckett, *Coord. Chem. Rev.* **1994**, *129*, 1-90.
[2] J. I. van der Vlugt, *Angew. Chem.* **2009**, *121*, 8990-9004.

Catalytic Sugar-assisted Transfer Hydrogenation with Ru[II], Rh[III] and Ir[III] Halfsandwich Complexes

Matthias Böge[a], Jürgen Heck[a]*

a: Hamburg University, Institute of Inorganic and Applied Chemistry,
Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

email: matthias.boege@chemie.uni-hamburg.de; juergen.heck@chemie.uni-hamburg.de
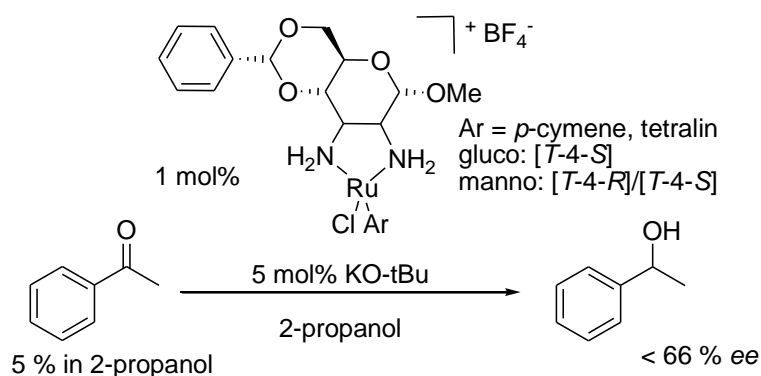
Halfsandwich ruthenium(II), rhodium(III) and iridium(III) complexes of methyl 4,6-*O*-benzylidene-2,3-diamino-2,3-dideoxy-α-D-hexopyranoside ligands have been applied in asymmetric transfer hydrogenation of acetophenone and display the highest enantiomeric excesses in the class of catalyst precursors with ligands containing two coordinating amino groups.

The configuration of the hexopyranosides and the type of arene ligands determine the formation of *R*- or *S*-1-phenylethanol up to 66 % ee despite the presence of two "mirrored" catalytic sites. A large influence of the substitution pattern of the arene ligands on the extent of the enantiomeric excess is demonstrated. The D-gluco- and D-mannopyranoside ligands behave as pseudo-enantiomers in asymmetric transfer hydrogenation.

DFT calculations allowed the identification of the favored transition states in transfer hydrogenation of acetophenone and revealed a site differentiation of the (pseudo)-trigonal deactivated catalyst in the formation of the diastereomeric active catalysts, which are (pseudo)-tetrahedral hydrido complexes. [1]

[1] M. Böge, J. Heck, *J. Mol. Catal. A.* **2015**, *408*, 107-122.

Activation of N₂ with Sterically Demanding Cyclopentadienyl Iron Complexes and the Synthesis of Ammonia

Matthias Reiners[a], Matthias Freytag[a], Peter G. Jones[a], Marc D. Walter[a]*

a: TU Braunschweig, Institute for Inorganic and Analytical Chemistry, Hagenring 30, 38106 Braunschweig, Germany

email: m.reiners@tu-braunschweig.de
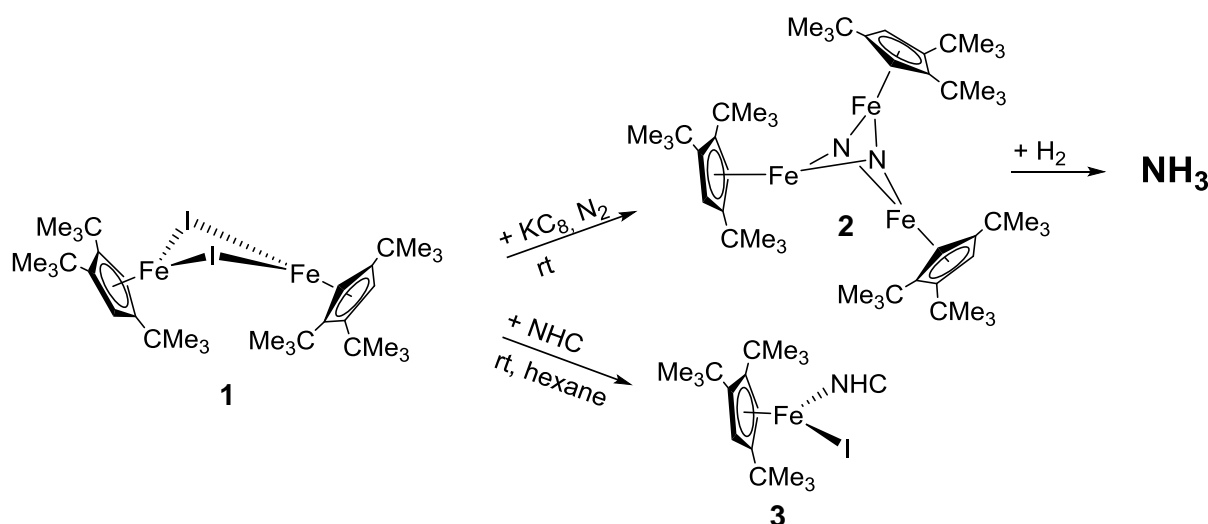
Scheme 1: Activation of N₂ and the synthesis of ammonia.

The cyclopentadienyl ligand (Cp) is one of the most investigated ligand in organometallic chemistry. Over the last six decades many cyclopentadienyl containing transition metal complexes were synthesized;[1-5] and depending on the metal these complexes were also used in many catalytic processes such as polymerization, hydrogenation or the activation of small molecules like CO, H_2 and N_2.[2,4] We are particularly interested in the reactivity of complexes with sterically demanding ligands such as 1,2,4-tri-*tert*-butyl-cyclopentadienyl (Cp'). Here we report on our recent results regarding the activation of molecular N_2 with [Cp'FeI]₂ (**1**) and potassium graphite. This activation product (**2**) can activate hydrogen and give ammonia. Furthermore we will report the synthesis of N-heterocyclic carbene adducts **3** to [Cp'FeI]₂ (**1**) and its reactivity, considering especially the ability of N_2 activation.[5]

[1] C. Janiak, H. Schumann, *Adv. Organomet. Chem.* **1991**, 33, 291-393.
[2] H. Braunschweig, F. Breitling, *Coord. Chem. Rev.* **2006**, 250, 2691–2720.
[3] M. Reiners, D. Baabe, P. Schweyen, M. Freytag, P. G. Jones, M. D. Walter, *Inorg. Chim. Acta* **2014**, 422, 167–180.
[4] M. D. Walter, J. Grunenberg, P. S. White, *Chem. Sci.* **2011**, 2, 2120–2130.
[5] M. Reiners, D. Baabe, K. Harms, M. Maekawa, C. G. Daniliuc, M. Freytag, P. G. Jones, M. D. Walter, *Inorg. Chem. Front.* **2016**, 3, 250-262.

Catalytic Cooperative Copolymerization of Epoxides with CO_2

Mike Schütze, Sebastian Dechert, Franc Meyer*

Georg-August-University Göttingen, Institute for Inorganic Chemistry, Tammannstr. 4, 37077 Göttingen, Germany

email: mike.schuetze@gwdg.de
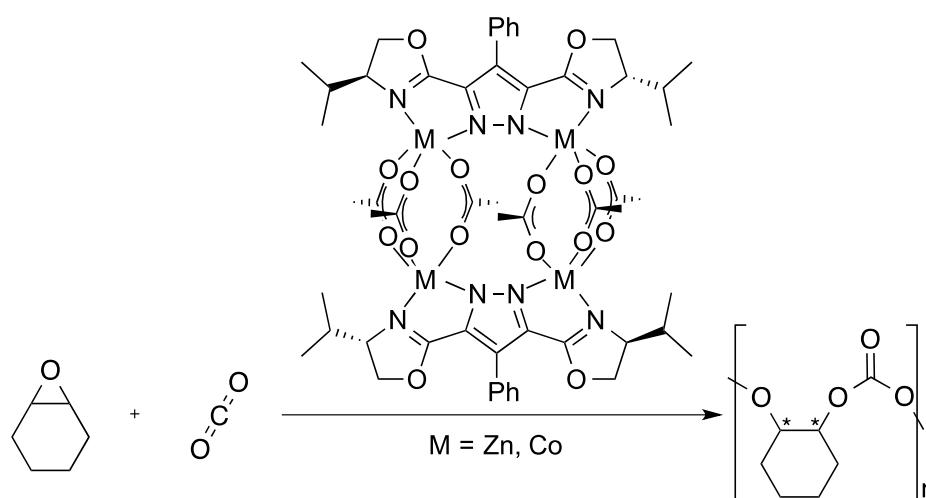
The necessity for sustainable polymers increases as the end of the fossil fuel feedstock approaches. Polycarbonates, prepared from epoxides with CO_2, provide 100% atom economics and qualify as Green Polymers, allowing the use of the industrial waste product CO_2 as a C1 feedstock. In the poly (cyclohexane carbonate) (PCHC) depicted above, 31% of the weight is contributed by CO_2.[1]

The C_2-symmetric pyrazolate-bridged bis(oxazoline) complexes here presented copolymerize cyclohexene oxide with CO_2. 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]

[1]   (a) Taherimehr, M.; Pescarmona, P. P. *J. Appl. Polym. Sci.* **2014**, *131*, 1–17. (b) Trott, G.; Saini, P. K.; Williams, C. K. *Philos. Trans. A. Math. Phys. Eng. Sci.* **2016**, *374*, 20150085.

[2]   Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans.* **2006**, *1*, 237–249.

Investigations of Reactivity and Coordination Chemistry of a Pyrrole Derived Pincer Ligand

<u>Nico Ehrlich</u>, Matthias Freytag, Peter G. Jones, Marc D. Walter*

TU Braunschweig, Institute for Inorganic and Analytical Chemistry, Hagenring 30, 38106 Braunschweig, Germany

email: <u>n.ehrlich@tu-bs.de</u>

Since the first synthesis of pincer type ligands in 1976 by Shaw and Moulton,[1] this structural motif and the corresponding metal compounds have been intensively investigated. This development is driven by the variability and unique properties of pincer compounds and their applications in catalytic processes such as alkane dehydrogenation, coupling reactions, hydrogen transfers and aldol condensations.[2] In the recent years our workgroup has synthesized several 5-membered ligands based on the *N*-heterocycles pyrrole or imidazole and introduced them into transition metal chemistry.[3]

We are particularly interested in the reactivity and coordination chemistry of the NNN-pincer type ligands such as **2** and its alkali metal salts **3** as transfer reagents for the synthesis of new transition- and rare earth metal compounds. The ligand synthesis proceeds by a Staudinger reaction of **1** with Me_3SiN_3. The corresponding alkali metal salts are obtained by deprotonation with strong non-nucleophilic bases such as MHMDS (M = Li, Na, K). Some additional results on PNP-pincer ligand derived transition metal compounds will also be reported.
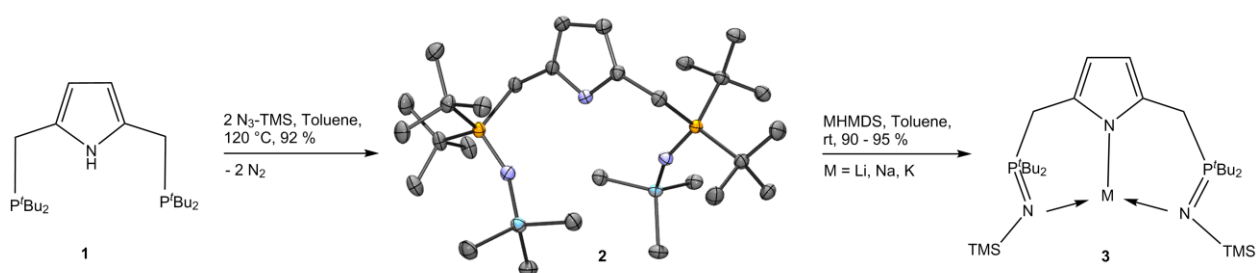
Scheme 1: Preparation of a new pyrrole derived pincer ligand

[1] C. J. Moulton, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1976**, 1020-1024.
[2] D. Morales-Morales, *Rev. Soc. Quim. Méx.* **2004**, *48*, 338.
[3] a) M. Kreye, A. Glöckner, C. G. Daniliuc, M. Freytag, P. G. Jones, M. Tamm, M. D. Walter, *Dalton Trans.* **2013**, *42*, 2192; b) M. Kreye, D. Baabe, P. Schweyen, M. Freytag, C. G. Daniliuc, P. G. Jones, M. D. Walter, *Organometallics.* **2013**, *32*, 5887; c) M. Kreye, J. W. Runyon, M. Freytag, P. G. Jones, M. D. Walter, *Dalton Trans.* **2013**, *42*, 16846; d) M. Kreye, C. G. Daniliuc, M. Freytag, P. G. Jones, M. D. Walter, *Dalton Trans.* **2014**, *43*, 9052; e) M. Kreye, M. Freytag, P. G. Jones, P. G. Williard, W. H. Bernskoetter, M. D. Walter, *Chem. Commun.* **2015**, *51*, 2946; f) M. Kreye, M. Freytag, C. G. Daniliuc, P. G. Jones, M. D. Walter, *Z. Anorg. Allg. Chem.* **2015**, *641*, 2109.

Cobalt-Catalyzed C–H Alkynylation and Alkenylation of Indole Derivatives

Nicolas Sauermann,[a] Marc Moselage,[a] María J. González[a] and Lutz Ackermann[a]*

[a] Georg-August-Universität Göttingen, Institut für Organische und Biomolekulare Chemie, Tammannstraße 2, 37077 Göttingen, Germany

email: Nicolas.Sauermann@chemie.uni-goettingen.de
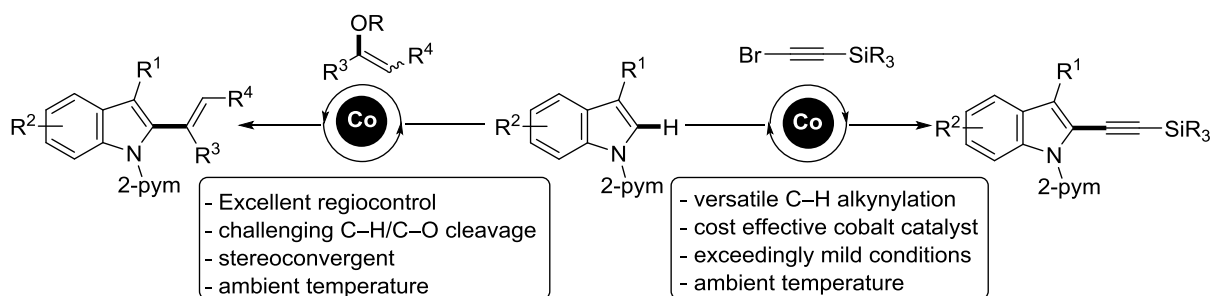
Base metal-catalyzed C–H activation represents a powerful alternative to the use of costly 4d and 5d transition metal catalysts for the sustainable and cost-effective synthesis of biologically relevant compounds.[1] In recent years, high-valent cobalt complexes as well as *in situ* generated low-valent catalytic systems have emerged as a versatile alternative to noble transition metal catalysis. While a wide range of C–H functionalizations, such as arylations, allylations, halogenations and hydroarylations have been reported,[1] direct C–H alkynylations as well as step-economical C–H alkenylations continued to be scarce.[2]

Herein, we present a cobalt-catalyzed direct C–H alkynylation using easily accessible bromoalkynes as alkynylation agents as well as a cobalt-catalyzed direct C–H alkenylation using alkenyl acetates via C–H/C–O cleavage.[3] Notable features of the presented reaction protocols include exceedingly mild reaction conditions, a broad substrate scope and excellent positional and stereocontrol.

[1] a) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498–525. b) K. Gao, N. Yoshikai,, *Acc. Chem. Res.* **2014**, *47*, 1208–1219. c) L. Ackermann, *J. Org. Chem.* **2014**, *79*, 8948–8954. and references therein.
[2] Selected examples: a) W.Song, L. Ackermann, *Angew. Chem. Int. Ed.* **2012**, *51*, 8251–8254. b) M. Moselage, N. Sauermann, J. Koeller, W. Liu, D. Gelamn, L. Ackermann *Synlett.* **2015**, 1596–1600. c) D.-G. Yu, T. Gensch, F. de Azambuja, S. Vásquez-Céspedes, F. Glorius, *J. Am. Chem. Soc.* **2014**, *136*, 17722–17725. d) H. Ikemoto, T. Yoshino, S. Matsunaga, M. Kanai, *J. Am. Chem. Soc.* **2014**, *136*, 5424–5431.
[3] a) N. Sauermann, M. J. González, L. Ackermann, *Org. Lett.* **2015**, *17*, 5316–5319. b) M. Moselage, N. Sauermann, S. C. Richter, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 6352–6355.

Ether-functionalised Alkyne Metathesis Catalysts

Òscar Àrias[a], Johanna Härdter[a], Matthias Freytag[a], Peter G. Jones[a], Matthias Tamm[a]*

a: Technische Universität Braunschweig, Institut für Anorganische und Analytische Chemie, Hagenring 30, 38106 Braunschweig, Germany

email: m.tamm@tu-bs.de

1: Ar = 2-(iPrO)Ph

2: Ar = 4-(MeO)Ph

3: Ar = 2,4,6-(MeO)$_3$Ph

4: Ar = 8-(MeO)Naph
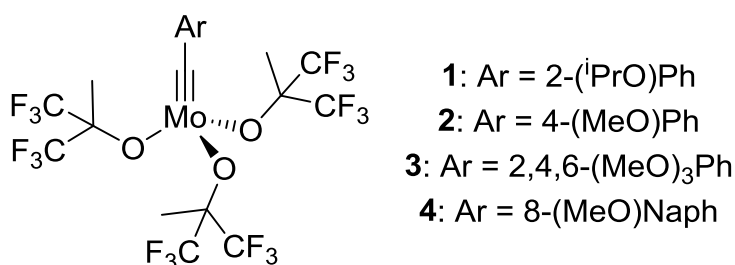
Alkyne metathesis – the catalytic cleavage and re-formation of a C–C triple bond – has increasingly found applications in polymer and organic synthesis in the past decades.[1,2] Although several alkylidyne complexes of Mo and W have been reported as active catalysts for this reaction,[1–3] the functional 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 alkylidyne complexes. In our group we focused on the variation of the benzylidyne moiety, for instance introducing an ether function at different positions of the ring (see Scheme). The synthetic strategy for the desired complexes **1–4** will be presented in this contribution, as well as the solid-state structure of **2** and **3** and their catalytic activity in internal and terminal alkyne metathesis.

[1] W. Zhang, J. S. Moore, *Adv. Synth. Catal.* **2007**, 349, 93–120.
[2] A. Fürstner, *Angew. Chem. Int. Ed.* **2013**, *52*, 2794–2819.
[3] X. Wu, M. Tamm, *Beilstein J. Org. Chem.* **2011**, *7*, 82–93.
[4] B. Haberlag, M. Freytag, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2012**, *51*, 13019–13022

Reactions of Donor-Acceptor Cyclopropanes with Carbonyl Ylides

Martin Petzold[a], P. G. Jones[b], D. B. Werz[a*]

a: Technische Universität Braunschweig, Institute of Organic Chemistry, Hagenring 30, 38106 Braunschweig, Germany
b: Technische Universität Braunschweig, Institute of Inorganic Chemistry, Hagenring 30, 38106 Braunschweig, Germany

email: m.petzold@tu-braunschweig.de

The formation of complex structural motifs within one step is the key to many synthetic strategies. Donor-acceptor (DA) cyclopropanes are of high value for this effort. Due to their high ring strain (~115 kJ·mol^{-1}) and a strongly polarized vicinal carbon-carbon-bond they offer unique reactivity and it is possible to unleash their full synthetic potential as C_3-building blocks in various transformations.[1-3]

In this study DA cyclopropanes were reacted with carbonyl ylides. These 1,3-dipoles are well known in literature for cycloadditions with *e.g.* olefins, alkynes, imines or carbonyls.[4,5] They can be easily prepared *in situ* from the corresponding diazo compounds. The reaction with DA cyclopropanes results in oxygen-bridged carbocycles (Scheme 1) with tunable substitution pattern.[6]
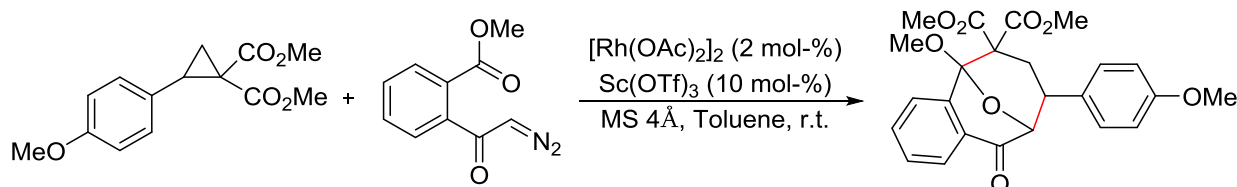
Scheme 3: [3+3]-Cycloaddition of a DA cyclopropane with an *in situ* generated carbonyl ylide.

[1] T. F. Schneider, J. Kaschel, D. B. Werz, *Angew. Chem. Int. Ed.* **2014**, *53*, 5504–5523.

[2] H.-U. Reissig, R. Zimmer, *Chem. Rev.* **2003**, *103*, 1151–1196.

[3] L. K. B. Garve, M. Petzold, P. G. Jones, D. B. Werz, *Org. Lett.* **2016**, *18*, 564–567.

[4] T. Hashimoto, K. Maruoka, *Chem. Rev.* **2015**, *115*, 5366–5412.

[5] Q.-Q. Cheng, J. Yedoyan, H. Arman, M. P. Doyle, *Angew. Chem. Int. Ed.* **2016**, *55*, 5573–5576.

[6] M. Petzold, D. B. Werz, *unpublished results*.

Synthesis of Unsymmetrically Substituted Fluorenols and 9,9´-Spirobifluorenes

Reinhard P. Kaiser[a], Martin Kotora[a]

[a:] Charles University, Faculty of Science, Department of organic Chemistry, Hlavova 8, 128 43 Praha 2, Czech Republic

email: kaiserr@natur.cuni.cz

X = H, OH, OTBDMS
R^1, R^2 = *n*-Pr, Ph, *p*-Tol
R^3 = Me, Et, *n*-Pr, CH$_2$OH
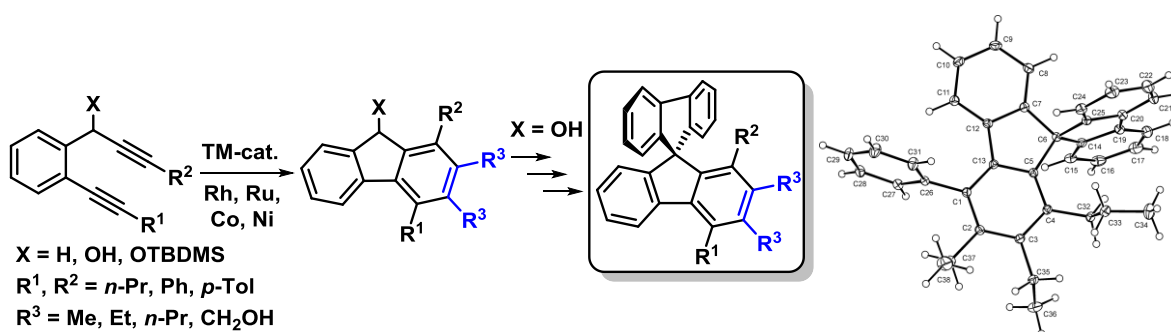
Cyclotrimerization reaction of substituted diynes with alkynes was investigated as a new synthetic pathway to regioselectively substituted fluorenes and fluorenoles. Compounds with the fluorene scaffold are often used as ligands in various transition metals complexes[1] and are important organic material chemistry components for light emitting devices like dyes in diodes.[2] Thus, appropriately substituted diynes with variable residues R^1 and R^2 (Scheme) as precursors for fluorenes or fluorenols were prepared. These compounds were suitable starting materials for the subsequent transition metal catalyzed cyclotrimerization reactions with symmetrically substituted alkynes, bearing various aliphatic substituents (Scheme, substituent R^3). Various cyclotrimerization catalysts based on Rh, Ru, Co and Ni were investigated to find the best reaction conditions. The scope of the reaction with respect to different aliphatic and aromatic R^1, R^2 and R^3 residues was assessed as well.

A series of the prepared unsymmetrically substituted fluorenoles was further transformed to the corresponding 9,9'-spirobifluorenes (Scheme) and their opto-physical properties were studied.[3]

[1] Š. Janková, P. Štěpnička, M. Kotora, *Eur. J. Org. Chem.* **2013**, 44-47.
[2] (a) C. Poriel, J. Rault-Berthelot, D. Thirion, *J. Org. Chem.* **2013**, *78*, 886-898.
     (b) D. Kumar, K. Thomas, C. Lee, K. Ho, *J. Org. Chem.* **2014**, *7*9, 3159-3172.
[3] R. P. Kaiser, F. Hessler, M. Kotora, *Chem. Eur. J.* **2015**, *21*, 13577-13582.

Phosphane-Substituted Troticenes – Ancillary Ligands in Palladium-Catalyzed Cross-Coupling Reactions

Sabrina Tröndle[a], Matthias Tamm[a]*

[a:] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig

email: s.troendle@tu-bs.de
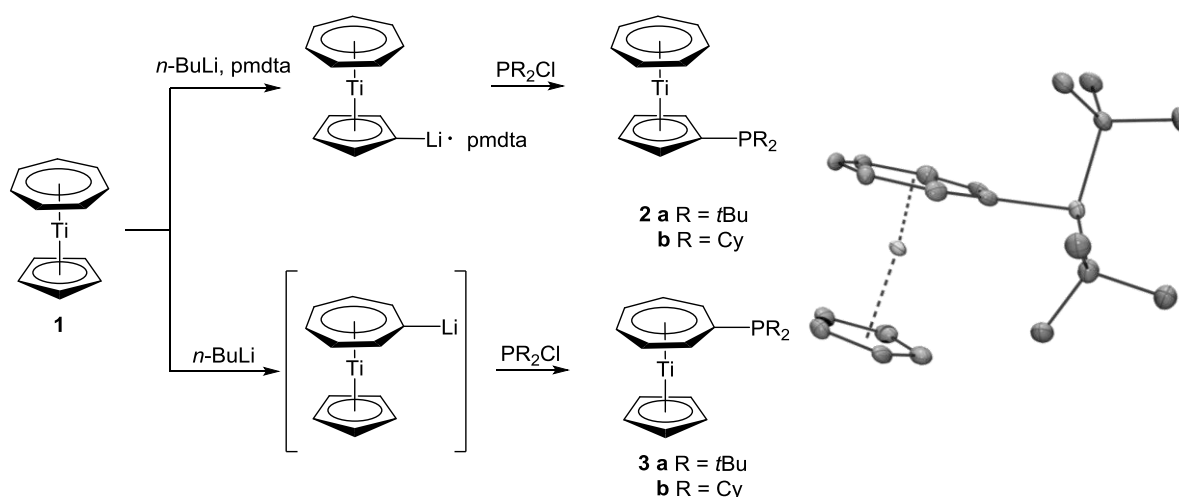
Phosphane ligands are widely employed for cross-coupling reactions in combination with palladium precursors.[1] Moreover, the application of ferrocenyl mono- and di-functionalized phosphanes as ligands was thoroughly investigated in catalytic reactions.[2] Based on these results, cycloheptatrienyl-cyclopentadienyl complexes of group IV elements bearing phosphanes have been synthesized and characterized in our group.[3]

Remarkably, functionalization of cycloheptatrienyl-cyclopentadienyl titanium (troticene) can occur selectively either at the five-membered or the seven-membered ring according to reaction conditions. Phosphane-substituted troticenes **2** and **3** are assumed to act as sterically demanding analogues of ferrocenylphosphanes in Suzuki-Miyaura coupling reactions. Complexes of type **2** and **3** rapidly react with palladium(II)-acetate and act themselves as a reducing agent. The resulting complexes are highly active in Suzuki-Miyaura reactions.[3]

[1] a) S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2004**, *43*, 1871-1876. b) W. F. Wu, H. Neumann, M. Beller*, Chem. Soc. Rev.* **2011**, *40*, 4986-5009.

[2] a) G. Mann, C. Incarvito, A. L. Rheingold, J. F. Hartwig*, J. Am. Chem. Soc.* **1999**, *121*, 3224-3225. b) N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002***, 67*, 5553-5566. c) C. C. C. Johansson Seechurn, S. L. Parisel, T. J. Colacot, *J. Org. Chem.* **2011**, *76*, 7918-7932.

[3] a) A. C. Tagne Kuate, S. Sameni, M. Freytag, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2013**, *52*, 8638-8642. b) S. Büschel, A.-K. Jungton, T. Bannenberg, S. Randoll, C. G. Hrib, P. G. Jones, M. Tamm*, Chem. Eur. J.* **2009**, *15*, 2176-2184.

Oxygen Reduction with a Bifunctional Dihydride Complex

C. Schiwek[a], J. Meiners[a], M. Förster[b], C. Würtele[a], M. Diefenbach[b], M. C. Holthausen[b], S. Schneider[a]*

a: Georg-August-Universität Göttingen, Institut für Anorganische Chemie, Tammannstraße 4, 37077 Göttingen, Germany
b: Goethe-Universität, Institut für Anorganische und Analytische Chemie, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany

email: christoph.schiwek@stud.uni-goettingen.de
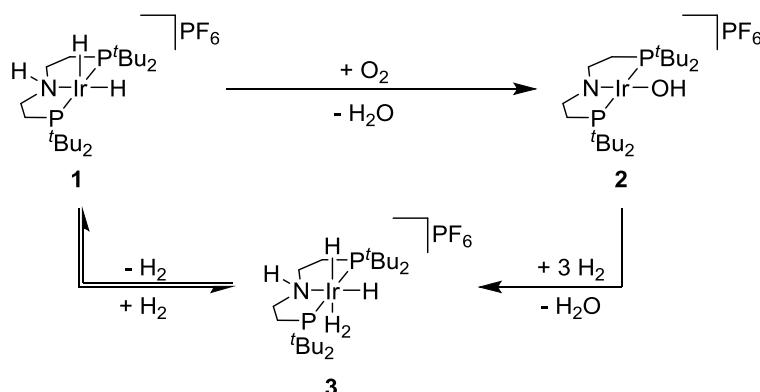
The oxygen reduction reaction (ORR), while of great interest in regards to sustainable catalysis and energy conversion processes, imposes particular challenges: the delivery of four protons, which is addressed in catalyst design by acidic groups in proximity of the O_2 reducing site, as well as four electrons for reduction of O_2, which need to be provided by multiple redox centers.[1-3] Inspired by previous work by the Rauchfuss group, in which two electrons were stored in a metal hydride bond,[3] we examined whether a single metal center ORR-catalyst can be designed by storage of the electrons within two covalent metal-hydride bonds: $[Ir^{iii}(H)_2\{NH(CH_2CH_2P^tBu_2)_2\}]PF_6$ **1**, using a bifunctional meridial, tridentate ('pincer') ligand, splits dioxygen with formation of water and the highly unusual square planar hydroxo complex $[Ir^{iii}(OH)\{N(CH_2CH_2P^tBu_2)_2\}]PF_6$ **2**. Heterolysis of H_2 completes the synthetic cycle. A mechanism, which is first order in **1** as well as O_2, is proposed based on kinetic studies, isotope labeling experiments and computations.[4]

[1] L. Que, W. B. Tolman, *Nature* **2008**, *455*, 333.
[2] D. K. Dogutan, S. A. Stoian, R. McGuire Jr., M. Schwalbe, T. S. Teets, D. G. Nocera, *J. Am. Chem. Soc.*, **2011**, *133*, 131
[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.

The Role of Ate Complexes in the Copper-Mediated Trifluoromethylation of Alkynes

Sebastian Weske[a], Ramona Schoop[a], Konrad Koszinowski[a]*

[a:] Georg-August-University Göttingen, Institute of Organic and Biomolecular Chemistry, Tammannstr. 2, 37077 Göttingen, Germany

email: sebastian.weske@stud.uni-goettingen.de
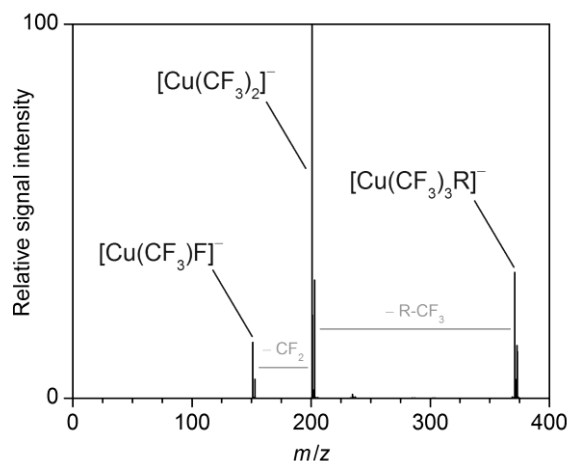
Figure 1. Mass spectrum of mass-selected $[Cu(CF_3)_3R]^-$ (R = CC-Ph) and its fragment ions produced upon collision-induced dissociation at E_{LAB} = 5 eV.

Trifluoromethylation reactions have recently received increased attention because of the beneficial effect of the trifluoromethyl group on the pharmacological properties of numerous substances.[1] A common method to introduce the trifluoromethyl group employs $Si(CH_3)_3CF_3$, together with a copper(I) halide.[2] We have applied this method to the trifluoromethylation of aromatic alkynes and used electrospray-ionization mass spectrometry to investigate the mechanism of these reactions.[3] In the absence of the alkyne component, the homoleptic ate complexes $[Cu(CF_3)_2]^-$ and $[Cu(CF_3)_4]^-$ were observed. In the presence of the alkynes RH, the heteroleptic complexes $[Cu(CF_3)_3R]^-$ were detected as well. These intermediates released the cross-coupling products R-CF$_3$ with perfect selectivity upon gas-phase fragmentation (Figure 1). Apparently, the $[Cu(CF_3)_3R]^-$ complexes did not originate from homoleptic cuprate anions, but from unobservable neutral precursors. The present results moreover point to the involvement of oxygen as oxidizing agent.

[1] K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881-1886.
[2] X. Liu, C. Xu, M. Wang, Q. Liu, *Chem. Rev.* **2015**, *115*, 683-730.
[3] S. Weske, R. Schoop, K. Koszinowski, *Chem. Eur. J.* **2016**, *22*, 11310-11316.

Investigations towards Ferrocene based Molecular Wires with Sulfur Alligator Clips

Sinem Schmiel[a], Holger Butenschön[a]*

[a:] Leibniz Universität Hannover, Institut für Organischen Chemie, Schneiderberg 1B, D-30167 Hannover, Germany

email: sinem.schmiel@oci.uni-hannover.de
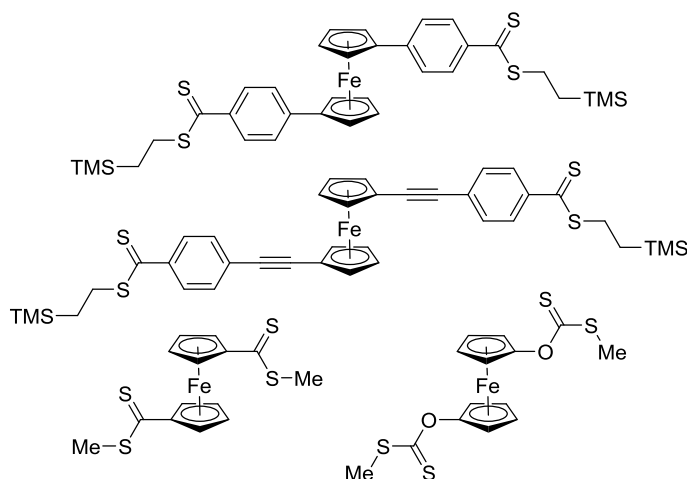
Molecular wires of the oligophenyleneethynylene-type (OPE) are of particular interest in the area of molecular electronics. The rigidity, which is characteristic for these compounds, can be evaded through replacing some 1,4-phenylene moieties with 1,1'-ferrocenylene units. This leads to a limited conformational flexibility comparable to a folding ruler as a consequence of the almost unrestricted rotation around the Cp-Fe-Cp axis.[1]

The synthesis of 1,1'-disubstituted ferrocenes with sulfur alligator clips follows the previously described concept. Since terminal sulfur groups show a relatively high junction conductance and a high tendecy to attach to gold surfaces, they are preffered vis-à-vis other groups, like nitrile.[2] Moreover, SCHÖNEBERGER *et al.* demonstrated that replacement of thiol terminal groups by carbodithioate alligator clips enhances the junction conductance.[3] Therefore syntheses of molecular wires with both types of sulfur alligator clips are of peculiar interest.

[1] I. Baumgardt, H. Butenschön, *Eur. J. Org. Chem.* **2010**, *6*, 1076-1087.

[2] W. Hong, D. Z. Manrique, P. Moreno-Garcia, M. Gulcur, A. Mishchenko, C. J. Lambert, M. R. Bryce, T. Wandlowsky, *J. Am. Chem. Soc.* **2012**, *134*, 2292-2304.

[3] Z. Li, H. Li, S. Chen, T. Fröhlich, C. Yi, C. Schönenberger, M. Calame, S. Decurtins, S.-X. Liu, E. Borguet, *J. Am. Chem. Soc.* **2014**, *136*, 8867-8870.

Oxidative Allylic Esterification of Alkenes by Cooper-ative Selenium-Catalysis using Air as the Sole Oxidant

Stefan Ortgies[a], Christian Depken[a], Alexander Breder[a]*

[a:] Georg-August-Universität, Institut für org. und biomol. Chemie, Tammannstr. 2, 37083 Göttingen, Germany

email: sortgie@gwdg.de
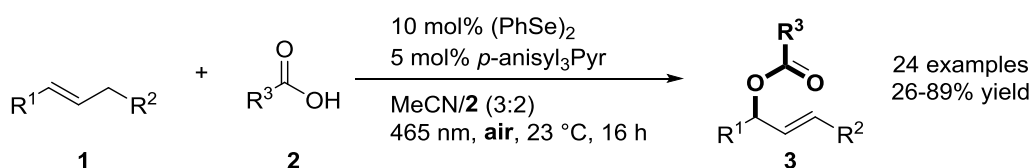
The carbophilic activation of simple alkenes for their oxidative allylic and vinylic functionalization remains one of the most important aspects of synthetic organic chemistry due to the pronounced step- and atom economy associated with such reaction regimes. To further improve on environmental innocuousness, practicability and cost efficiency of oxidative alkene derivatizations, there has been an increasing interest in the development of new reaction manifolds that rely on the use of molecular oxygen as the sole oxidant. While numerous metal-catalyzed reactions in which O_2 exclusively acts as an electron acceptor are known today,[1] only very few cognate organocatalytic variants have been reported to date.[2] With regard to this methodological dearth and in continuation of our work on selenium-catalyzed alkene activation,[3] we developed a cooperative seleno-/photoredoxcatalytic system that allows for the application of aerial oxygen as the terminal oxidant in the allylic acyloxylation of simple alkenes. We found that the combination of 10 mol % of diphenyl diselenide and 5 mol % of 2,4,6-tri-*p*-anisylpyrylium tetrafluoroborate (*p*-anisyl$_3$Pyr) proved optimal for the allylic functionalization of diversely substituted alkenes using carboxylic acids as nucleophiles and air as the terminal oxidant under visible light irradiation, giving rise to the acyloxylation products in up to 89% yield.[4]

[1] for selected reviews, see: (a) B. L. Ryland, S. S. Stahl, *Angew. Chem. Int. Ed.* **2014**, *53*, 8824-8838; (b) I. J. S. Fairlamb, *Angew. Chem. Int. Ed.* **2015**, *54*, 10415-10427.

[2] M. Shibuya, Y. Osada, Y. Sasano, M. Tomizawa, Y. Iwabuchi, *J. Am. Chem. Soc.* **2011**, *133*, 6497-6500.

[3] (a) J. Trenner, C. Depken, T. J. Weber, A. Breder, *Angew. Chem. Int. Ed.* **2013**, *52*, 8952-8956; (b) F. Krätzschmar, M. Kaßel, A. Breder, *Chem. Eur. J.* **2015**, 21, 7030-7034; (c) S. Ortgies, A. Breder, *Org. Lett.* **2015**, *17*, 2748-2751.

[4] S. Ortgies, C. Depken. A. Breder, *Org. Lett.* **2016**, *18*, 2856-2859.

Novel Dinuclear Nickel *N*-heterocyclic Carbene Complexes for the Activation of Small Molecules

S.G. Resch[a], S. Dechert[a], F. Meyer[a]*

[a:]Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstr. 4, 37077, Göttingen, Germany

email: stefan.resch@chemie.uni-goettingen.de

Cooperative effects[1] in di- and multinuclear metal systems play a key role in many enzymatic reactions as for example in urease, hydrogenase, nitrogenase and methane monooxygenases.[2] Such cooperative effects can lead to a more efficient, selective transformation and conformational control of substrates, to a higher local reagent concentration at the metal centers, a stabilization of reactive species and complex intermediates.[3] Additionally, they can facilitate accessibility of bimolecular reaction pathways and be used to overcome entropic control.[3] Organometallic catalysis might cooonceptually benefit from exploiting these functional principles in a bioinspired approach, and cooperative effects in bimetallic systems have indeed been successfully applied in, e.g. epoxidation reactions[4] and olefin hydrogenations[5]. We have been working on the development of various dinuclear metal complexes based on bridging pyrazole-based ligands and their use for the cooperative transformation of small molecules, such as water oxidation and dioxygen activation.[6] Here the syntheses and characterization of novel dinuclear nickel complexes based on compartemental pyrazole/NHC hybrid ligands will be presented, and first reactivity experiments towards the cooperative activation of small molecules will be discussed.

[1] a) E. Jabri, M. B. Carr, R. P. Hausinger, P. A. Karplus, *Science* **1995**, *268*, 998-1004.
   b) R. Haak, S. J. Wezenberg, A. W. Kleij, *Chem. Commun.* **2010**, *46*, 2713-2723.
[2] a) S. W. Ragsdale, *J. Biol. Chem.* **2009**, *284*, 18571-18575.
   b) R. Balasubramanian, S. M. Smith, L. A. Yatsunyk, T. L. Stemmler, A. C. Rosenzweig, *Nature* **2010**, *465*, 115-119.
   c) L. C. Seefeldt, B. M. Hoffman, D. R. Dean, *Annu. Rev. Biochem.* **2009**, *78*, 701-722.
[3] S. Liu, A. R. Mouat, M. Delferro, T. J. Marks, *J. Am. Chem. Soc.* **2014**, *136*, 10460-10469.
[4] T. Sone, A. Yamaguchi, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2008**, *130*, 10078-10079.
[5] D. G. H. Hetterscheid, S. H. Chikkali, B. de Bruin, J. N. H. Reek, *ChemCatChem.* **2013**, *5*, 2785-2793.
[6] a) S. Neudeck, S. Maji, I. López, S. Meyer, F. Meyer, A. Llobet, *J. Am. Chem. Soc.* **2014**, *136*, 24-27.
   b) K. E. Dalle, T. Grüne, S. Dechert, S. Demeshko, F. Meyer, *J. Am. Chem. Soc.* **2014**, *136*, 7428-7434.

Tetrasubstituted Enol Ethers via an *anti*-Carbopalladation/Alkoxylation Cascade

Theresa Schitter[a], Daniel B. Werz[a]*

a: Technische Universität Braunschweig, Institut für Organische Chemie, Hagenring 30, 38106 Braunschweig, Germany

email: t.schitter@tu-braunschweig.de

The formation of two or more bonds in one single step is becoming more and more important, especially in terms of efficiency and atom economy. Such transformations are referred to as 'domino reaction', a term which was first defined by Tietze, when they take place under the same reaction conditions without adding additional reagents and catalysts, and in which the subsequent reactions result as a consequence of the functionality formed in the previous step.[1] Recently, our group developed a formal *anti*-carbopalladation of alkynes.[2] Since such a process leads to a tetrasubstituted vinyl palladium species a terminating step, e.g. a Heck reaction, needs to be added.[3]
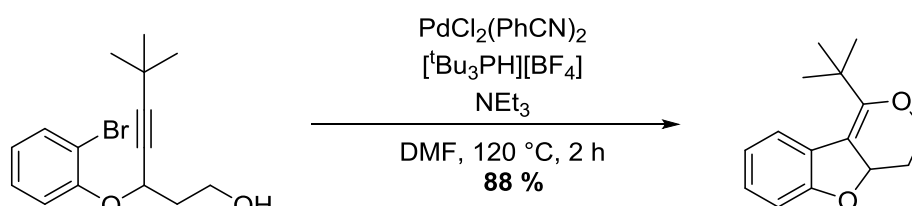
Scheme 4: Example of an *anti*-carbopalladation/alkoxylation cascade.

In the present study a nucleophilic attack by a hydroxyl group is used as terminating process. By this *anti*-carbopalladation/alkoxylation cascade tetrasubstituted enol ethers are easily available (Scheme 1).[4]

[1] L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136.
[2] M. Pawliczek, T. F. Schneider, C. Maaß, D. Stalke, D. B. Werz, *Angew. Chem. Int. Ed.* **2015**, *54*, 4119–4123.
[3] M. Pawliczek, B. Milde, P. G. Jones, D. B. Werz, *Chem. Eur. J.* **2015**, *21*, 12303–12307.
[4] T. Schitter, P. G. Jones, D. B. Werz, *unpublished results*.

Metal-Metal reactivity in Dinuclear Pincertype Ligands

Thomas Kothe, Dennis Manz, Stamatia Katsiaouni, Frank Meyer*

a: Georg-August-Universität Göttingen, Institut für Anorganische Chemie, Department, Tammannstr. 4, 37077 Göttingen, Germany

email: tkothe@chemie.uni-goettingen.de
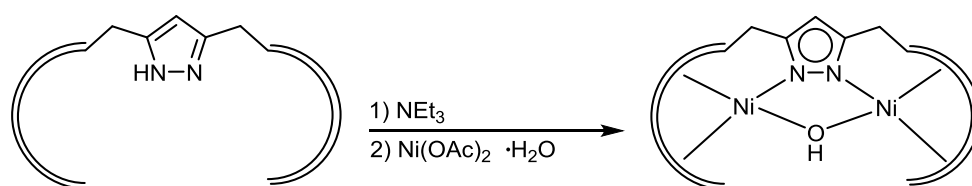
The catalytic conversion of dinitrogen was one of the most groundbreaking accomplishments in the beginning of the 20th century. The biological counterpart of the Haber-Bosch synthesis involves an enzyme complex containing essential metalloproteins based on iron.[1] Literature concerning nickel complexes including dinitrogen was rather scarce compared to analog iron compounds. Recent examples show that nickel complexes bearing *β*-diketiminates can be used to activate dinitrogen. The resulting two-metal-centered species is stabilized by the sterically demanding substituents of the ligand.[2]

Pyrazol bridging ligand systems are suitable to produce dinuclear complexes. Featuring *β*-diketiminate sidearms or similar they can be used to synthesize two-centered nickel pincer complexes with a sterically protected pocket. Experiments indicate that those have a low reactivity which can be substantial for the stabilization of low-valent metal complexes and therefore for the reaction with small molecules like dinitrogen.[3]

[1]   B. E. Smith, *Science* **2002**, *297,* 1654-1655.
[2]   S. Pfirrmann, C. Limberg, C. Herwig, R. Stößer, B. Ziemer, *Angew. Chem. Int. Ed.* **2009**, *48*, 3357-3361.
[3]   D. Manz, S. Katsiaouni, F. Meyer, *unpublished.*

Ate Complexes in Iron-catalyzed Cross-Coupling Reactions

Tobias Parchomyk[a], Prof. Dr. Konrad Koszinowski[a]

a: Georg-August-Universität Göttingen, Institut für Organische und Biomolekulare Chemie, Tammannstraße 2, 37077 Göttingen, Germany

email: tobias.parchomyk@chemie.uni-goettingen.de
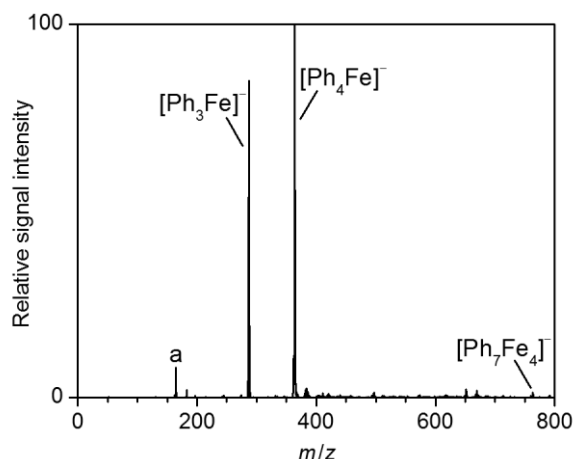
Fe-catalyzed cross-coupling reactions have an outstanding potential for sustainable organic synthesis, but their application is still limited due to an insufficient mechanistic understanding. The nature of the in-situ formed intermediates is discussed controversially with suggested oxidation states of Fe ranging from −II to +II (for the reduced species of the redox couple).[1] Growing evidence points to a prominent role of ate complexes in Fe-catalyzed cross-coupling reactions.[2] As we have shown previously,[3] an ideal method to analyze in-situ formed ate complexes is electrospray-ionization mass spectrometry (ESI MS). This technique also appears well-suited for probing ate complexes in Fe-catalyzed cross-coupling reactions.

Transmetalation of $Fe(acac)_3$ with PhMgCl in THF produces iron ate complexes, whose aggregation and oxidation states crucially depends on the presence of additives and ligands. Addition of *i*PrCl results in the formation of a heteroleptic species Ph_3FeiPr^-. Upon gas-phase fragmentation of the latter, reductive elimination of the cross-coupling product Ph-*i*Pr is observed, proving this elementary reaction as a key step in Fe-catalyzed cross-coupling reaction.

[1] R. B. Bedford, *Acc. Chem. Res.* **2015**, *48*, 1485-1493.
[2] R. B. Bedford et. al., *Angew. Chem. Int. Ed.* **2014**, *53*, 1804-1808; S. B. Muñoz III, S. L. Daifuku, S. W. Brennessel, M. L. Neidig, *J. Am. Chem. Soc.* **2016**, *138*, 7492-7495.
[3] A. Putau, H. Brand, K. Koszinowski, *J. Am. Chem. Soc* **2012**, 134, 613-622; C. Schnegelsberg, S. Bachmann, M. Kolter, T. Auth, M. John, D. Stalke, K. Koszinowksi, *Chem. Eur. J.* **2016**, *22*, 7752-7762.

Molybdenum corrolocenes

<u>Marc-Kevin Zaretzke</u>, Peter N. Schweyen, Benedikt Wolfram, Martin Bröring*

TU Braunschweig, Institute of Inorganic and Analytical Chemistry, Haagenring 30, 38106 Braunschweig, Germany

email: m.zaretzke@tu-braunschweig.de

Corrolocenes are half-sandwich complexes in which the central metal atom is coordinated by one porphyrin-like corrole and one cyclopentadienyl ligand[1,2] This novel, organometallic substance class constitutes a conceptual link between the research fields of porphyrinoids and sandwich complexes, and archetypical issues from both worlds, like electron transfer and catalysis, are interesting objects of study for corrolocene derivatives.
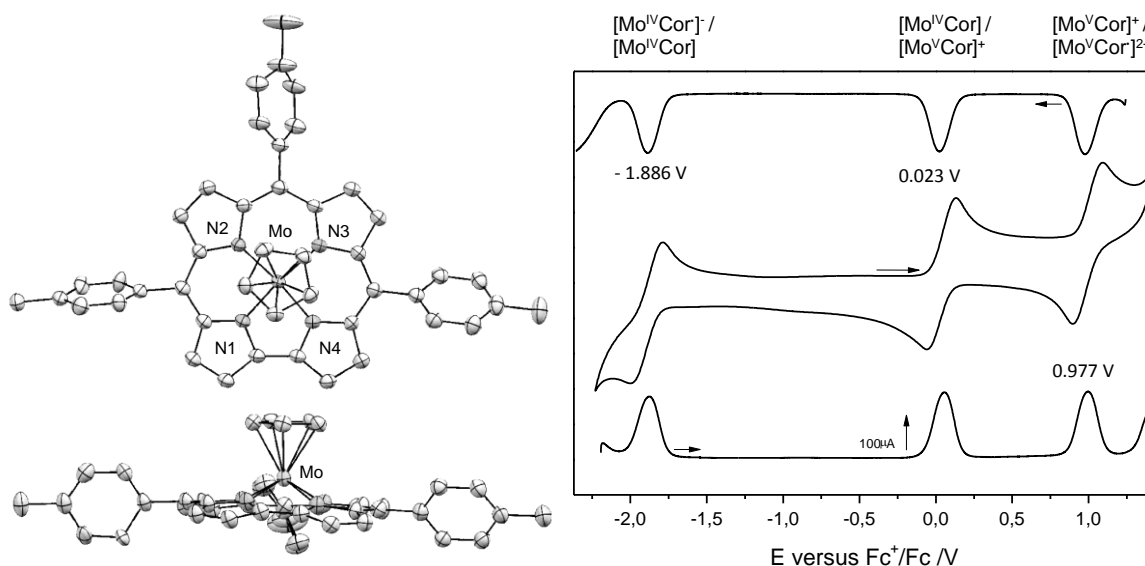
For molybdenum, corrolocenes are available from inreactive oxidomolybdenum(V)[3,4] precursors by a chlorination - reductive coordination sequence in excellent yields, making use of the recently developed *Viking Helmet-corroles*[2] as reactive intermediates. We have now started to conduct electrochemical and spectroelectochemical studies as well as investigations into the catalytic potential of such molybdenum corrolocenes and will present first results on the poster.

[1] H.L. Buckley, W.A. Chomitz, B. Koszarna, M. Tasior, D.T. Gryko, P.J. Brothers, J. Arnold, *Chem Commun.* **2012**, *48*, 10766-10768.
[2] P. Schweyen, *Dissertation*, Technische Universität Carolo-Wilhelmina zu Braunschweig, Braunschweig, **2016**.
[3] I. Luobenznova, M. Raizman, I. Goldberg, Z. Gross, *Inorg. Chem.* **2006**, *45*, 386-394.
[4] I. Niegler-Etinger, I. Goldberg, Z. Gross, **2013**, *52*, 4139-4141.

Chemistry of [1.1]-Ferrocenophane-1,12-dione

Wing-Yin Tsang, Holger Butenschön[*]

Leibniz University of Hannover, Institute of Organic Chemistry, Schneiderberg 1 B, 30167 Hannover, Germany

email: *wing-yin.tsang@oci-hannover.de*
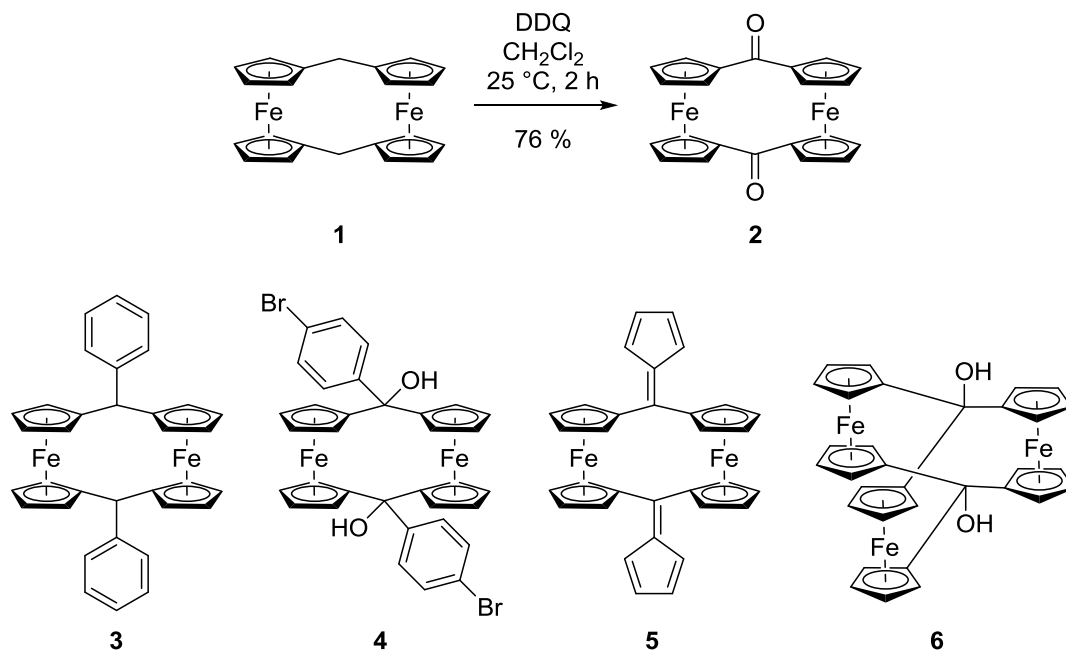
[m.n]Ferrocenophanes are connected by C_mH_n or C_mH_nX chains and are linked together by at least two ferrocene units. [1.1]Ferrocenophane **2** was first reported by Watts *et al.* in 1967. This compound was synthesized by Friedel Crafts alkanoylation and self-condensation but only gave low yields. [1], [2] Butenschön *et al.* reported an improved access of ferrocenophane **2** by oxidizing ferrocenophane **1** with DDQ. Starting from **2** new ferrocenophane derivatives **3-5** were synthesized. Moreover, compound **2** is a potential precursor for trinuclear ferrocenophanes but the synthesis was not successful yet. [3]

Current work of our group is the synthesis of new ferrocenophane derivatives and its investigation in chemical and physical properties. We are especially focused on ferrocenophane derivatives, in which C1 and C12 are linked together by a C_mH_n chain. Additionally, we attempt to synthesize a trinuclear ferrocenophane, such as compound **6**.

[1] U. T. Mueller Westerhoff, *Angew. Chem. Inr. Ed. Engl. 25*, **1986**, 702-717.
[2] T. H. Barr, H. L. Lentzner, W. E. Watts, *Tetrahedron*, **1969**, 6001-6013.
[3] J. R. Garabatos-Perera, T. Wartchow, H. Butenschön, *Adv. Synth. Catal.*, **2009**, *351*, 1139-1147.

Late-Stage Peptide Diversification by Bioorthogonal Catalytic C–H Arylation at 23 °C in H₂O

Alexandra Schischko, Yingjun Zhu, Michaela Bauer and Lutz Ackermann*

Institut für Organische und Biomolekulare Chemie, Georg-August-Universität,
Tammannstraße 2, 37077 Göttingen, Germany

alexandra.schischko@chemie.uni-goettingen.de
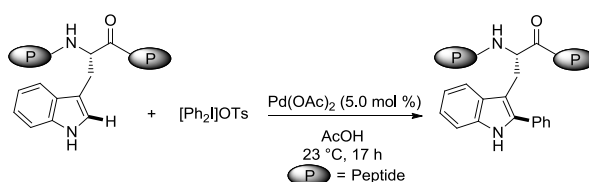
In the past decade, peptides and proteins have been identified as increasingly potent therapeutics, including important applications in proteomics, asymmetric catalysis, diagnosis and drug delivery.[1] Non-proteinogenic amino acids and peptides derived thereof have drawn considerable attention, as they frequently exhibit enhanced activities and improved pharmacokinetics as compared to their natural counterparts. The direct C–H functionalization of natural amino acids has been recognized as a more step-economical tool for the post-synthetic peptide modification.[2] Among the natural amino acids tryptophan is an interesting target, because it alters the structure and function of proteins, has a relatively low natural abundance and is furthermore a fluorescent marker.[3] So far there are only a few transition-metal-catalyzed direct arylations of tryptophan-containing oligopeptides.[4]

Herein, we present a protocol for palladium-catalyzed direct C–H arylations of tryptophan-containing peptides with user-friendly diaryliodonium salts.[5] The reaction system proved applicable to various substitution pattern on the aryl moity, including halogen-containing motifs. Tri- and even hexapeptides were arylated with excellent levels of site-selectivity without racemization. To our delight, the protocol proceeded also in H₂O as the reaction medium, illustrating the potential for *in-vitro* late-stage diversification of biopolymers.

[1] K. Fosgerau, T. Hoffmann, *Drug Discovery Today* **2015**, *20*, 122-128.
[2] A. F. M. Noisier, M. A. Brimble, *Chem. Rev.* **2014**, *114*, 8775-8806.
[3] J. T. Vivian, P. R. Callis, *Biophys. J.* **2001**, *80*, 2093-2109.
[4] S. Preciado, L. Mendive-Tapia, F. Alberico, R. Lavilla, *J. Org. Chem.* **2013**, *78*, 8129-8135; J. Ruiz-Rodríguez, F. Alberico, R. Lavilla, *Chem. Eur. J.* **2010**, *16*, 1124-1127; T. J. Williams, A. J. Reay, A. C. Whitwood, I. J. S. Fairlamb, *Chem. Commun.* **2014**, *50,* 3052-3054.
[5] Y. Zhu, M. Bauer, L. Ackermann, *Chem. Eur. J.* **2015**, *21*, 9980-9983.

Overcoming the Limitations of C–H Activation with Strongly Coordinating N–Heterocycles by Cobalt Catalysis

Hui Wang,[a] Mélanie M. Lorion,[a] Lutz Ackermann*[a]

Georg-August-Universität Göttingen, Institut für Organische und Biomolekulare Chemie, Tammannstraße 2, Göttingen, 37077, Germany

email: Lutz.Ackermann@chemie.uni-goettingen.de
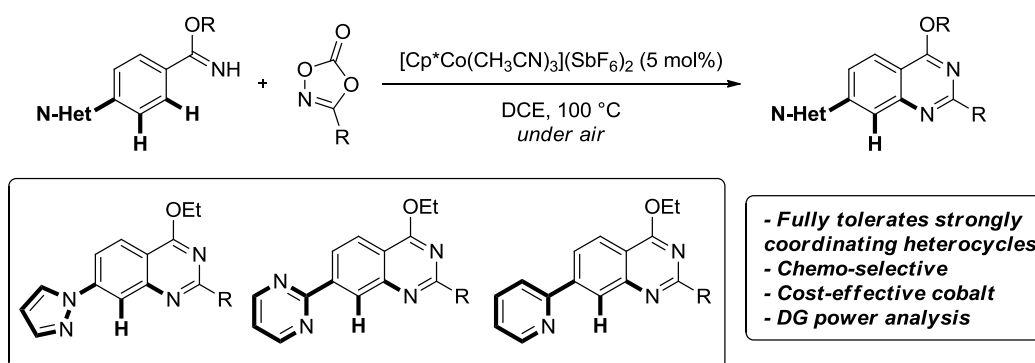
C–H functionalization technology has emerged as an increasingly powerful platform in modern organic synthesis.[1] Despite tremendous advances during the past decades, strongly coordinating N–heterocycles continue to pose major challenges to transition metal catalyst, often resulting in inhibition of catalytic turnover. More importantly, biologically relevant N–heterocycles, such as pyrazoles, pyrimidines or pyridines, strongly coordinate to the active transition metal catalyst, resulting in proximity-induced C–H activation in the *ortho* position,[2] which severely limits further applications.[3]

Here, we report on the first cobalt(III)–catalyzed C–H amidation of imidates, which the strongly coordinating heterocycles, including pyrazole, pyrimidine or pyridine being fully tolerated.[4] Thereby, structurally diverse quinazolines were accessed in a step-economical fashion with ample substrate scope. Our findings further provide a first comparative study on the directing group power in cobalt(III)–catalyzed C–H functionalization chemistry.

[1] (a) J. K. Kim, K. Shin, S. Chang, *Top. Organomet. Chem.* **2016**, *55*, 29-51; (b) M. Moselage, J. Li, L. Ackermann, *ACS Catal.* **2016**, *6*, 498-525.
[2] (a) D. A. Collby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624-655; (b) L. Ackermann, *Top. Organomet. Chem.* **2007**, *24*, 35-60.
[3] L. G. Mercier, M. Leclerc, *Acc. Chem. Res.* **2013**, *46*, 1597-1605.
[4] H. Wang, M. M. Lorion, L. Ackermann, *Angew. Chem. Int. Ed.* **2016**, *55,* 10386-10390.

List of Participants

Invited Speakers

Prof. Dr. Suzanne A. Blum

Department of Chemistry

University of California

Irvine, California (USA)

Prof. Dr. Burkhard König

Institute of Organic Chemistry

Faculty of Chemistry and Pharmacy

University of Regensburg

Regensburg (Germany)

Prof. Dr. Pedro J. Pérez

Laboratorio de Catálisis Homogénea

Centro de Investigación en Química

Sostenible

Universidad de Huelva

Huelva (Spain)

Prof. Dr. Regina Palkovits

Institut für Technische und

Makromolekulare Chemie (ITMC)

RWTH Aachen University

Aachen (Germany)

Prof. Dr. Kálmán J. Szabó

Department of Organic Chemistry

Stockholm University

Stockholm (Sweden)

Dr. Thomas Schaub

Catalysis Research Laboratory Heidelberg

& Synthesis and Homogeneous Catalysis

BASF SE

Ludwigshafen (Germany)

Prof. Dr. Sylviane Sabo-Etienne

Laboratoire de Chimie de Coordination du

CNRS (LCC-CNRS)

Université de Toulouse

Toulouse (France)

Prof. Dr. Moris S. Eisen

Schulich Faculty of Chemistry

Technion −Israel Institute of Technology

Haifa (Israel)

Prof. Dr. Lutz Gade

Anorganisch-Chemisches Institut

University of Heidelberg

Heidelberg (Germany)

Prof. Dr. Shigeki Matsunaga

Laboratory of Synthetic and Industrial

Chemistry

Faculty of Pharmaceutical Sciences

Hokkaido University

Sapporo (Japan)

Prof. Dr. Michael L. Neidig

Department of Chemistry

University of Rochester

Rochester, New York (USA)

Participants

Name	Institute	University
Prof. Dr. Ackermann, Lutz	Institute of Organic Chemistry	Georg-August-University of Göttingen
Dr. Doddi, Adinarayna	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Ahlburg, Nils Lennart	Institute of Organic Chemistry	TU Braunschweig
Anke, Felix	Leibniz Institute for Catalysis	University of Rostock
Àrias, Òscar	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Baabe, Dirk	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Bannenberg, Thomas	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Prof. Dr. Bauer, Matthias	Inorganic Chemistry	Paderborn University
Bednarova, Eva	Faculty of Science, Organic Chemistry	Charles University in Prague
Bittner, Celine	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Bockfeld, Dirk	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Böge, Matthias	Institute of Inorganic and Applied Chemistry	Hamburg University

Dr. Borner, Corinna	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Böser, Richard	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Bothe, Elena	Institute of Technical Chemistry	TU Braunschweig
Dr. Brandhorst, Kai	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Breder, Alexander	Institute of Organic Chemistry	Georg-August-University of Göttingen
Prof. Dr. Bröring, Martin	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Dorazio, Sarina	Institute of Inorganic Chemistry	University of Göttingen
Dr. Döring, Cindy	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Du, Jia-Pei	Institute of Inorganic Chemistry	University of Göttingen
Ehrhorn, Henrike	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Ehrlich, Nico	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Eltaher, Ashraf	Faculty of Pharmacy	Zagazig University
Enachi, Andreea	Institute of Inorganic and Analytical Chemistry	TU Braunschweig

Dr. Frank, Rene	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Franz, Heiko	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Frosch, Jenni	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Glüer, Arne	Institute for Inorganic Chemistry	Georg-August-University of Göttingen
Hackl, Ludwig	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Han, Delong	Leibniz Institute for Catalysis	University of Rostock
Heinisch, Lauren	Institute of Organic Chemistry	Leibniz University of Hannover
Hoffmann, Martin	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Höhne, Martha	Leibniz Institute for Catalysis	University of Rostock
Homolya, Gabor	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Jess, Kristof	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Joksch, Markus	Leibniz Institute for Catalysis	University of Rostock
Kaiser, Reinhard Peter	Faculty of Science, Organic Chemistry	Charles University in Prague
Kindjajev, Andrei	Inorganic Chemistry	Christian-Albrecht-University of Kiel

Dr. Kleeberg, Christian	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Kleeberg, Kirstin	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Köhne, Ingo Dennis	Institute of Inorganic Chemistry	University of Göttingen
Köllmann, Christoph	Institute of Organic Chemistry	TU Braunschweig
Kolter, Marlene	Institute of Organic and Biomolecular Chemistry	University of Göttingen
Koneczny, Marvin	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Prof. Dr. Koszinowski, Konrad	Institute of Organic and Biomolecular Chemistry	University of Göttingen
Kothe, Thomas	Institute of Inorganic Chemistry	University of Göttingen
Kreft, Alexander	Institute of Organic Chemistry	TU Braunschweig
Kuhn, Vitali	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Lau, Caroline	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Lücht, Alexander	Institute of Organic Chemistry	TU Braunschweig
Lücke, Ana-Luiza	Institute of Organic Chemistry	Clausthal University of Technology

Maftei, Catalin	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Maftei, Elena	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Melcher, Daniel	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Prof. Dr. Menzel, Henning	Institute of Technical Chemistry	TU Braunschweig
Prof. Dr. Meyer, Franc	Institute of Inorganic Chemistry	University of Göttingen
Prof. Dr. Neda, Ion	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Nekkanti, Phani Kumar	Institute of Organic Chemistry	Georg-August-University of Göttingen
Oelmann, Julian	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Ortgies, Stefan	Institute of Organic Chemistry	Georg-August-University of Göttingen
Oschmann, Wiebke	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Paesch, Alexander	Institute of Organic Chemistry	University of Göttingen
Parchomyk, Tobias	Institute of Organic Chemistry	University of Göttingen
Patalag, Lukas	Institute of Organic Chemistry	TU Braunschweig

Peters, Marius	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Petzold, Martin	Institute of Organic Chemistry	TU Braunschweig
Pfeil, Mareike	Inorganic Chemistry	Christian-Albrecht-University of Kiel
Raeder, Jan	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Reiners, Matthias	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Resch, Stefan	Institute of Inorganic Chemistry	University of Göttingen
Rode, Katharina	Institute of Organic Chemistry	University of Göttingen
Rösner, Jörn	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Sachse, Florian	-	University of Leipzig
Sauermann, Nicolas	Institute of Organic Chemistry	University of Göttingen
Dr. Scepaniak, Jeremiah	Institute of Inorganic Chemistry	University of Göttingen
Schitter, Theresa	Institute of Organic Chemistry	TU Braunschweig
Schischko, Alexandra	Institute of Organic and Biomolecular Chemistry	Georg-August-University of Göttingen

Schiwek, Christoph	Institute of Inorganic Chemistry	University of Göttingen
Schmiel, David	Institute of Organic Chemistry	Leibniz University of Hannover
Schmiel, Sinem	Institute of Organic Chemistry	Leibniz University of Hannover
Schmutzler, Felix	-	University of Leipzig
Schnabel, Tobias	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Schütze, Mike	Institute of Inorganic Chemistry	University of Göttingen
Dr. Schweyen, Peter	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Seeba, Marten	Institute of Inorganic Chemistry	University of Göttingen
Dr. Siewert, Inke	Institute of Organic Chemistry	University of Göttingen
Silva Valverde, Miguel	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Tamai, Hideki	Institute of Organic Chemistry	TU Braunschweig
Prof. Dr. Tamm, Matthias	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Tamm, Victoria	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Triebert, Dominik	-	University of Leipzig

Tröndle, Sabrina	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Tsang, Wing-Yin	Institute of Organic Chemistry	Leibniz University of Hannover
Volkmann, Christian	Institute of Inorganic Chemistry	Georg-August-University of Göttingen
Wagner, Jannik	Institute of Physical Chemistry	University of Göttingen
Dr. Walter, Marc	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Wang, Hui	Institute of Organic and Biomolecular Chemistry	Georg-August-University of Göttingen
Warratz, Svenja	Institute of Organic Chemistry	Georg-August-University of Göttingen
Weber, Sebastian	-	University of Leipzig
Prof. Dr. Werz, Daniel	Institute of Organic Chemistry	TU Braunschweig
Weske, Sebastian	Institute of Organic and Biomolecular Chemistry	University of Göttingen
Dr. Winkler, Andrea	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Dr. Wolfram, Bennedikt	Institute of Inorganic and Analytical Chemistry	TU Braunschweig
Zaretzke, Marc-Kevin	Institute of Inorganic and Analytical Chemistry	TU Braunschweig

Useful Information

Phone numbers

Emergency: 112

Police: 110

On-duty medical unit: 116117

On-duty pharmacy: 22833, www.aponet.de

Taxi: +49 531 5991

       +49 531 55555

       +49 531 62121

       +49 531 66666

Technische Universität Braunschweig:

       +49 531 391-0 (General)

       +49 531 391-5303 (Inorganic Chemistry Department)

Conference Hotels

Hotel Deutsches Haus

Ruhfäutchenplatz 1
38100 Braunschweig
Phone: +49 531 1200-0
resi@deutscheshaus24.de

Hotel "An der Stadthalle"

Leonhardstraße 21
38102 Braunschweig
Phone: +49 531 73068
info@hotel-an-der-stadthalle.de

Stadthotel Magnitor

Am Magnitor 1
38100 Braunschweig
Phone: +49 531 4713-0
info@stadthotel-magni.de

Steigenberger Parkhotel

Nîmes-Straße 2
38100 Braunschewig
+49 531 48222-0
braunschweig@steigenberger.de

Advance Hotel

Mittelweg 7
38106 BraunschweigTelefon:
Phone: +49 531 390770
info@advance-hotel.de

Places of interest

Tourist Information Office

Kleine Burg 14
38100 Braunschweig
Phone: +49 531 470-2040
www.braunschweig.de/english

Burgplatz (Castle Square):

- Braunschweig Lion Statue
- St. Blasii Cathedral (Dom)
- Dankwarderode Castle
- Braunschweig State Museum (Landesmuseum)

Rathaus (Town Hall)

Platz der Deutschen Einheit 1

Altstadtmarkt:

- Old Town Hall (Altstadtrathaus)
- Church of St. Martin
- Old Customs House (Altes Zollhaus)
- Cloth Merchant's House (Gewandhaus)

Magni District:

- many half-timbered houses (and the oldest one in Braunschweig)
- Happy RIZZI House
- Church of St. Magni
- Municipal Museum

Ducal Palace and Quadriga (and shopping mall)

Schlossplatz 1
38100 Braunschweig

Richmond Palace

Wolfenbütteler Straße 55
38124 Braunschweig

Riddagshausen District and St. Maria Abbey

Klostergang 64
38104 Braunschweig

Where to eat

Student cafeteria (Mensa)

Katharinenstr. 1

**Falafelhaus
(Arab street food)**

Schleinitzstr. 1

**La Cupola
(Italian cuisine)**

Pockelsstraße 11

**QUARTIER
(burger, pasta and backed potatoes)**

Bültenweg 89

**McMurphy´s
(salads and sandwiches)**

Bültenweg 10

**Eusebia Bar & Café
(varied cuisine)**

Spielmannstraße 11

**Parco am Botanischen Garten
(Italian cuisine)**

Bültenweg 95

**Troja
(Anatolian cuisine)**

Bültenweg 6

**Zu den Vier Linden
(German cuisine)**

Wiesenstraße 5

**Mutter Habenicht
(German cuisine)**

Papenstieg 3

**Schadt's-Brauerei-Gasthaus
(German cuisine)**

Marstall 2 / Höhe 28

**Rheinische Republik
(Rhenish cuisine)**

Neue Str. 10

**Wirtshaus "am Kohlmarkt"
(Bavarian cuisine)**

Kohlmarkt 10

Conference Venue

The lectures will be held at the **old building** of the Technische Universität Braunschweig (Pockelsstr. 4). The conference room **SN 19.1** is located to the right on the ground floor.

Nearest bus or tram stations:

- Mühlenpfordstraße (M1, M2)
- Pockelsstraße (bus 419, 429)
- Theaterwall or Botanischer Garten (M3)
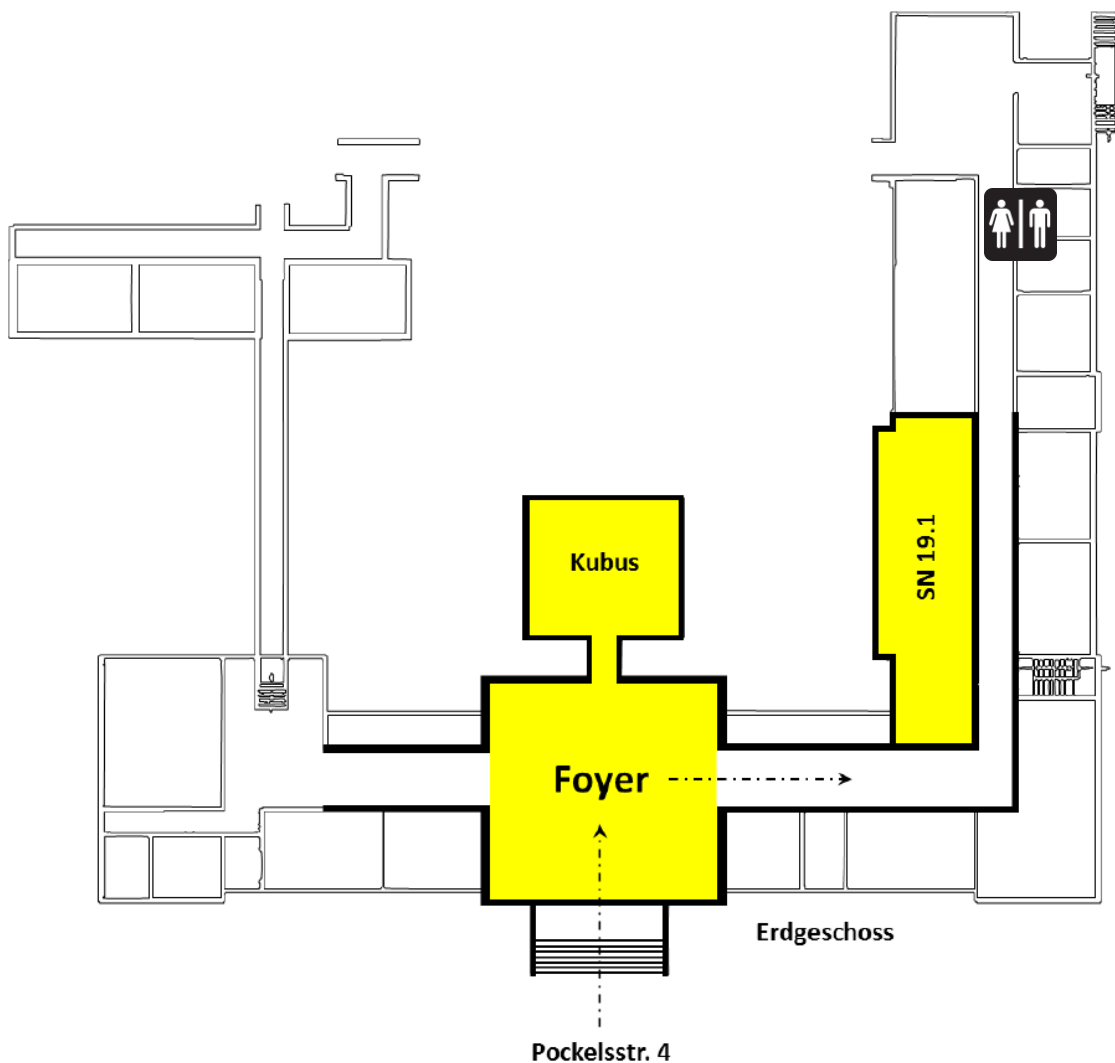
Conference Dinner

The conference dinner will take place in the ballroom of the old town hall (Altstadtrathaus). This room is called in Braunschweig with the historic name *Große Dornse*, meaning Great Heated Room.

How to get there:

- ➢ **walking**: 18:15 get together in front of the Foyer

- ➢ **nearest bus or tram stations:**
    - ❖ Altstadtmarkt (bus 411, 413, 416, 418, 422, 433)
    - ❖ Friedrich-Wilhelm-Platz (M3, M5)

Old City Hall / Uwe Gehring / Wikimedia Commons / CC-BY-SA-3.0

Public transport map

Legende
Endhaltestelle
Zeitweise Endhaltestelle
Haltestelle wird nur in angezeigter Richtung bedient
Straßenbahnlinie mindestens im 15-Minuten-Takt
Buslinie mindestens im 15-Minuten-Takt
Buslinie im 30-Minuten-Takt
Buslinie im 60-Minuten-Takt
Regionalbuslinie
Anruf-Linien-Taxi (ALT)
Während der Baumaßnahme gesperrter Linienweg
einzelne Fahrten
Kundenzentrum/Ticketverkauf Verkehrs-GmbH
Park+Ride
Bike+Ride
Braunschweiger Stadtteil

Ihre Braunschweiger Verkehrs-GmbH

Querum
Hondelage
Flughafen
Kralenriede
Flughafen
Richard-Strauß-Weg
Am Büten
Nordstr.
Hans-Sommer-Str.
Bültenweg
Pockelsstr.
Siegfriedviertel
Gliesmaroder Str.
Volkmarode
Bebelhof
Riddagshausen
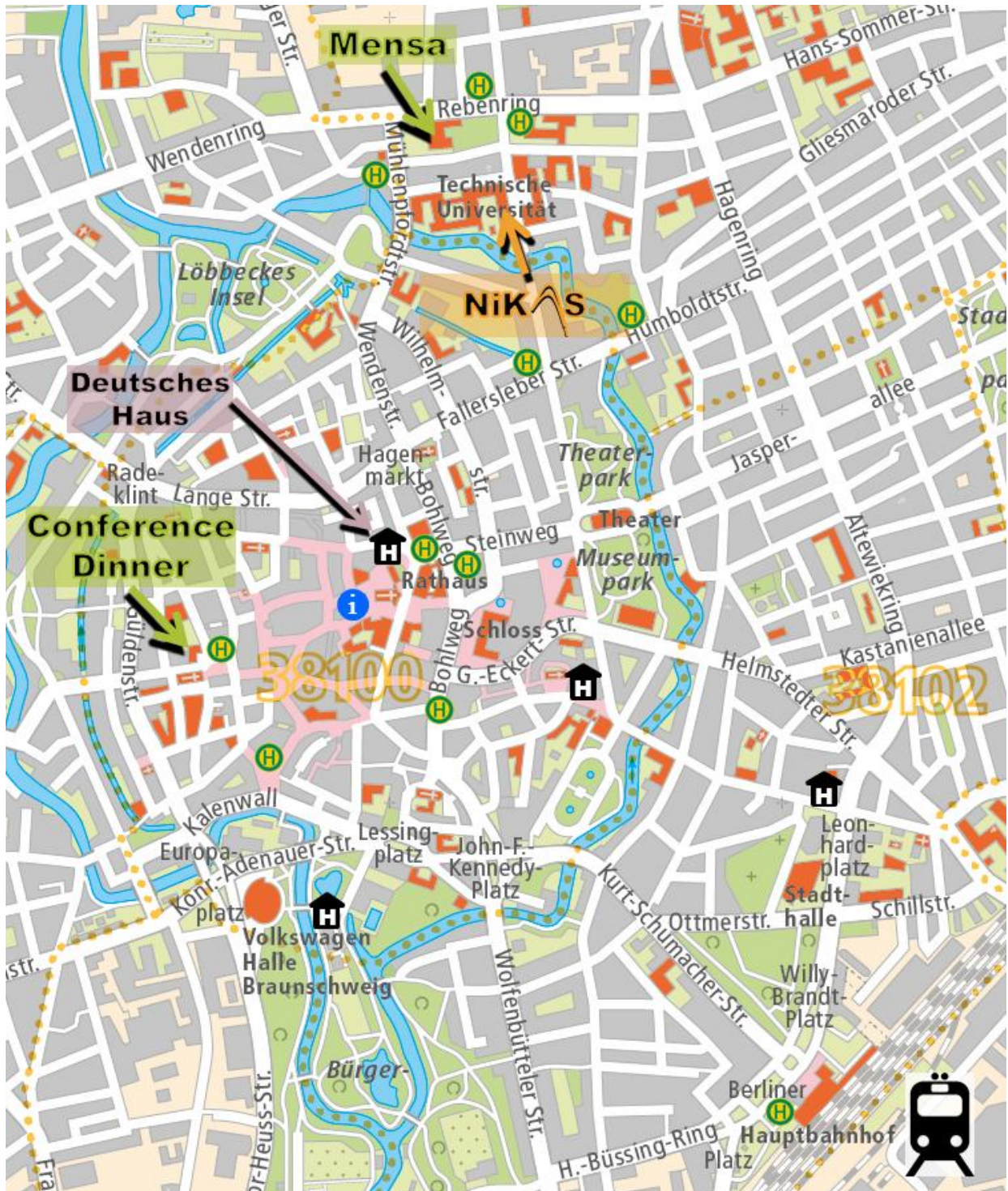Jasperallee
Querumer Forst, Bevenrode
Kasernenstr.
Botanischer Garten
Museumstr.
Steintor
Kastanienallee
Hochstr.
Helmstedter Str.
Willy-Brandt-Platz
Leonhardplatz (Stadthalle)
TU Braunschweig
Staatstheater
Theaterwall
Mühlenpfordtstr.
Schützenplatz
Ludwigstr.
Siegfriedviertel
Wenden
Nordstadt
Hamburger Str.
Am Wendentor
Hagenmarkt
Georg-Eckert-Str.
Schloss
St. Magni
Am Magnitor
Stadthalle
Viewegs-Garten
Campestr.
Hauptbahnhof
Heinrich-Büssing-Ring
Mascherode
Helmstedter Str.
Rathaus
Kundenzentrum Verkehrs-GmbH
Packhof
Alte Waage
Innenstadt
Dom
Burglöwe
Münzstr.
Burg
Friedrich-Wilhelm-Str.
Friedrich-Wilhelm-Platz
John-F.-Kennedy-Platz
Leisewitzstr.
Bürgerpark
Wolfenbüttel Bahnhof
Heidberg
Stöckheim
Inselwall
Radeklint
Hintern Brüdern
Altstadtmarkt
Gildenstr.
Südstr.
Am Wassertor (Volkswagen Halle)
Volkswagen Halle
Holzhof (Volkswagen Halle)
Ekbertstr.
Messegelände Nordeingang
Otto-von-Guericke-Str.
Am Klosterkamp
Leiferde
Amalienplatz
Klinikum Celler Str.
Petristr.
Rudolfplatz
Kälberwiese
Tuckermannstr.
Goslarsche Str.
Westliches Ringgebiet
Johannes-Selenka-Platz
Europaplatz
Luisenstr.
Helenenstr.
Fabrikstr.
Cyriaksring
Maschplatz
Maschstr.
Groß Schwülper
Völkenrode
Lehndorf
Hermannstr.
Hildesheimer Str.
Vechelde
Maienstr.
Madamenweg
Pfingststr.
Raffteich
Hochschule für Bildende Künste
Weststadt
Broitzem
Am Jödebrunnen
Westbhf.
Weststadt
Wipshausen
Prt.B.
Völkenrode
Lamme

Oker

City map

www.braunschweig.de/geodaten

Scientific Program

	Monday, September 19	Tuesday, September 20
		Session 3
8:45–9:30		**I6** T. Schaub
9:30–10:15		**I7** S. Sabo-Etienne
10:15–10:45		Coffee Break
		Session 4
10:45–11:30	11:00–13:00 Arrival & Registration	**I8** M. S. Eisen
11:30–12:15		**I9** L. Gade
12:15–13:00		Lunch
13:00–13:15	Welcome	
	Session 1	Session 5
13:15–14:00	**I1** S. A. Blum	**I10** S. Matsunaga (GDCh)
14:00–14:45	**I2** B. König	**I11** M. L. Neidig
14:45–15:00	Foto	Closing Remarks & Prizes
15:00–15:30	Coffee Break	15:00 Departure
	Session 2	
15:30–16:15	**I3** P. J. Pérez	
16:15–17:00	**I4** R. Palkovits	
17:00–17:45	**I5** K. J. Szabó	
19:00–23:00	Poster Session & Conference Dinner	

Catalysis for Sustainable Synthesis

https://www.tu-braunschweig.de/iaac/casus