Max-Planck-Institut
für Kohlenforschung

Report for the Scientific Advisory Board

2014 – 2016

Max-Planck-Institut
für Kohlenforschung

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Max-Planck-Institut
für Kohlenforschung

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Emeritus Scientific Members of the Max-Planck-Institut für Kohlenforschung

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Professor Dr. Manfred Reetz

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Elected Members of the Scientific Council of the Max Planck Society, Section of Chemistry, Physics and Technology

Dr. Christian Lehmann (July 2012 – July 2016)
Dr. Michael Felderhoff (since July 2016)

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CHAPTER 1

The Max-Planck-Institut für Kohlenforschung

1.1 History

The decision to found a Kaiser-Wilhelm-Institut für Kohlenforschung (coal research) in Mülheim/Ruhr was taken in 1912 by the Kaiser Wilhelm Society, representatives of the coal industry and the town of Mülheim/Ruhr. In 1913 Franz Fischer (1877-1947), who in 1911 had been appointed professor for electrochemistry at the Technical University in Berlin-Charlottenburg, was chosen as the first Director.

Franz Fischer and his co-workers carried out basic research in a number of areas concerning the formation and chemical composition of coal as well as on its conversion into solid, liquid and gaseous products. The most important contribution culminated in the so-called Fischer-Tropsch process for coal liquefaction. In 1925, Franz Fischer and the group leader Hans Tropsch reported that liquid hydrocarbons (alkanes) can be produced from carbon monoxide and hydrogen in the presence of solid metal catalysts. The mixture of the two gases (synthesis gas) necessary for this new process was prepared by the "gasification" of coal with steam and oxygen at 900°C. In 1925 the "Studien- und Verwertungsgesellschaft mbH" was founded for the purpose of exploiting the patents. By the early 1940s nine industrial plants were operating in Germany producing ca. 600 000 tons of liquid hydrocarbons per year. Today there is a renewed interest in Fischer-Tropsch technology with plants in Sasolburg/South Africa, Malaysia, and Qatar (using natural gas instead of coal). In 1939 Franz Fischer instigated a change in the status of the Institute; it became a foundation of private law with the objective of supporting the scientific investigation of coal for the public benefit.

Following Fischer's retirement in 1943 Karl Ziegler (1898-1973) was appointed Director of the Institute. After the founding of the Max Planck Society as the successor of the Kaiser Wilhelm Society in 1948, the Institute obtained its present name in 1949. As a consequence of Ziegler's appointment, the main research efforts shifted to organometallic chemistry. Based upon his earlier experience with the organic compounds of the alkali metals, Ziegler and his co-workers turned their attention to aluminum. In 1949 they reported the multiple addition of ethylene to aluminum alkyls which became known as the "Aufbau" reaction. The product of this oligomerization was a mixture of aluminum alkyls having long, linear alkyl chains attached to the metal; these compounds could be converted into α-olefins or primary alcohols, the latter being important for the production of biodegradable detergents. An unexpected observation during the systematic investigation of this reaction led to the discovery that transition metals have a dramatic effect on the "Aufbau" reaction; in particular, the addition of

compounds of titanium or zirconium led to the coupling of up to 100 000 ethylene molecules at normal pressure and temperature. The optimized process employed the so-called organometallic “Mischkatalysatoren” consisting of an aluminum alkyl and a transition metal salt. It was patented in 1953 and led to a dramatic development of the industrial production of polyethylene and polypropylene as cheap and versatile polymers. The licensing of the patents enabled the Institute to be operated on an independent financial basis for nearly 40 years. As a result the Institute expanded and a number of new buildings such as the library, the main research laboratory, pilot plant facilities, high pressure workshops and an instrumental analysis building were constructed. Karl Ziegler was awarded the Nobel Prize for Chemistry in 1963 (together with Guilio Natta who analyzed the stereochemistry of polypropylene). Ziegler subsequently created the Ziegler-Fund (in 1968) and the Ziegler-Foundation (in 1970), which still play an important role in financing the Institute.

In recognition of the fundamental importance of Karl Ziegler’s discoveries and their tremendous implications for industry, the German Chemical Society (GDCh) bestowed the title “Historische Stätte der Chemie” (Historical Landmark of Chemistry) on the Institute in 2008. A bronze plaque on the historic building commemorates this event.

Günther Wilke followed Karl Ziegler as Director in 1969. His research concentrated on the organometallic chemistry of the transition metals (especially nickel) and their application in homogeneous catalysis. For example, the developed cyclodimerization and the cyclotrimerization of butadiene using homogeneous nickel catalysts were exploited industrially. Ligand-control led to the development of highly selective homogeneous catalysts, including catalysts bearing chiral enantiopure ligands. The Institute also pursued research in electrochemistry, contributing an efficient electrochemical synthesis of iron(II) ethanolate which became industrially important for the production of ferrocene. Investigations on the use of supercritical gases for purification purposes, which were first described by Kurt Zosel at the Institute in 1963, led to a large-scale industrial process for the decaffeination of green coffee beans using supercritical carbon dioxide. Roland Köster, a Scientific Member of the Max Planck Society since 1969, headed his own group during these years, which was primarily concerned with organoboron chemistry.

In 1993 Manfred T. Reetz was appointed Director of the Institute. He initiated projects pertaining to catalysis, transition metal colloids and directed evolution of enzymes. He also re-defined the scientific activities of the Institute as a whole, a development which

resulted in the establishment of five Departments comprising Synthetic Organic Chemistry, Homogeneous Catalysis, Heterogeneous Catalysis, Organometallic Chemistry and Theory. This plan foresaw the appointment of Scientific Members as Directors of these Departments. In 1995 Andreas Pfaltz joined the Institute as the Director of the Department of Homogeneous Catalysis, while Manfred T. Reetz headed the Department of Synthetic Organic Chemistry. Thereafter the appointments of Ferdi Schüth (Heterogeneous Catalysis), Alois Fürstner (Organometallic Chemistry) and Walter Thiel (Theory) followed. Thus, the scientific activities of the Institute were put on a broad and interdisciplinary basis.

Following Andreas Pfaltz' move back to Basel, the position of the Director of the Department of Homogeneous Catalysis remained vacant for some time. Benjamin List from the Scripps Research Institute, La Jolla, was identified as a pioneer in the then emerging field of organocatalysis. He was hired on a C3-position (associate professor) in 2003, and promoted to become the Director of the Department in 2005.

Manfred Reetz, although Emeritus since 2011, remains an External Group Leader of the Institute; his laboratory is physically located at the Philipps-Universität Marburg, where he is Hans Meerwein Research Professor.

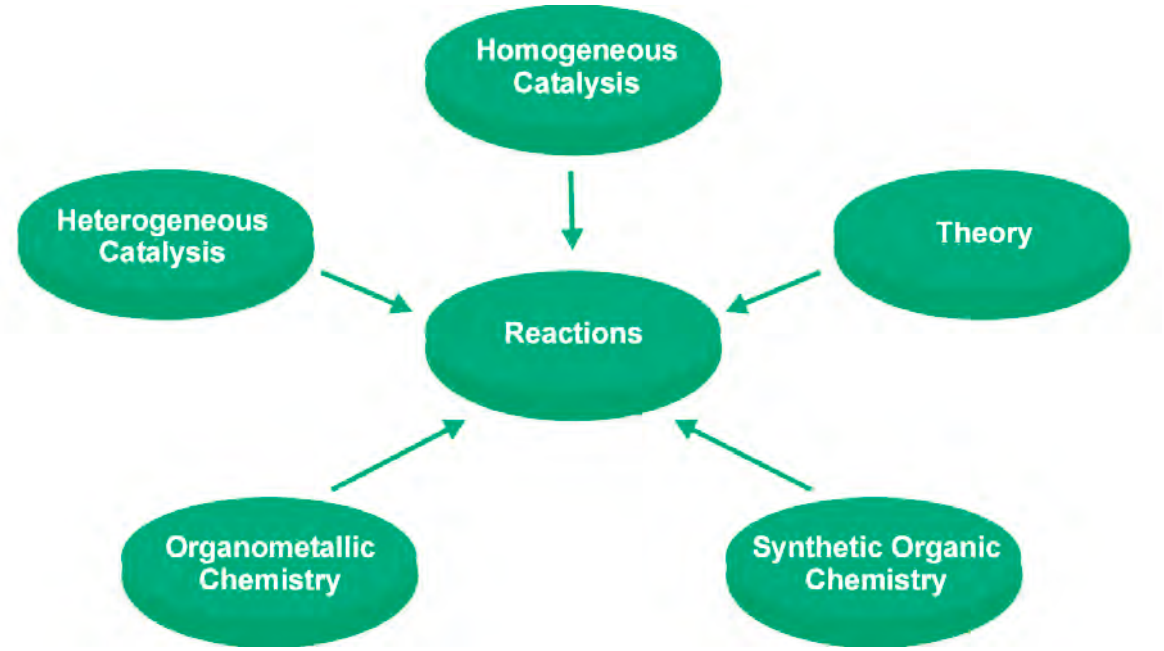
In 2015, Tobias Ritter was appointed as new Director of the Department of Synthetic Organic Chemistry. His research interests are focused on the discovery of new reactivity that provides practical access to compounds of interest for catalysis, medicine and material science. The portfolio encompasses late-stage fluorination and its application to radiolabeling for positron emission tomography (PET); this particular line of research is made possible by a new radiochemistry laboratory.

The Directors of the Departments form a Board which is responsible for all decisions; the Managing Director is elected from this Board. As successor to Manfred Reetz, Ferdi Schüth served as Managing Director from 2003-2005, followed by Walter Thiel (2006-2008), Alois Fürstner (2009-2011), Benjamin List (2012-2014), Walter Thiel (2015) and Alois Fürstner (2016-2017).

In 2014 the Institute celebrated its 100th anniversary with a series of special events. A book entitled "*Katalyse auf dem Kahlenberg*" was published that provides a detailed overview over the historic development and the current status. For more information, see the Chapter "Public Relations".

1.2 Current Research Areas

The research areas of the Max-Planck-Institut für Kohlenforschung are defined by the five Departments comprising Synthetic Organic Chemistry, Homogeneous Catalysis, Heterogeneous Catalysis, Organometallic Chemistry and Theory. The central theme pervading all Departments is basic research in the catalytic transformation of compounds and materials with the highest degree of chemo-, regio- and stereoselectivity under conditions which maximize efficient use of natural resources.



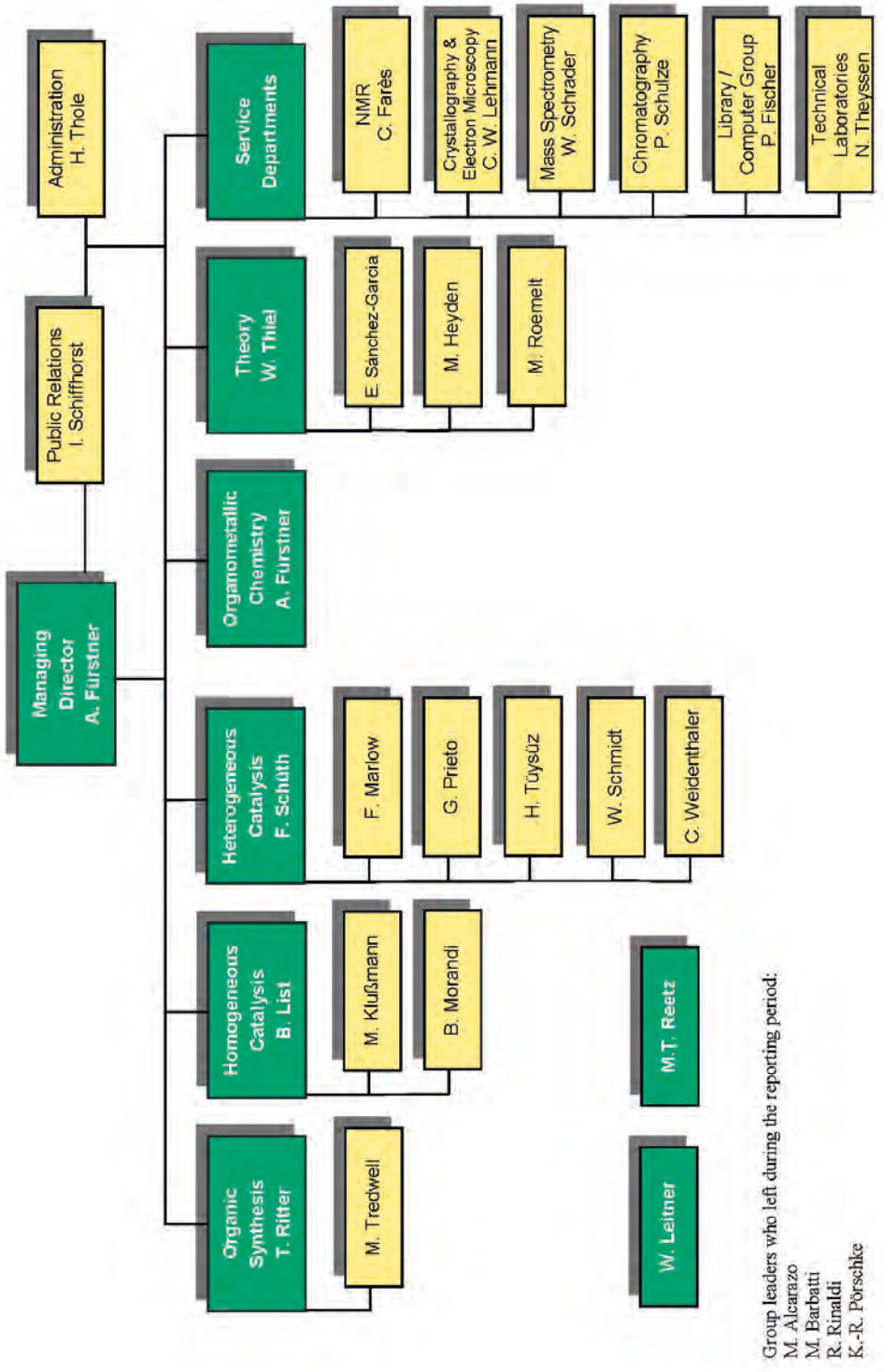
Catalysis is viewed world-wide as the key technology in the establishment of economically viable and ecologically benign chemical processes of the future. However, the efficiency of numerous catalytic systems is far from ideal and for many important chemical transformations appropriate catalysts have not even been found. Moreover, many fundamental aspects of catalysis are still poorly understood. Research in catalysis from a fundamental point of view calls for a high degree of interdisciplinarity. For a truly integrated approach, expertise is needed in homogeneous and heterogeneous catalysis, organocatalysis, biocatalysis, organometallic chemistry, organic as well as inorganic synthesis, and theory. By necessity, this requires the appropriate laboratories, equipment and instrumentation all in one unit. The idea of assembling five research Departments encompassing all major branches of catalysis under one roof therefore ensures the “critical mass” and the diversity necessary for meeting the scientific

challenges in this field. It is this factor which distinguishes research in Mülheim/Ruhr from related activities at universities. Indeed, the organizational concept of the Institute fosters an atmosphere conducive to scientific cross-fertilization and various kinds of synergisms. Traditional “gaps” between homogeneous and heterogeneous catalysis as well as biocatalysis are losing significance, and specific links between the Departments have developed. Moreover, a number of collaborations between the Institute and university groups are in operation, leading to significant scientific output as well as efficient use of the available instrumentation.

Specific projects in the experimentally oriented Departments include the design and evolution of unusual kinds of achiral and chiral ligands, novel solid materials displaying specific functional properties, catalytic reactions using small organic molecules as catalysts, new transformations catalyzed by noble and non-noble metals, methods for radio-labeling of clinically relevant compounds, and directed evolution of selective enzymes for use in organic chemistry. Much emphasis is also placed on the development of atom-economical strategies for catalysis-based syntheses of natural products of biological signifiance, the investigation of catalytically relevant reactive intermediates, the creation of combinatorial techniques in catalysis, and the study of how solid materials nucleate from solutions of relevant precursors. The results of many of these studies are expected to stimulate further research in actual catalyst design. The development of theoretical methods in quantum mechanics and molecular modeling in the Theory Department is also of prime importance, not only for extending the scope of computational methodology, but also for specific applications in homogeneous transition metal catalysis and biocatalysis.

In summary, the Institute has been organized to meet the needs for concerted interdisciplinary catalysis research from a fundamental point of view. Its objective is to carry out basic research to the point where industry and/or institutions dedicated to applied science can take over.

1.3 Organigram 2016



1.4 Members of the Scientific Advisory Board

For the period 2015-2017:

Prof. Dr. Janine Cossy	École Supérieure de Physique et Chimie Associé au CNRS, UMR 7084 10, rue Vauquelin 75231 Paris cedex 05, France
Prof. Dr. Dirk de Vos	KU Leuven Centrum voor Oppervlaktechemie en Katalyse Kasteelpark Arenberg 23 – bus 2461 3001 Leuven, Belgium
Prof. Dr. Jeremy Harvey	KU Leuven Theoretical and Computational Chemistry Group Celestijnenlaan 200f – box 2404 3001 Leuven, Belgium
Prof. Dr. Paul Knochel	Ludwig-Maximilians-Universität München Fakultät Chemie und Pharmazie Butenandtstr. 13 81377 München, Germany
Prof. Dr. Scott J. Miller	Yale University Department of Chemistry Chemistry Research Building – 110 PO Box 208107 New Haven, CT 06520-8107, USA
Prof. Dr. Javier Pérez-Ramírez	ETH Zürich Institute for Chemical and Bioengineering Vladimir-Prelog-Weg 1 8093 Zürich, Switzerland
Prof. Dr. Peter R. Schreiner	Justus-Liebig-University Gießen Institut für Organische Chemie Heinrich-Buff-Ring 17 35392 Gießen, Germany
Prof. Dr. Helma Wennemers	ETH Zürich Laboratory of Organic Chemistry, HCI H313 Vladimir-Prelog-Weg 3 8093 Zürich, Switzerland

Previous members (since 2005): Prof. Avelino Corma (Valencia, Spain); Prof. Pierre H. Dixneuf (Rennes, France); Prof. Dieter Enders (Aachen, Germany); Prof. Ben L. Feringa (Groningen, The Netherlands); Prof. J. A. Gladysz (Erlangen, Germany); Prof. Peter Hofmann (Heidelberg, Germany); Prof. Graham Hutchings (Cardiff, UK); Prof. Eric N. Jacobsen (Cambridge, USA); Prof. Henri Kagan (Orsay, France); Prof. Rutger A. van Santen (Eindhoven, The Netherlands); Prof. Joachim Sauer (Berlin, Germany); Prof. Richard R. Schrock (Cambridge, USA); Prof. Jens Weitkamp (Stuttgart, Germany

1.5 Members of the Board of Governors ("Verwaltungsrat") 2012-2016

Representative of the Ministerium für Innovation, Wissenschaft und Forschung des Landes Nordrhein-Westfalen

Dr. Thomas Grünewald

Representative of the Municipality of Mülheim an der Ruhr

Ulrich Scholten, Mayor

Representatives of the Max Planck Society

Dr. Ludwig Kronthaler, Secretary General of the Max Planck Society

Prof. Dr. Klaus Müllen

Dr. Jörn Rüter (Chairman)

Representatives of the Studiengesellschaft Kohle mbH

Prof. Dr. Michael Dröscher

Dr. Peter Schuhmacher

Dr. Peter Nagler (until 2016)

Prof. Dr. Stefan Buchholz (since 2016)

Honorary Members

Dr. Werner Schwilling

Prof. Dr. Günther Wilke *(deceased 9 December 2016)*

CHAPTER 2

Research Programs

2.1 Department of Organic Synthesis

Director:

Tobias Ritter (born 1975)

Further group leaders:

Matthew Tredwell (born 1981)
Group leader since August 2015

Curriculum Vitae: Tobias Ritter

1975	Born in Lübeck, Germany
1995-1997	Technische Universität Braunschweig, Germany
1997-1997	University of Bordeaux, Bordeaux, France
1997-1998	Swiss Federal Institute of Technology, Lausanne, Switzerland
1998-1999	Master Thesis, Stanford University, Stanford, CA, USA
1999-2004	Ph. D. Organic Chemistry, ETH Zürich, Switzerland
2004-2006	Post-Doctoral Fellow, California Institute of Technology, Pasadena, USA
2006-2010	Assistant Professor of Chemistry and Chemical Biology, Harvard University, Cambridge, USA
2010-2012	Associate Professor for Chemistry and Chemical Biology, Harvard University, Cambridge, USA
Since 2010	Chemist, Department of Radiology, Massachusetts General Hospital, Boston, USA
2011	Founder, SciFluor Life Sciences, Cambridge, USA
2012-2015	Professor of Chemistry and Chemical Biology, Harvard University, Cambridge, USA
2015-2017	Visiting Professor, Harvard University, Cambridge, USA
2015-	Director, Max-Planck-Institut für Kohlenforschung, Mülheim / Ruhr, Germany

Awards and Honors

1996-1999	Scholarship of the Konrad-Adenauer-Foundation
1997	Scholarship of the European Union
1997-1998	Scholarship of the Swiss National Science Foundation
1998-1999	Fellowship of the Konrad-Adenauer-Foundation
2000	Winterfeld Award - Towards the Total Synthesis of Teretifolione B
2000-2002	Kekulé-Scholarship of the Fond der Chemischen Industrie e.V.
2004-2006	Postdoctoral Fellowship (DAAD)
2007	Thieme Chemistry Journals Award
2008	Milton Fund Award, Harvard Medical School
2008-2011	Smith Family Award for Excellence in Biomedical Research
2009-2011	Massachusetts Life Science Center Young Investigator Award
2009	Bayer Early Excellence in Science Award
2010-2012	Eli Lilly Grantee Award
2010-2013	Air Force Young Investigator Award

2010-2015	NSF Career Award
2010	Alfred P. Sloan Research Fellowship
2010	Amgen Young Investigator Award
2010	AstraZeneca Excellence in Science Award
2010	Roslyn Abramson Award for Excellence in Teaching Undergraduates
2011	BASF Catalysis Award
2011	Camille Dreyfus Teacher Scholar Award
2011	Popular Science Brilliant 10 Award
2012	Klung-Wilhelmy-Weberbank Preis, Berlin, Germany
2013	RSC Fluorine Chemistry Prize

Special Activities

2011-2016	Chief Scientific Adviser SciFluor Life Sciences
2016-	Member, Scientific Advisory Board *Chem*
2016-	Member, Scientific Advisory Board *ACS Central Science*

Organic Synthesis

We seek to discover molecular reactivity to develop practical access to molecules of interest in catalysis, medicine and materials.

The new director assumed responsibilities for the Department of Organic Synthesis in July 2015. The infrastructure of the Department was finalized throughout the first year, culminating in the completion of the brand-new, state of the art radiochemistry facility in the spring of 2016. The quadruple glove-box suite with four double glove boxes and fully integrated solvent purification systems is another equipment highlight of the new Department.

The director currently has additional appointments at the Department of Chemistry and Chemical Biology at Harvard University and at the Department of Radiology at Massachusetts General Hospital, and the split of the director's effort is roughly 4:1 MPI/Harvard. Approximately one third of the original Harvard research group transitioned from Harvard to the MPI in 2015, and roughly a third of the original research group force is still active at Harvard at the end of this reporting period. The transition Harvard – MPI is anticipated to be completed in 2017 with additional three researchers transitioning from Harvard to the Max-Planck-Institut für Kohlenforschung.

The department was reinforced in 2015 with Dr. Tredwell. Dr. Tredwell joined from the University of Oxford and assumed responsibilities as group leader and director of the radiochemistry facilities. It is anticipated that Dr. Tredwell works collaboratively with the director on selected projects, but mainly builds his own research group to establish independent research to secure a professorship within roughly five years.

Research in the department currently focuses on four topics. The largest research efforts deal with Late-Stage Fluorination and its application to Positron Emission Tomography (PET) with the unnatural isotope ^{18}F, ultimately for use in clinical research. Reaction development for C–F bond formation with detailed mechanistic investigations builds the foundation for fundamental advances. A substantial effort is also devoted to translation of novel ^{18}F fluorination chemistry into radiopharmacies that require simple and practical reaction conditions. We now attempt to develop ^{18}F fluorination reactions that combine the operational simplicity of conventional ^{18}F fluorination chemistry with the increased substrate scope of modern late-stage fluorination chemistry.

C–H functionalization chemistry is another important area of the group's research, with the focus being on the development of late stage functionalization, with substrate as the limiting reagent. Lastly, catalysis with first row metals is being developed, informed by an advanced understanding of reaction mechanisms including the electronic structure of the catalysts.

The Tredwell group has initiated their own program in stereoselective fluorination chemistry, broadly defined, including both ^{18}F and ^{19}F chemistry.

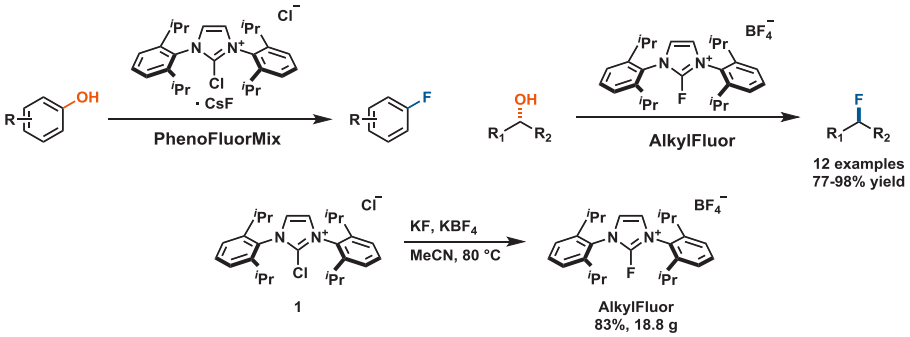
2.1.1 Research Area "Fluorination" (T. Ritter)

Involved: F. Becker, J. Boergel, G. Boursalian, J. Brandt, M. Campbell, T. Fujimoto, N. Goldberg, C. Kleinlein, E. Lee, J. Li, T. Liang, A. Mazzotti, E. McNeill, C. Neumann, X. Shen, H. Shi, F. Sladojevich

Objective: Advances in modern fluorination chemistry rely heavily on the availability of novel fluorinating reagents and an increased mechanistic understanding of the challenging C–F bond formation step. We aim to develop practical reagents for the conversion of alcohols and phenols to alkyl- and aryl-fluorides. In the pursuit of new reaction chemistry we strive to gain detailed mechanistic insight into unusual C−F bond formation reactions, such as concerted nucleophilic aromatic substitution reactions with fluoride, as well as oxidative fluoride transfer from high-valent transition metal complexes.

Results:

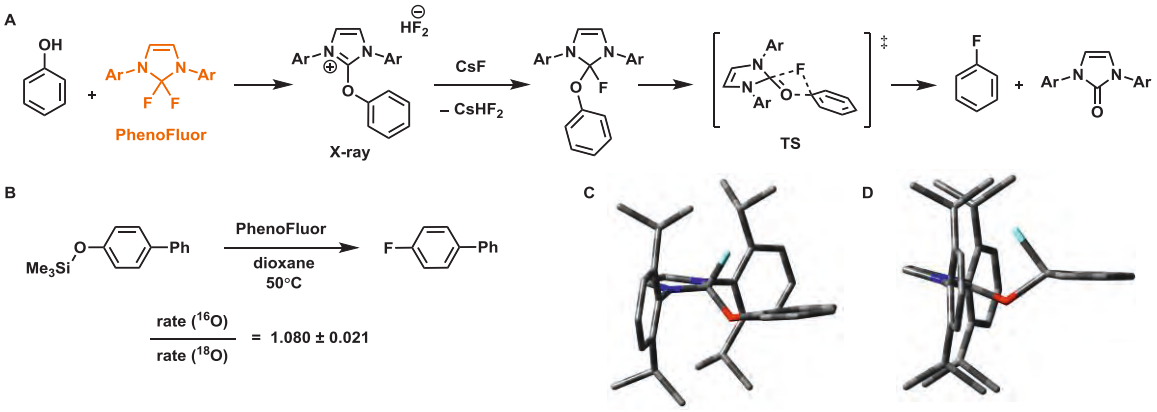
Novel Deoxyfluorinating Reagents: Our group reported the PhenoFluor deoxyfluorinating reagent, which converts a wide range of phenols and alcohols to the corresponding aromatic and aliphatic fluorides. The reagent is moisture-sensitive, necessitating long-term storage under inert atmosphere and complicating large-scale synthesis and commercialization. We have developed the deoxyfluorination reagents PhenoFluorMix for phenols and AlkylFluor for alcohols, which replicate PhenoFluor reactivity but lack its sensitivity to water. Large-scale synthesis of both reagents is feasible and commercialization has taken place for PhenoFluorMix and is underway for AlkylFluor.



PhenoFluorMix and AlkylFluor overcome the moisture sensitivity associated with PhenoFluor.

Mechanistic insight allows the development of new transformations: In addition to the availability of more convenient and powerful fluorinating reagents, increased

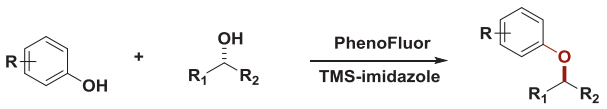
mechanistic understanding of C–F bond formation processes can lead to improved reaction protocols and reagents as well as the discovery of novel transformations.



A proposed mechanism of the concerted nucleophilic aromatic substitution mechanism of deoxyfluorination with PhenoFluor. **B** $^{16}O/^{18}O$ kinetic isotope effect. **C** DFT optimized structure of the tetrahedral adduct. **D** DFT optimized structure of the transition state.

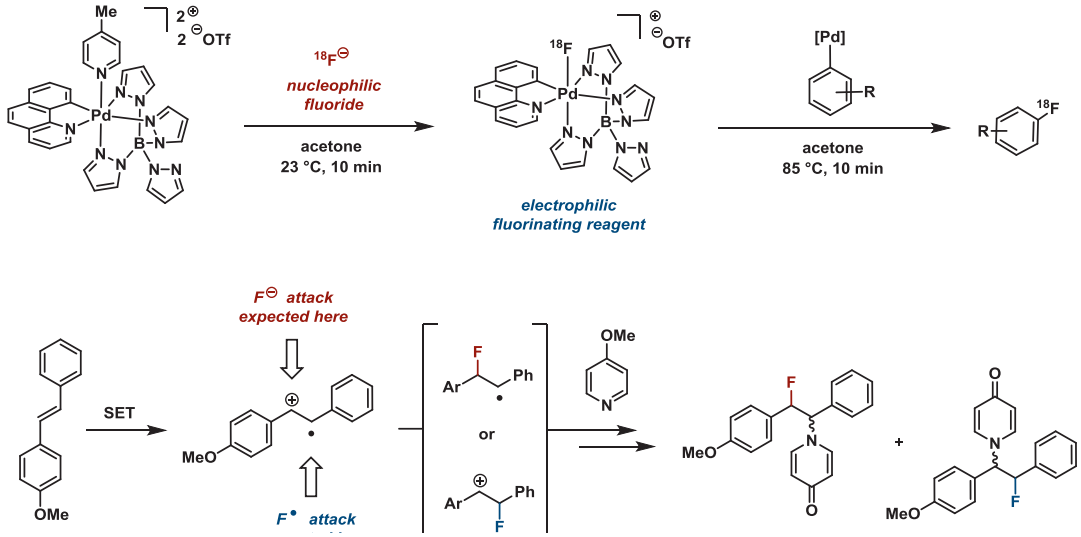
The PhenoFluor-mediated deoxyfluorination is an unusually powerful transformation given that, despite the use of a nucleophilic fluoride source, the hydroxide group of electron-poor as well as electron-rich arenes can be displaced by fluoride. We have found that the PhenoFluor reagent forms an uronium bifluoride adduct, which upon HF abstraction by added CsF is converted to a tetrahedral adduct. Detailed mechanistic investigation, including a $^{16}O/^{18}O$ kinetic isotope effect and a DFT study, corroborate a concerted nucleophilic aromatic substitution mechanism where C–F bond formation and C–O bond cleavage occur simultaneously. The concerted nature of the nucleophilic displacement prevents the build-up of a formal negative charge on the arene core and thus extends the scope of nucleophilic aromatic substitution to arenes substituted with electron-donating substituents in the *para* position. Formation of the PhenoFluor urea upon C−O bond cleavage is highly exergonic; because partial C−O bond cleavage occurs in the transition state, the exothermicity of urea formation serves to lower the activation barrier for deoxyfluorination. Further mechanistic work established the origin of the fluoride atom, which is incorporated into the aryl fluoride product. A precise understanding of the mechanism of fluoride incorporation into the product enabled us to extend the deoxyfluorination chemistry to ^{18}F fluoride.

Based on our detailed understanding of the PhenoFluor reaction mechanism, we were able to develop a C–O bond formation reaction using a combination of PhenoFluor and a silylating reagent that traps fluoride nucleophiles. A wide range of phenols and alcohols can be coupled to form the desired alkyl-aryl ethers in high yields.



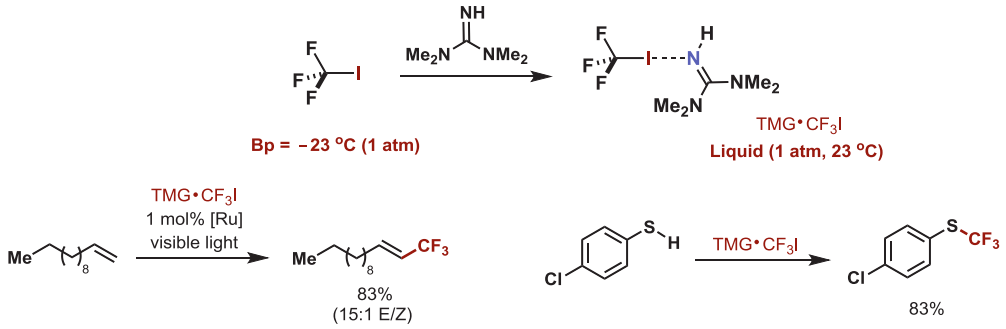
PhenoFluor-mediated ether bond formation.

Umpolung of fluoride: We have previously developed a formal Umpolung reaction of fluoride that proceeds *via* the capture of fluoride anion from solution by a Pd(IV)–picoline complex, displacing picoline to form a Pd(IV)–F complex. The Pd(IV)–F complex undergoes oxidative fluoride transfer to a Pd(II)–aryl complex, and C–F reductive elimination furnishes the fluorinated arene. Mechanism studies indicate that formation of an outer-sphere complex between fluoride and the Pd(IV)–picoline complex enables formation of Pd(IV)–F with high rates even at the nano- to micromolar fluoride concentrations typical for ^{18}F synthesis. Electrophilic fluorination by the Pd(IV)–F complex occurs via an oxidative fluoride transfer mechanism: single-electron transfer oxidation of the substrate precedes fluoride transfer, which is in turn followed by a second single-electron transfer.



Formal Umpolung of fluoride occurs via a sequence involving fluoride capture followed by SET/fluoride transfer/SET.

Convenient trifluoromethylation reagents: Similar to the PhenoFluor reagent class, we have developed a more convenient form of the reagent CF_3I through formation of halogen-bonded adducts. Use of the liquid TMG•CF_3I instead of gaseous CF_3I does not reduce reactivity but simplifies reaction set-up.



Halogen-bonding with suitable bases converts CF_3I into a more convenient trifluoromethylation reagent.

Future directions: Develop a catalytic version of the PhenoFluor deoxyfluorinating reagent. Use the mechanistic insight into the PhenoFluor reaction to disfavor decay of the tetrahedral adduct and lower the deoxyfluorination barrier through the introduction of hydrogen-bonding substituents into the reagent.

Publications resulting from this research area: 1, 3, 5, 6, 9- 16, 22, 23, 25, 27

External funding: NIH-NIGMS (GM088237), NIH-NIBIB (EB013042-02), NSF (CHE-0952753), NSF GRFP (DGE0644491) - graduate fellowship to G. B. Boursalian, Daiichi-Sankyo Co – fellowship to T. Fujimoto, NIH/NIDA (K01DA038000) – career development award to H. Shi

Cooperations: none

2.1.2 Research Area "[^{18}F]-Fluorination for PET Imaging" (T. Ritter)

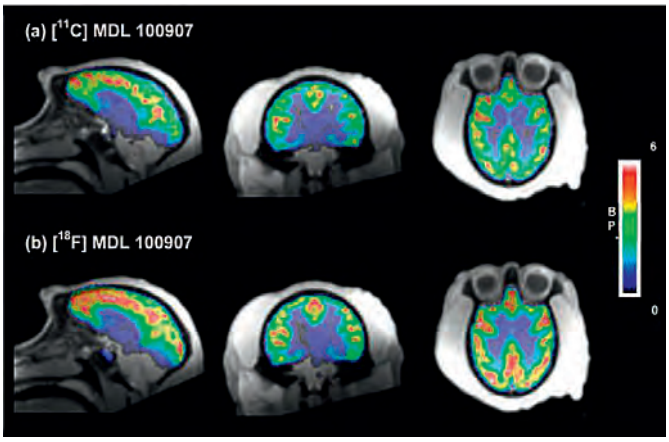
Involved: A. Braun, J. M. Hooker, A. J. Hoover, E. Lee, C. N. Neumann, H. Ren, T. Ritter, H. Shi, M. G. Strebl

Objective: Fluorine-18 is the most commonly used radioisotope in Positron Emission Tomography (PET), a functional molecular imaging technique with far-reaching potential in biomedical research. Despite significant advances in radiofluorination, the need for operationally simple, reliable and functional group tolerant reactions remains. Our goal is the development of more general, simpler and more practical reactions for the synthesis of aryl [^{18}F] fluorides, as well as other [^{18}F]fluorine-containing small molecules.

Results: Previously, we demonstrated for the first time the conversion of [^{18}F]fluoride into a reagent for electrophilic radiofluorination. The concept was an exciting novelty in the field of radiochemistry. PET was historically limited by the availability of radiotracers. Even though our initial disclosure of Pd(IV)-mediated radiofluorination has offered new perspectives, it quickly became evident that operational simplicity is paramount for the success of any given radiolabeling methodology. With the goal of *practical* radiolabeling strategies in mind, two distinct pathways were investigated: A) Nickel-mediated radiofluorination and B) Radiodeoxyfluorination via organic uronium intermediates.

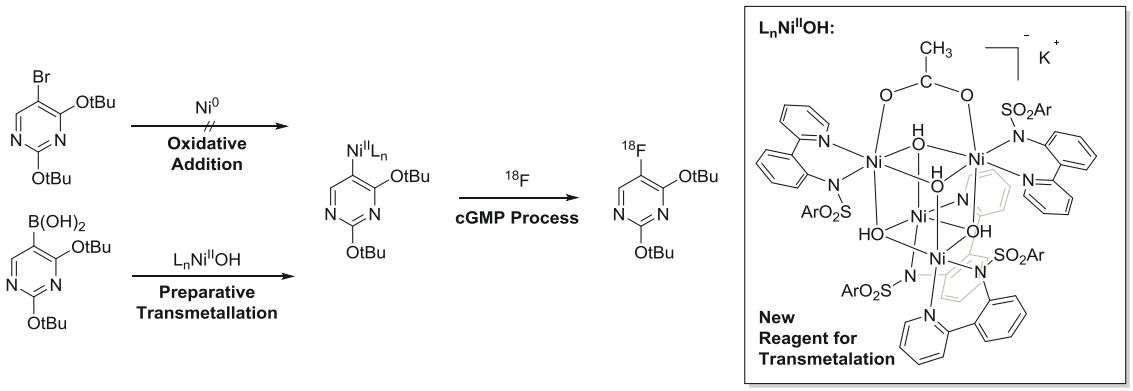
Scale up

Our group reported a nickel-mediated radiofluorination with reaction rates that allow radiolabeling within seconds to minutes in aqueous media. To demonstrate the usefulness, we chose an established PET tracer, MDL100,907, and successfully performed a radiosynthesis with our new method. Basic amines were problematic for nickel-mediated fluorination initially, but reaction



Voxel-wise binding potential (BPND) maps of (a) [^{11}C]MDL100907 (90 min) and (b) [^{18}F]MDL100907 (120 min) overlaid on structural MRI.

development for the production of MDL100,907 allowed us to overcome that limitation and produce sufficient quantities of radiolabeled product for imaging studies with the newly synthesized molecule. Through PET imaging in non-human primates we established the bioequivalence of our newly synthesized [^{18}F]MDL1000,907 to the previously used [^{11}C]MDL100,907 for the study of serotonin receptors. Thereby, we demonstrated that nickel-mediated fluorination is scalable and suitable for full automation.

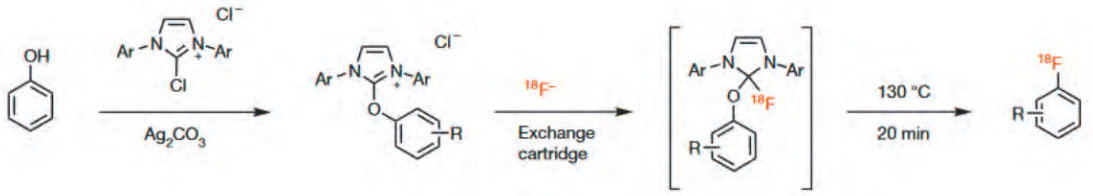


When the conventional synthetic protocol via oxidative addition failed to yield the labeling precursor, a new transmetallation reagent was developed to access a nickel complex, which was used to develop a cGMP radiopharmaceutical production process of [^{18}F]5FU.

GMP Process for Production of 5-Fluorouracil for Human Use: The ultimate challenge for any radiofluorination is the development of a reliable, efficient and fully automated GMP radiosynthetic process for human radiopharmaceutical production. 5-Fluorouracil (5FU) is a known radiotracer designed for oncological imaging applications. Despite interest in the tracer, its application has been very limited due to the difficult, unreliable radiosynthesis. Our methodology was challenged by initial complications in the synthesis of the labeling precursor. The nickelated uracil was inaccessible through oxidative insertion of nickel(0) into a carbon bromine bond and new organometallic reactions had to be developed to obtain the labeling precursor. We overcame this synthetic challenge through an unprecedented transmetallation from boron onto nickel, enabled by a polynuclear nickel-cube. With the precursor in hand, we developed a fully automated, GMP certified radiosynthetic process that allowed us to produce [^{18}F]5FU in a sufficient quantity for imaging applications under the stringent quality requirements for human radiopharmaceutical production. Despite improvements and simplifications in the labeling precursor synthesis, nickel-mediated radiofluorination still requires the use of air and moisture sensitive materials. As a consequence, even though GMP radiopharmaceutical production has been demonstrated,

the process is too complex for routine applications and does not meet our standards for operational simplicity yet.

User-Friendly Radiochemistry: A distinct approach to radiofluorination was enabled by mechanistic understanding of non-radioactive carbon fluorine bond formation through deoxyfluorination. A chloroimidazolium reagent is able to convert phenols into uronium salts, which are unique in their ability to undergo nucleophilic aromatic substitution via a concerted mechanism. The method is general for electron poor arenes and heteroarenes and affords aryl fluorides in high specific activity through an operationally simple procedure.



Radiodeoxyfluorination using a chloroimidazolium chloride reagent. After formation of an uronium intermediate, ^{18}F fluoride incorporation occurs on an ion exchange cartridge. The resulting tetrahedral intermediate undergoes C–F bond formation upon heating.

Through extensive mechanistic work, a process was designed that omits the need for azeotropic drying of ^{18}F, but instead leverages the ionic nature of the uronium intermediate to elute fluoride off an anion exchange cartridge. The ion exchange process is crucial for a successful reaction: If free fluoride is added to the reaction vessel, no ^{18}F aryl fluoride formation is observed. ^{18}F needs to be tightly bound in the tetrahedral intermediate in order to form a carbon-fluorine bond through concerted nucleophilic substitution on the arene. Radiodeoxyfluorination cannot currently be used to fluorinate electron-rich arenes: if the electron density at the tetrahedral carbon center becomes too high, the neutral intermediate releases fluoride. At the low fluoride concentrations typical for radiochemistry, the fluoride anion engages in unproductive side-reactions that compete with fluoride re-association required for productive fluorination. Current work is aimed at understanding the process in more detail and circumventing the release of fluoride in order to extend the substrate scope to electron-rich phenols. We are furthermore in the process of demonstrating scalability of the method.

Beyond Aryl Fluorides: Our group has also developed a practical method for the synthesis of [^{18}F]difluoromethylarenes from (pseudo)halides. Labeling precursors were

prepared in one step from aryl chlorides, bromides, iodides and triflates and (non decay-corrected) radiochemical yields ranged from 10-60%. The reaction is general and several drug analogues and radiopharmaceuticals were prepared, including Claritin and Prozac. A wide range of functional groups as well as air and moisture can be tolerated.

Future directions: Increase the substrate scope and operational simplicity of radiofluorination; Demonstrate usefulness of new methods in radiotracer development

Publications resulting from this research area: 8, 13, 20, 22, 23, 25, 26

External funding: NIH-NIGMS (GM088237), NIH-NIBIB (EB013042-02), Phelps Foundation

Cooperations: J. M. Hooker, N. Vasdev (both Massachusetts General Hospital), R. M. van Dam (Associate Professor, Crump Institute for Molecular Imaging, Molecular & Medical Pharmacology, UCLA University of California Los Angeles), A. Guimaraes (Oregon Health & Science University)

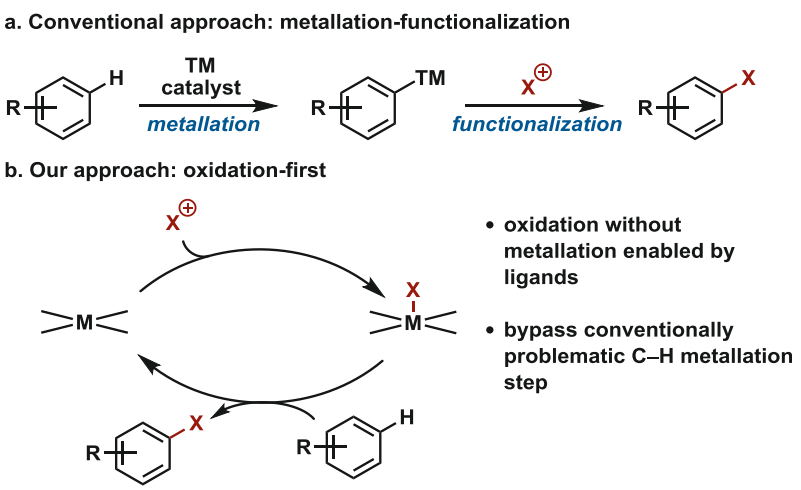
2.1.3 Research Area "C–H Functionalization" (T. Ritter)

Involved: G. B. Boursalian, W. S. Ham, A. R. Mazzotti, J. Börgel, F. Sladojevich, E. McNeill, E. D'Amato, C. N. Neumann

Objective: Efficient C–H functionalization reactions have the potential to streamline organic synthesis by obviating the requirement for pre-functionalized starting materials to access value-added products. To fully realize the potential of C–H functionalization, sufficient reactivity must be elicited to enable high-yield conversion of the targeted C–H bonds. Furthermore, selectivity is required for a specific C–H bond in a given molecule, otherwise mixtures of constitutional isomers result, which hampers the efficiency gains of C–H functionalization. We aim to develop broadly useful C–H functionalization reactions which address these challenges of reactivity and selectivity by exploring new, unconventional strategies.

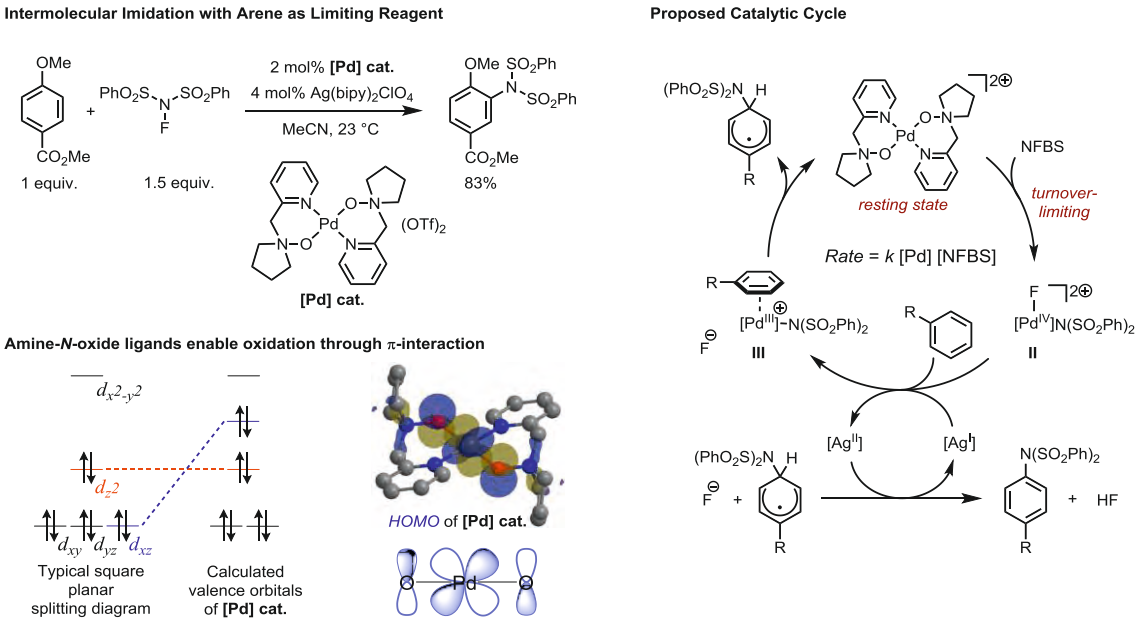
1. Oxidation-first approach to C–H Functionalization

A common approach towards C–H functionalization is the use of electrophilic transition metal (TM) catalysts capable of cleaving aromatic C–H bonds to yield an organometallic intermediate, which is subsequently functionalized to yield the product. Unless a coordinating directing group is utilized, this conventional metalation-functionalization approach, with few exceptions, requires multiple equivalents of the arene substrate. We have pioneered a new approach for aromatic C–H functionalization, in which ancillary ligands on the TM catalyst promote oxidation prior to any interaction with the arene substrate. We have found that the high-valent metal thus generated can have augmented reactivity towards arenes, enabling high yields of functionalized products even when the arene is used as limiting reagent.



We had reported an aromatic C–H imidation reaction catalyzed by a palladium complex that is ligated by unusual tertiary amine-*N*-oxide ligands, in conjunction with a silver

co-catalyst. In this imidation reaction, the arene can be used as limiting reagent, even though no coordinating directing group is required. The amine-*N*-oxide ligand was designed to promote oxidation of palladium: π-repulsion between a filled nonbonding *d*-orbital on Pd and the *N*-oxide lone pairs results in a high-energy electronic configuration, easing oxidation. Mechanistic studies confirmed oxidation of the Pd complex prior to oxidation-H functionalization, consistent with the design of the *N*-oxide ligands. Other highly unusual features of the mechanism include redox cooperativity between the two transition metal catalysts, and a lack of organometallic intermediates, which are ubiquitous in C–H functionalization.

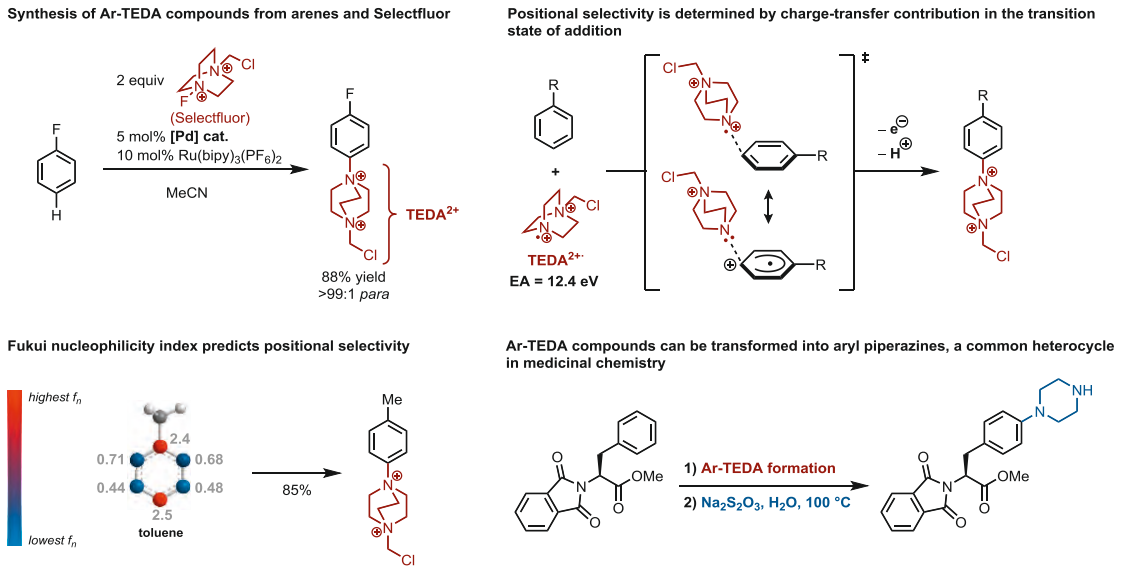


Our work with amine-*N*-oxides as ligands for transition metals had made us aware of inconsistencies in the treatment of orbital splitting diagrams of TM complexes in several standard inorganic chemistry textbooks. Such confusion led us to publish an educational article on *d*-orbital splitting diagrams, in order to clarify the issue for students in the field.

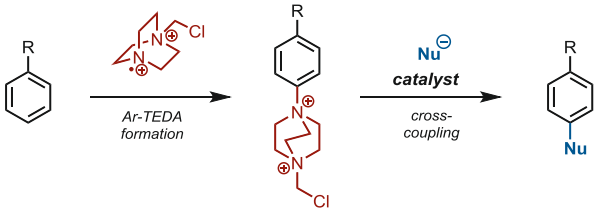
Future directions: We will continue to expand the scope and applicability of the oxidation-first approach to C–H functionalization. Work is underway towards the design of new transition metal complexes that can undergo oxidation without C–H metalation, with the expectation that such complexes will exhibit unprecedented reactivity.

2. Aromatic C–H Functionalization by Electrophilic Radicals

We have published a new approach to C–H functionalization, which involves aromatic substitution by highly electrophilic radicals. We have discovered that the radical dication $TEDA^{2+\bullet}$, generated from the reagent Selectfluor by single-electron reduction, undergoes aromatic substitution with nearly perfect positional selectivity for a variety of arenes. For monosubstituted arenes, the *para* isomer is formed almost exclusively (>99:1 for fluorobenzene). To the best of our knowledge, this is the only C–H functionalization reaction that exhibits perfect positional selectivity for a broad range of substrates. The unprecedented degree of positional selectivity owes to the extremely high electron affinity of the $TEDA^{2+\bullet}$ radical (12.4 eV), which engenders a significant degree of charge transfer in the transition state of addition; attack is favored at the position which can best accommodate this charge transfer, which is predicted to be the *para* position by Fukui nucleophilicity indices. The Ar–TEDA molecules thus generated can be converted to aryl piperazines, a very important motif in pharmaceuticals, through a simple and convenient procedure.



Future directions: One corollary of the above results is that highly *para*-selective radical additions are not in principle limited to the $TEDA^{2+\bullet}$ radical. Potentially any radical of sufficiently high electron affinity can afford very high *para* selectivity, and incorporation of multiple positive charges is the best way to increase the electron affinity of a radical. Work is currently underway to expand the scope of charge-transfer-directed radical



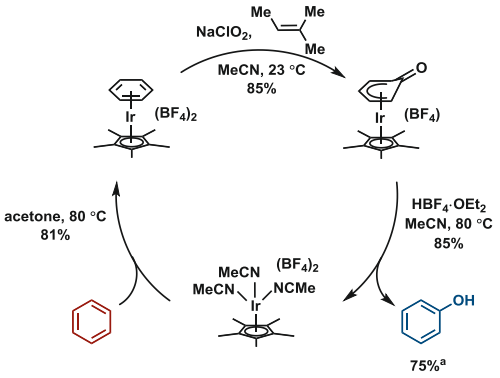
General strategy for *para*-selective C–H functionalization through Ar–TEDA cross-coupling.

substitution to new high-electron-affinity radicals to enable the selective installation of synthetically interesting functional groups.

Additionally, the Ar–TEDA compounds may have potential as electrophiles in transition-metal catalyzed cross coupling reactions, with the TEDA moiety acting as a pseudohalide. The identification of an appropriate catalyst, capable of selective cleavage of the Ar–TEDA bond, could in principle enable coupling with an arbitrary nucleophile, and thus open the way to a general strategy for *para*-selective aromatic C–H functionalization.

3. η^6-Coordination to Transition Metals as a Novel Approach to C–H Functionalization

η^6-Binding of arenes to transition metals can augment the arene's ability to undergo various reactions, such as nucleophilic attack, deprotonation, and oxidation. We have identified η^6-binding as a potential platform for a unique approach to C–H functionalization. As a step towards this goal, we have reported a new transformation of η^6-coordinated arenes. An η^6-arene iridium complex undergoes oxidation by hypochlorite, through nucleophilic attack followed by elimination, to yield an η^5-bound phenolate. The phenol product can be liberated through treatment with strong acid, leading to displacement of the arene by solvent. The starting η^6-arene complex can be regenerated by heating the solvento complex in the presence of benzene, completing a synthesis cycle for transition metal mediated hydroxylation through η^6-activation.

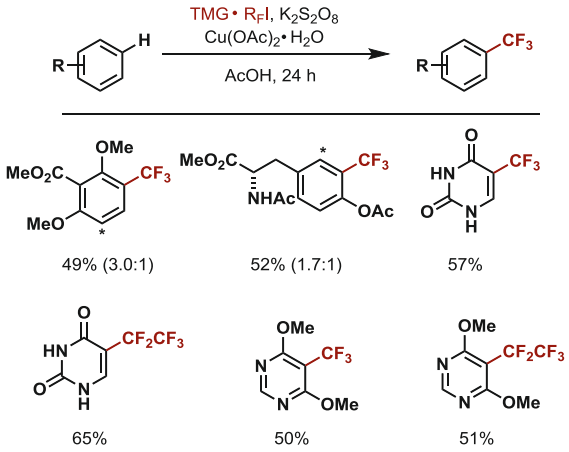


Synthesis cycle for aromatic C–H hydroxylation promoted by η^6 binding.

Future directions: A precondition for catalysis by η^6-activation of arenes is the possibility of arene exchange to occur under the same conditions as oxidation. Thus, work is underway in our laboratories to develop strategies to promote arene exchange, such as through the design of appropriate ancillary ligands and reaction conditions.

4. Condensed-phase Halogen-bonding Adducts as Convenient Reagents for Aromatic Perfluoroalkylation

Perfluoroalkyl iodides are effective sources for perfluoroalkyl radicals, which are intermediates in a variety of useful perfluoroalkylation reactions. However, the lighter perfluoroalkyl iodides, such as F_3CI and F_5C_2I are gaseous at standard temperature and pressure, and thus can be inconvenient to handle and measure in a synthetic laboratory setting. We have developed several halogen-bonded adducts of F_3CI and F_5C_2I, which are easily handled liquid and solid forms of these reagents. Using the tetramethylquanidine (TMG) adducts of F_3CI and F_5C_2I, we developed a convenient, direct aromatic C–H perfluoroalkylation reaction.



Publications resulting from this research area: 2, 4, 5, 7, 12, 17, 19, 21, 23

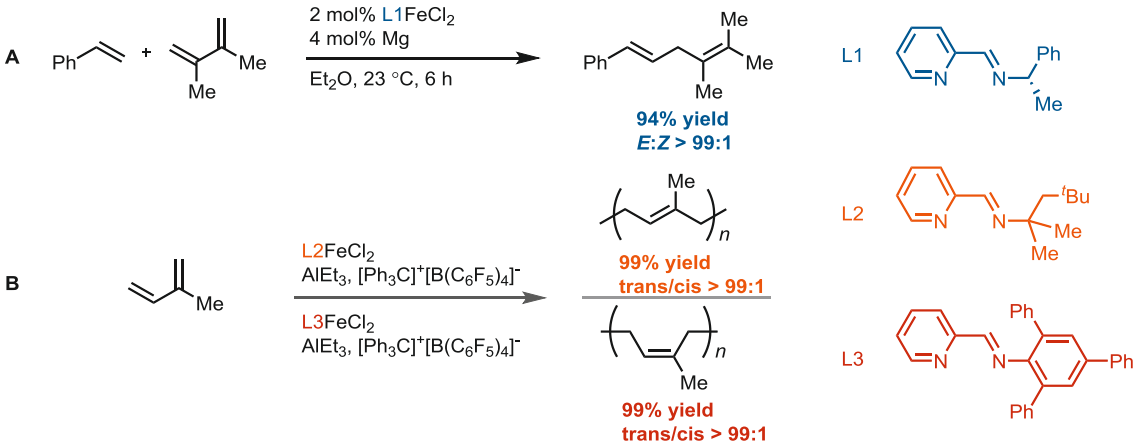
External funding: NSF (CHE-0952753), UCB Pharma

Cooperations: none

2.1.4 Research Area "Well-defined Fe Catalysts" (T. Ritter)

Involved: H. Lee, J. Börgel

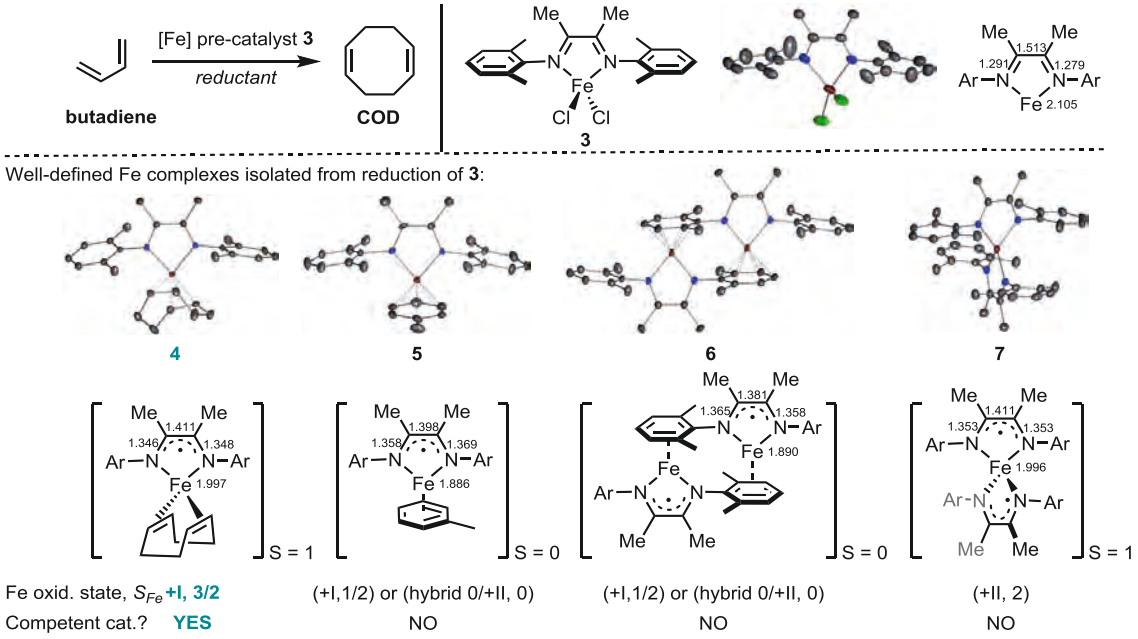
Objective: Iron-catalyzed or -mediated transformations of organic substrates have been important throughout the development of organic chemistry due to iron's abundance, low cost, and favorable toxicity profile. We have previously reported redox-active iminopyridine-ligated low-valent iron catalysts that can be used in a variety of 1,4-selective functionalization of 1,3-dienes including hydrovinylation, hydroboration, hydrosilylation and polymerization.



A Iron-catalyzed 1,4-addition of olefins to 1,3-dienes. **B** Stereoselective polymerization of isoprene enabled by iminopyridine-ligated iron catalyst.

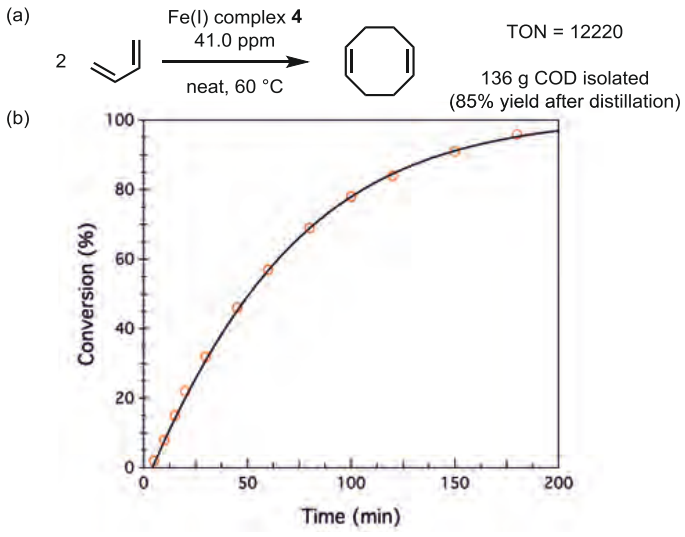
While the promise of low-valent iron catalysis is high, as shown in the synthetic utility of our catalysts and others, the lack of understanding of the mechanism of low-valent iron catalysis in general often complicates improvements of reactions and makes rational design of catalysts challenging. Therefore we aimed to study the mechanism of a low-valent iron-catalyzed diene dimerization reaction featuring a redox-active diimine ligand, to provide greater understanding of the structure-reactivity relationships of low-valent iron complexes which would be valuable in the development and rational design of iron catalysts.

Results: We identified and isolated an active catalyst for diene dimerization that features a high-spin Fe(I) center, where partial metal–ligand antibonding orbital population is proposed to allow for facile ligand exchange during catalysis.



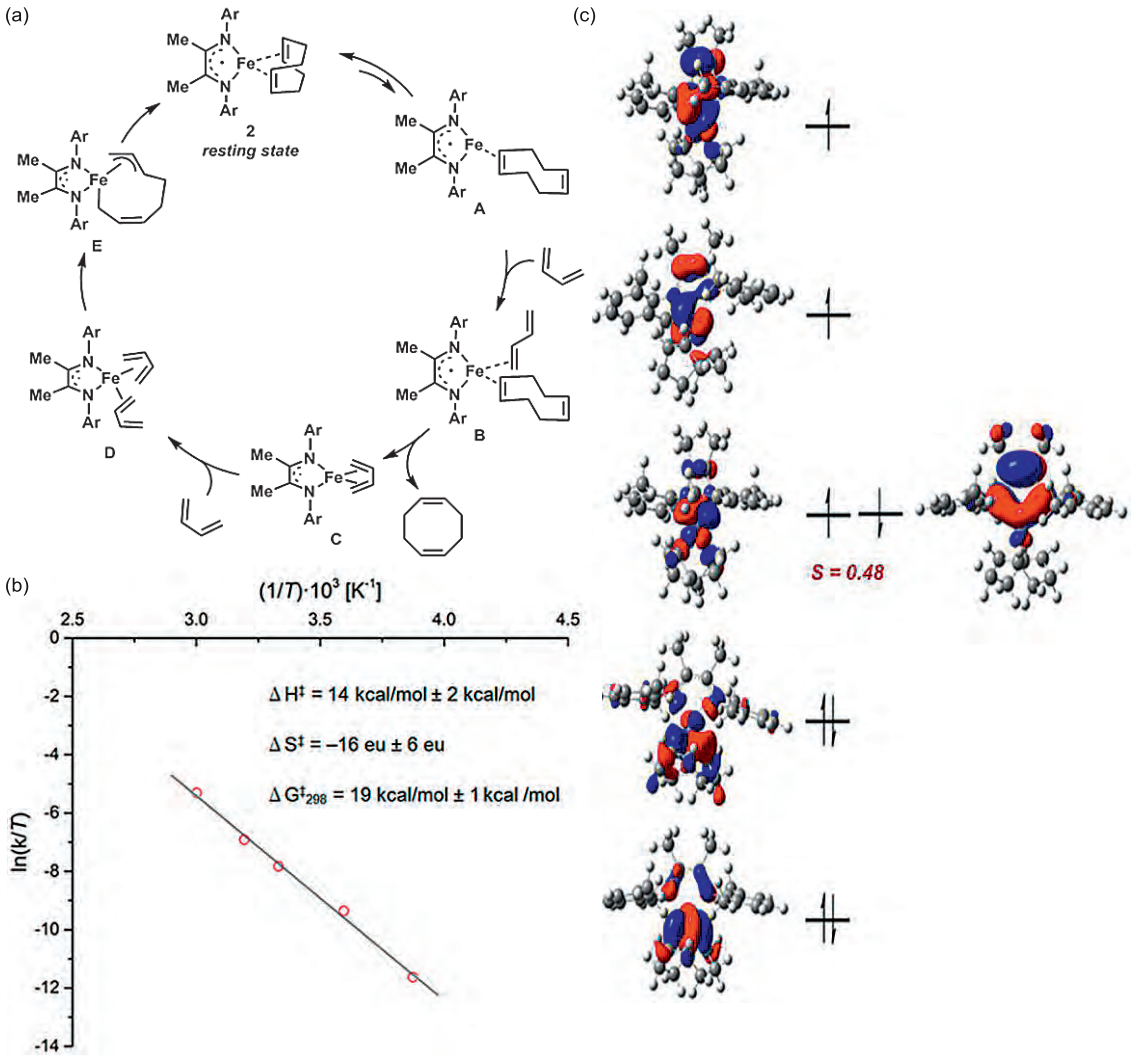
Well-defined iron complexes **4**–**7** isolated from reduction of **3**, and their activities in the synthesis of COD from butadiene; X-ray structures are drawn with 50% probability ellipsoids, H-atoms omitted for clarity; selected bond lengths are given in Å.

Among structurally related low-valent iron complexes **4**–**7** isolated from reduction of precatalyst **3**, we identified that formally 16-electron Fe(I) complex **4** is a chemically and kinetically competent catalyst in the synthesis of COD from butadiene, in contrast to complexes **5**–**7** that require additional activating reagents such as trialkylaluminum compounds to generate a catalytically active species for butadiene dimerization. The bond metrics analyzed by single crystal X-ray diffraction indicate a radical anion form of the diimine ligand, suggesting an oxidation state of +I for the Fe center in **4**.



A Catalytic activity of **4** in butadiene dimerization.
B Kinetic profile of butadiene dimerization with **4**.

Catalyst **4** produces COD from butadiene, without any additional activating reagent, and 41 ppm catalyst loading is sufficient on >100 g scale. Catalyst **4** provides high selectivity for COD, the major side product being the formal [4+2] addition product vinylcyclo-hexene (VCH), which is a common byproduct in COD synthesis.



(a) Proposed catalytic cycle for iron-catalyzed [4+4] butadiene dimerization. (b) Eyring plot for dimerization of butadiene catalyzed by **4** (0.18 mol%) with data collected over a temperature range of –15 to –60 °C. (c) Qualitative MO diagram of Fe (I) complex **4** derived from BS (3,1) B3LYP/TZVP calculations.

COD synthesized with isolated catalyst **4** shows COD:VCH ratios ranging from 97:3 up to 99:1, higher than previously reported for iron-catalyzed COD synthesis with precatalyst **3**. While dimerization of butadiene with Fe(II) precatalyst **3** and MeMgCl displays an induction period of 80 minutes at the same catalyst loading, the reaction with **4** displays first order kinetics, with no induction period. Fe catalyst **4** achieved a rate of more than 8 kg butadiene/ g (Fe)/ h at 60 °C, an order of magnitude higher than that reported for the conventional nickel-phosphite catalysts that described in Wilke's seminal work.

Isolation of the kinetically competent catalyst **4** enabled us to conduct a detailed mechanistic study of diene dimerization. We determined that the catalyst resting state is the Fe(I) complex **4** by monitoring the reaction using ^{1}H NMR. A kinetic order of 1 was

measured with respect to Fe catalyst **4**. Furthermore, first-order kinetics were observed for butadiene and zero-order kinetics were observed for COD. Eyring analysis suggests an associative turnover-limiting step, such as butadiene coordination to Fe ($\Delta S^{\ddagger} = -16 \pm 6$ eu). Taken together, these data are consistent with the proposed catalytic cycle: reversible dissociation of one of the olefins of COD forms steady-state intermediate **A**, followed by turnover-limiting butadiene association.

The significant difference in reactivity between **4** and structurally similar low-valent Fe complexes such as **5** prompted us to probe the electronic structures of related iron complexes, using zero-field ^{57}Fe Mössbauer spectroscopy and SQUID magnetometry. Experimental data and DFT calculations support the assignment of active catalyst **4** as a high-spin $S = {}^{3}/_{2}$ Fe(I) center coupled antiferromagnetically to the diimine ligand radical ($S = {}^{1}/_{2}$), in contrast to **5** which features a low-spin Fe(I) center antiferromagnetically coupled to the diimine ligand radical. In complex **4**, the molecular orbital on the iron that is magnetically coupled to the diimine ligand is singly occupied and shows an antibonding interaction along the Fe–π bond of the COD ligand. We speculate that this antibonding interaction is weakens the COD ligand–metal bond and enables the fast dissociation of the COD ligand during catalysis.

We reported a detailed mechanistic study of a low-valent iron catalyst with a redox-active ligand for diene dimerization, to provide a better understanding of the structure-reactivity relationship of low-valent iron complexes for rational design of improved catalysts. In contrast to related Fe(I) complexes that are not catalytically competent, detailed electronic structure characterization of a new, active catalyst **4** establishes a high-spin ($S = {}^{3}/_{2}$) Fe center, which allows for rapid ligand substitution and catalyst turnover enabled by partial Fe–COD ligand antibonding orbital population. The direct relationship between electronic structure and reactivity established here may be valuable in the development of improved low-valent iron catalysis.

Future directions: Design a novel, well-defined Fe catalysts for selective functionalization of alkenes, alkynes and arenes based on an understanding of the electronic structure.

Publications resulting from this research area: 18, 24

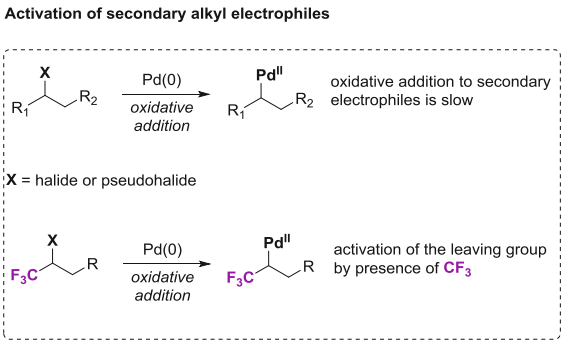
External funding: Fonds der Chemischen Industrie (stipends to J. Börgel)

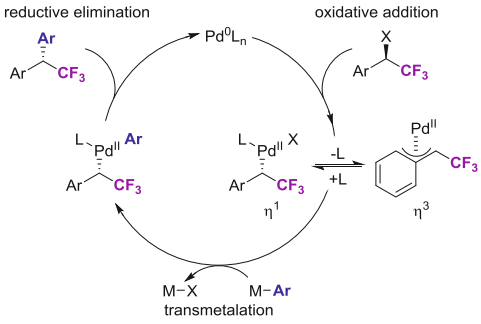
2.1.5 Research Area "Synthesis of C_{sp3}-CF_3 Stereogenic Centers" (M. Tredwell)

Involved: M. Brambilla, R. Petzold

Objective: Fluorinated motifs have found application in a wide variety of fields from agrochemicals to molecular imaging. The impact a fluorinated functional group has on a material or molecule is highly dependent on the degree of fluorination and the precise site of its introduction. Our objective was to develop new methods for the selective construction of C_{sp3}-CF_3 stereocenters.

Results: The majority of existing methods for the synthesis of stereogenic C_{sp3}-CF_3 centers are based on the stereocontrolled introduction of a CF_3 group into the target of interest. Whilst this approach has been applied successfully to highly activated systems such as aldehydes and ketones, methods for installation at other positions is comparatively rare, and thus stimulated our interest towards addressing this limitation. We considered an alternative synthetic route in which rather than introducing the CF_3, we would use a trifluoromethylated building block and take advantage of the unique reactivity of the fluorinated compound in order to promote a reaction that is challenging in its absence.

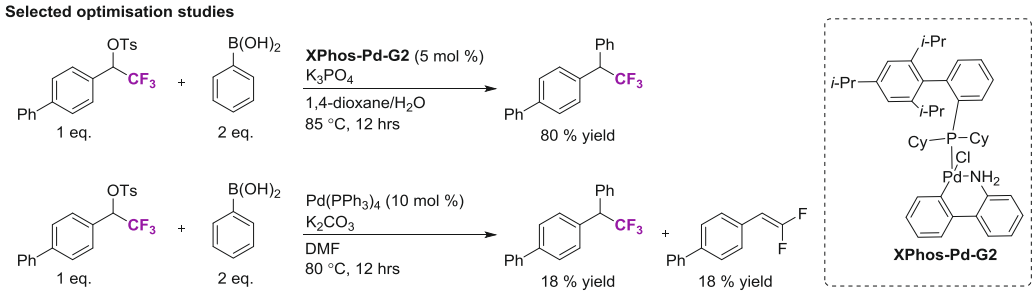




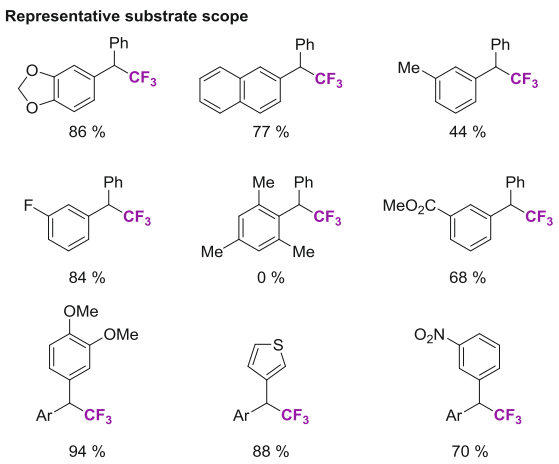
In this context we focused our attention on the use of secondary alkyl electrophiles in palladium cross-coupling reactions. In contrast to nickel catalysis, secondary alkyl electrophiles are seldom used with palladium catalysts due to the slow oxidative addition step and facile β-hydride elimination of the resultant alkyl–Pd(II) species. We hypothesized that the electron-withdrawing effect of a proximal trifluoromethyl group to a leaving group in a secondary electrophile would sufficiently activate it towards oxidative addition (OA) with a Pd catalyst, and that judicious selection of the ligand could minimize the undesired β-hydride elimination. The trifluoromethylated Pd(II)

species could potentially be used in the myriad of known transformations to give access to a diverse range of compounds bearing a stereogenic C_{sp3}-CF_3 stereocenter.

In our preliminary screening study we opted to study the Suzuki-Miyaura cross-coupling of 1-([1,1'-biphenyl]-4-yl)-2,2,2-trifluoroethanol derivatives with aryl boronic acids. This model system was selected as it removed the possibility of competitive β-hydride elimination and allowed us to focus our attention on the key OA step, and whether β-fluoride elimination would be a detrimental side reaction. The resultant 1,1-diaryl-2,2,2-trifluoroethanes are also structurally interesting compounds and have been investigated as alternatives to dichlorodiphenyltrichloroethane (DDT). Our initial results demonstrated that conversion of the benzylic alcohol to the corresponding tosylate provided a suitably activated starting material that undergoes OA with Pd(0) and the subsequent transmetalation and reductive elimination steps to yield the anticipated products. The optimal catalyst was identified as XPhos-Pd-G2 which gave the highest yields whilst minimizing β-fluoride elimination, which was formed in significant quantities when employing other Pd catalysts such as $Pd(PPh_3)_4$.

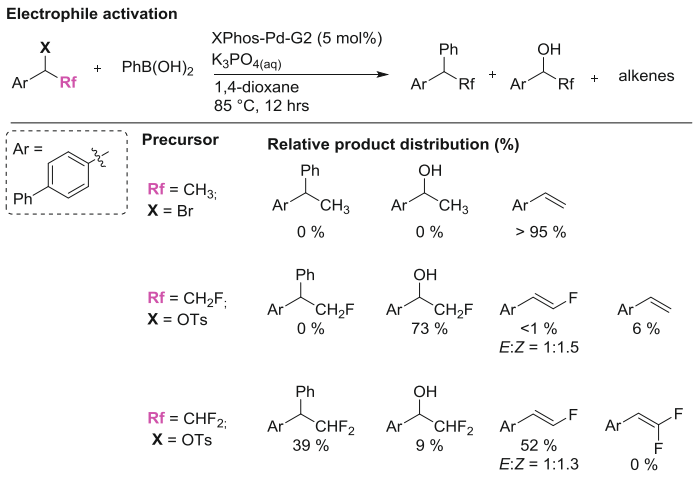


A wide range of electron-donating and –withdrawing functional groups were tolerated on the arene ring bearing the 2,2,2-trifluoroethyl tosylate moiety. *ortho*-Substitution resulted in decreased yield, presumably due to increased steric hindrance in the initial OA step. When examining the substrate scope with regard to the boronic acid coupling partner, a wide range of functional groups were compatible, in addition to those bearing *ortho*-substituents and a range of heteroarenes.



To demonstrate the activating effect of the CF_3 group for secondary alkyl electrophiles, a series of compounds were

synthesized where the number of fluorine atoms present was sequentially decreased. 1-([1,1'-Biphenyl]-4-yl)-2,2-difluoroethyl tosylate (**1a**) when subjected the optimized reaction conditions, a 39 % yield of the desired cross-coupled product was recorded. However, hydrolysis and elimination side reactions are also present. It is noteworthy that in this system only β-fluoride elimination was observed. The monofluorinated substrate 1-([1,1'-biphenyl]-4-yl)-2-fluoroethyl tosylate (**1b**) gave none of the desired product under the optimal conditions, with hydrolysis to the starting alcohol being the predominate reaction. Attempts to prepare the corresponding non-fluorinated tosylate were unsuccessful due to the instability of this compound and so a direct comparison was not possible. However, we were able to synthesize 4-(1-bromoethyl)-1,1'-biphenyl (**1c**) that when subjected to the reaction conditions gave only the product of elimination. These results clearly demonstrate the activating effect of the CF_3 group on secondary alkyl tosylates in Pd catalyzed cross-coupling reactions.



Future directions: Expand the substrate scope to include non-benzylic secondary substrates and alkyl boronic acids. Further explore the utility of this fluorinated building block in additional transformations.

2.1.6 Publications 2014-2016 from the Department of Organic Synthesis

Ritter Group

(1) Brand, J. R.; Lee, E.; Boursalian, G. B.; Ritter. T. *Chem. Sci.* **2014**, *5*, 169-179.

(2) Kornecki, K. P.; Berry, J. F.; Powers, D. C.; Ritter, T. *Prog. Inorg. Chem.* **2014**, *58*, 223-300.

(3) Liang, T.; Ritter, T. In *Comprehensive Organic Synthesis II*, Knochel, P., Ed., 2nd ed.; Elsevier: Amsterdam, 2014; Vol. 6; pp 210-238.

(4) Powers, D. C.; Ritter, T. In *Comprehensive Organic Synthesis II*, Knochel, P., Ed., 2 nd ed.; Elsevier: Amsterdam, 2014; Vol. 6; pp 719-743.

(5) Regalado, E. L.; Kozlowski, M. C.; Curto, J. M.; Ritter, T.; Campbell, M. G.; Mazzotti, A. R.; Hamper, B. C.; Spilling, C. D.; Mannino, M. P.; Wan, L.; Yu, J.-Q.; Liu, J.; Welch, C. J. *Org. Biomol. Chem.* **2014**, *12*, 2161-2166.

(6) Campbell, M. G.; Ritter, T. *Org. Proc. Res. Develop.* **2014**, *18*, 474-480.

(7) Parker, S. E.; Börgel, J.; Ritter, T. *J. Am. Chem. Soc*. **2014**, *136*, 4857-4860.

(8) Ren, H.; Wey, H.-Y.; Strebl, M.; Neelamegam, R.; Ritter, T.; Hooker, J. *ACS Chem. Neurosci*. **2014**, *5*, 611-615.

(9) Fujimoto, T.; Becker, F.; Ritter, T. *Org. Process Res. Dev.* **2014**, *18*, 1041-1044.

(10) Campbell, M. G.; Ritter, T. *Chem. Rev*. **2015**, *115*, 612-633.

(11) Fujimoto, T; Ritter, T. *Org. Lett.* **2015**, *17*, 544-547.

(12) Sladojevic, F.; McNeill, E.; Börgel, J.; Zheng, S.-L.; Ritter, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 3712-3716.

(13) Neumann, C. N.; Ritter, T. *Angew. Chem., Int. Ed*. **2015**, *54*, 3216-3221.

(14) Shi, H.; Babinski, D.; Ritter, T. *J. Am. Chem. Soc*. **2015**, *137*, 3775-3778.

(15) Shen, X.; Neumann, C. N.; Kleinlein, C.; Goldberg, N.; Ritter, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 5662-5665.

(16) Campbell, M. G.; Hoover, A. G.; Ritter, T. *Top. Organomet. Chem.* **2015**, *52*, 1-53.

(17) D'Amato, E. M.; Neumann, C. N.; Ritter, T. *Organometallics* **2015**, *34*, 4626-4631.

(18) McNeill, E.; Ritter, T. *Acc. Chem. Res.* **2015**, *48*, 2330-2343.

(19) Börgel, J.; Campbell, M. G.; Ritter, T. *J. Chem. Educ*. **2016**, 93, 118-121.

(20) Hoover, A. J.; Lazari, M.; Ren, H.; Narayanam, M. K.; Murphy, J. M.; van Dam, R. M.; Hooker, J. M.; Ritter, T. *Organometallics* **2016**, *35*, 1008-1014.

(21) Boursalian, G. B.; Ham, W. S.; Mazzotti, A. R.; Ritter, T. *Nat. Chem.* **2016**, *8*, 810-815.

(22) Neumann, C. N.; Hooker, J. M.; Ritter, T. *Nature* **2016**, *534*, 369-373.

(23) Shi, H.; Braun, A.; Wang, L.; Liang, S. H. Vasdev, N.; Ritter, T. *Angew. Chem., Int. Ed.* **2016**, *36*, 10786-10790.

(24) Lee, H.; Campbell, M. G.; Hernández Sánchez, R.; Börgel, J.; Raynaud, J.; Parker, S. E.; Ritter, T. *Organometallics* **2016**, *35*, 2923-2929.

(25) Neumann, C. N.; Ritter, T. *Nat. Chem.* **2016**, *8*, 882-883.

(26) Kumar, V.; Boucher, Y.; Liu, H.; Ferreira, D.; Hooker, J.; Catana, C.; Hoover A.; Ritter, T.; Jain, R.; Guimaraes, A. *Transl. Oncol.* **2016**, 9, 431-437.

(27) Goldberg, N. W.; Shen, X. Li, J.; Ritter, T. *Org. Lett.* **2016**, 18, 6102-6104

2.2 Department of Homogeneous Catalysis

Director:

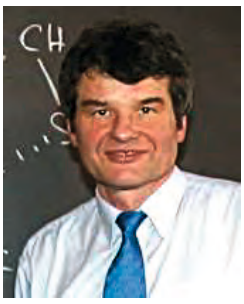
Benjamin List (born 1968)

Further group leaders:

Martin Klußmann (born 1974)

Bill Morandi (born 1983)

Klaus-Richard Pörschke (born 1949)
until March 2016



Curriculum Vitae: Benjamin List

1968	Born in Frankfurt / Main, Germany
1993	Chemistry Diploma, Freie Universität Berlin
1997	Ph.D., Johann Wolfgang Goethe-Universität Frankfurt, with Prof. J. Mulzer
1997-1998	Postdoc, Scripps Research Institute, La Jolla, USA, with Prof. R. Lerner
1999-2003	Assistant Professor (Tenure Track), Scripps Research Institute, La Jolla, USA
2003-2005	Group Leader at the Max-Planck-Institut für Kohlenforschung
2004-	Honorary Professor at the Universität zu Köln
2005-	Director at the Max-Planck-Institut für Kohlenforschung
2012-2014	Managing Director of the Max-Planck-Institut für Kohlenforschung

Awards and Honors

1997-1998	Feodor-Lynen Fellowship of the Alexander von Humboldt Foundation
1994-1995	NaFoeG-Graduate Fellowship of the Senate of Berlin
2000	Synthesis-Synlett Journal Award
2003	Carl-Duisberg-Memorial Award
2004	Degussa Prize for Chiral Chemistry
2004	Lieseberg Prize
2004	Lecturer Award of the German Chemical Industry Fund
2005	Visiting Professorship, Gakushuin University, Tokyo, Japan
2005	Society of Synthetic Chemistry, Japan: 2005 Lectureship Award
2005	AstraZeneca European Lecturer
2005	Novartis Young Investigator Award
2006	JSPS Fellowship, Japan
2006	100 Masterminds of Tomorrow, Germany
2006	Wiechert Lectureship, FU Berlin, Germany
2007	Fonds der Chemischen Industrie Award, Germany
2007	OBC Lecture Award
2007	AstraZeneca Research Award in Organic Chemistry
2008	Visiting Professorship, Sungkyunkwan University, Korea
2009	Organic Reactions Lectureship, USA
2009	Boehringer-Ingelheim Lectureship, Canada
2009	Thomson Reuters Citation Laureate

2010	High Levels Lectureship for Graduate Students, University of Science and Technology of China, Hefei
2010	New Honors Program Lectureship, National University of Singapore
2011	Boehringer-Ingelheim Lectureship, Harvard University, USA
2011	ERC-Advanced Grant
2012	Novartis Chemistry Lectureship Award 2012-2013
2012	Otto-Bayer-Prize, Germany
2013	Musher Memorial Lecture, Jerusalem, Israel
2013	Novartis Lectureship, UC Berkeley, USA
2013	Horst-Pracejus-Prize, Germany
2013	Mukaiyama Award, Japan
2013	Ruhrpreis, Mülheim, Germany
2014	Arthur C. Cope Scholar Award, USA
2014	Thomson Reuters Highly Cited Researcher Prize
2015	Carl Shipp Marvel Lectures in Organic Chemistry of Illinois
2016	Gottfried Wilhelm Leibniz-Prize
1999-2016	ca. 250 Plenary and Name Lectureships

Other Activities / Committees

2004	Co-Editor (with C. Bolm), Special Edition: "Organocatalysis", *Advanced Synthesis & Catalysis*
2004	Co-Editor (with K. N. Houk), Special Edition: "Enantioselective Organocatalysis", *Accounts on Chemical Research*
2005-	Co-Editor, *Synfacts* (Thieme)
2005-2011	Coordination of the DFG Priority Program (SPP1179) "Organocatalysis"
2006	Editor "Organocatalysis", *Chemical Reviews*
2006-	Member of the Selection Committee for Max Planck Group leaders
2008-	Editorial Advisory Board, *Beilstein Journal of Organic Chemistry*
2008-2009	Editor "Asymmetric Organocatalysis", *Topics in Current Chemistry*
2009-2010	Co-Editor (with K. Maruoka) "Asymmetric Organocatalysis", *Science of Synthesis Reference Library*
2010-	Editorial advisory panel, *Nature Communications*
2011-	Regional Editor of *Synlett* (Thieme)
2011-	Academic Advisory Board *Advanced Synthesis and Catalysis*
2011	Co-Editor (with K. Maruoka) "Asymmetric Organocatalysis", *Science of Synthesis* (Thieme)

2011 Editor “Asymmetric Organocatalysis”, *Beilstein Journal of Organic Chemistry*

2015- Editor in Chief of *Synlett* (Thieme)

Research in the Department of Homogeneous Catalysis

Researchers in our department continue focusing on the development of new catalysis concepts within the areas of organocatalysis and transition metal catalysis. We explore new catalysts and new catalytic reactions, expand the substrate scope of other catalytic transformations, apply asymmetric catalysis in natural product and pharmaceutical synthesis, study mechanisms of homogeneous catalytic reactions, and explore catalysis with textile-supported catalysts (B. List, K.-R. Pörschke, M. Klußmann, B. Morandi).

During the last three years, the department grew again noticeably, mainly due to the formation of the group of Bill Morandi comprising now thirteen co-workers. During the evaluation period between 2014 and 2016, the department consisted altogether of four groups, in addition to that of the head of the department, Professor Benjamin List, those led by Professor K.-R. Pörschke, who has been a group leader at the institute since over twenty years and retired in 2016, by Dr. M. Klußmann, who has been a group leader here since 2007, and of Dr. B. Morandi, who has joined the department in 2014.

The group of **Professor List** primarily advances enantioselective organocatalysis as a fundamental approach complementing the already more advanced fields of biocatalysis and transition metal catalysis. The List group has a profound interest in developing “new reactions”, designs and identifies new principles for the development of organocatalysts, expands the scope of already developed catalysts such as proline, uses organocatalysis in the synthesis of natural products and pharmaceuticals, and also investigates the mechanisms by which organocatalysts activate their substrates.

Since 2005, the group has first conceptualized, provided the proof of concept, and then significantly advanced “asymmetric counteranion directed catalysis” (ACDC). Initially merely an idea, this approach has progressed within the department, but now also at many other institutions around the globe, into a truly general strategy for highly enantioselective synthesis and has found utility in organocatalysis but also in transition metal catalysis and Lewis acid catalysis. This area is now the main research field in the List group. More recently, a new approach to heterogeneous catalysis was developed, in which organic catalysts are immobilized on inexpensive textile materials and used as efficient and recyclable catalysts.

Professor Pörschke has a longstanding expertise in the coordination and catalytic chemistry of Ni, Pd, and Pt, which often have been used in combination with main

group metal compounds (Li, Mg, Al, Ge, Sn). During the last decade, additional lines of research came into focus, such as Organometallic Plastic Crystals (OMPCs) of Ni, Co, Rh, and Ir, and bispidine-modified cisplatin-related Pt complexes as potential cytostatic compounds. Most recently, the group has discovered a process (in several variations) which allows cesium and rubidium to be separated quantitatively and with 100% selectivity from about any given source. Publications on this topic are forthcoming.

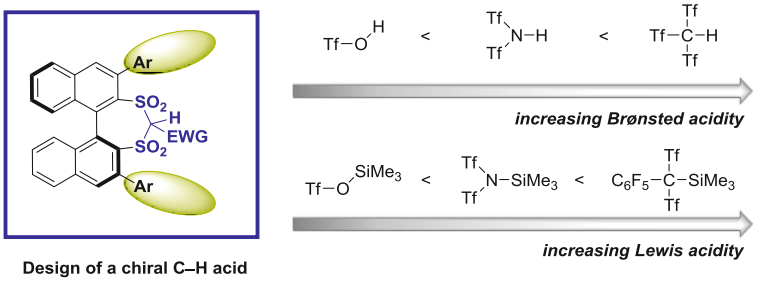
The group of **Dr. Klußmann** is developing novel synthetic methods and investigating reaction mechanisms in homogeneous catalysis, with an emphasis on oxidative methods for the functionalization of C-H bonds. Such reactions hold a great potential for sustainable chemistry, yet their mechanisms are often poorly understood. The mechanistic studies in the group thus aim at uncovering novel reactivities, understanding fundamental principles and providing inspiration for new applications.

The group of **Dr. Morandi** was established in 2014 after its leader had obtained a prestigious and highly competitive Max-Planck Research Group Leader position, which is fully supported from central MPG funds. The group has diverse activities in the design of novel catalytic reactions for the efficient and sustainable transformation of widely available starting materials. Among other projects, the group has already pioneered three different major areas: (1) the conceptualization of “shuttle catalysis” and its application to HCN-free reversible transfer hydrocyanation; (2) the invention of selective approaches to the defunctionalization of polyols; (3) the development of catalytic amination methods for the direct preparation of unprotected primary amines. As a result, several awards have been given to Bill Morandi.

2.2.1 Research Area "C–H Acids for Organic Synthesis" (B. List)

Involved: T. Gatzenmeier, D. Höfler, M. Leutzsch, M. van Gemmeren, Y. Xie, P. Wedemann

Objective: Despite the recent success in enantioselective catalysis with chiral Brønsted acids and Lewis acids, many unreactive substrate classes, such as unsaturated esters, remained out of reach for reasons of insufficient catalyst activity. Based on the well-established acidity trends for Brønsted and Lewis acids (Scheme 1), we proposed the design and synthesis of novel catalysts, whose enhanced activity would rely on a highly acidified C–H bond. The aim of this project is to establish C–H acids as a novel, highly acidic catalyst class. We introduce tetrasulfonyl propenes as a new motif for organocatalysis.

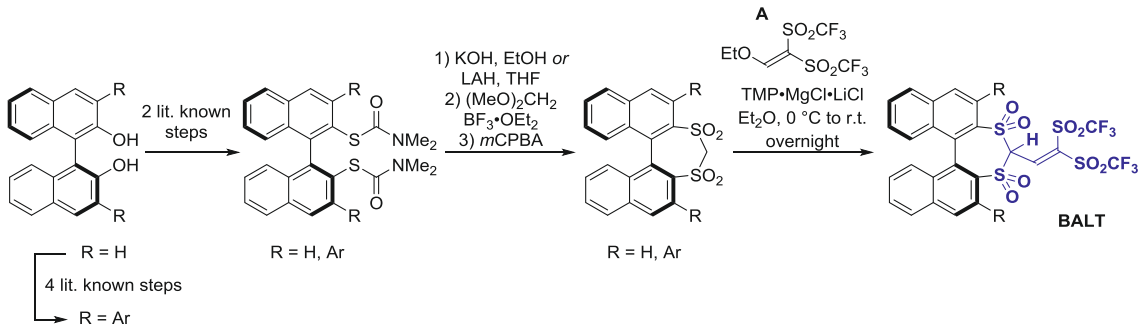


Scheme 1. Design of a chiral C–H acid catalyst (left); trend of Brønsted and Lewis acidities on triflated center-atoms (right).

Results:

A) BINOL-Derived Chiral C–H Acids

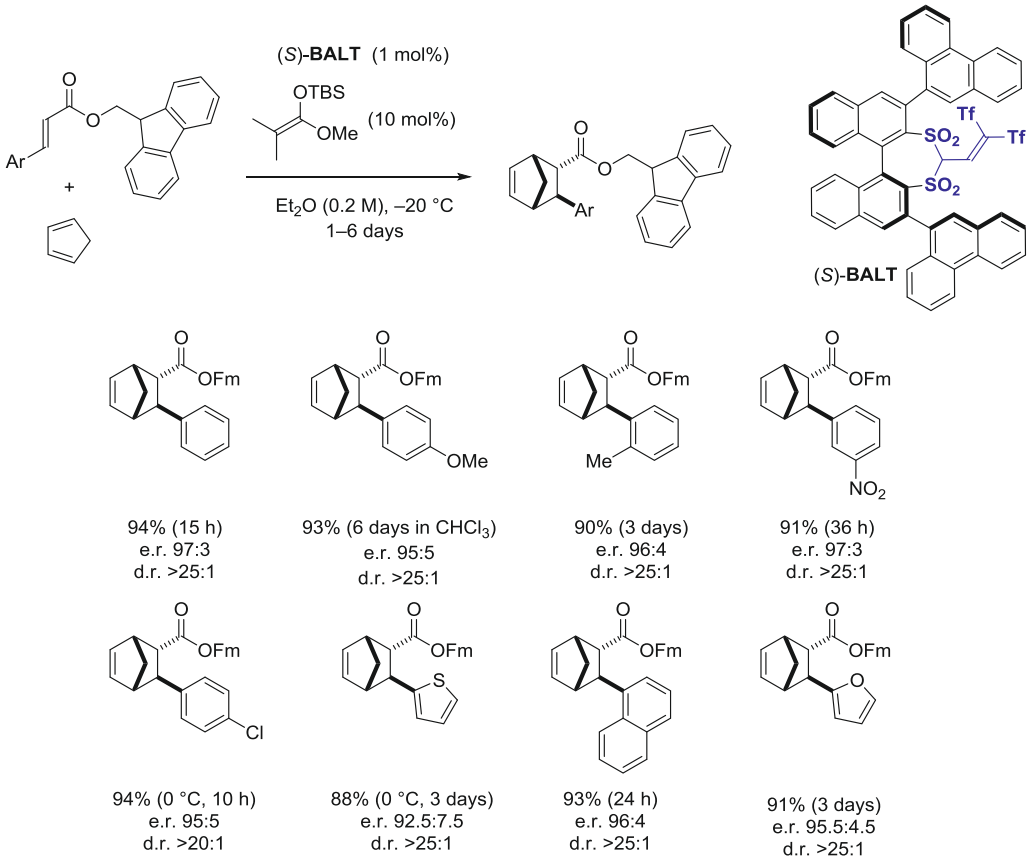
Based on the rationale of acidifying the C–H bond with electron-withdrawing groups, preferentially triflyl groups, a variety of chiral C–H acid catalysts have been designed, synthesized and tested. The first chiral C–H acid catalysts with stronger acidity than disulfonimides were obtained from 3,3'-substituted BINOL-derived disulfones and bistriflyl vinyl enol **A**.



Scheme 2. Synthetic strategy for novel chiral C–H acids.

These binaphthyl-allyl-tetrasulfones (BALTs) show very high activities, both in Brønsted and Lewis acid-catalyzed reactions. Upon silylation the newly developed C–H

acids become extremely active Lewis acid catalysts for highly enantioselective Diels–Alder reactions of cinnamates with cyclopentadiene. The reaction of various 9-fluoroenylmethyl cinnamates and cyclopentadiene gave very high yields and excellent enantioselectivities using only 1 mol% catalyst loading and a catalytic amount of a silyl ketene acetal.



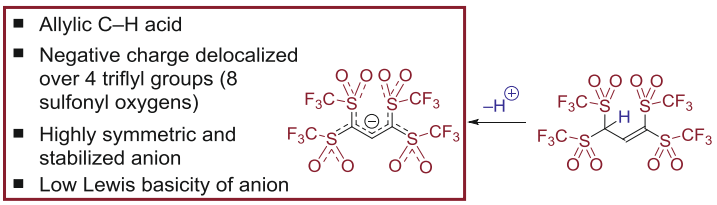
Scheme 3. Asymmetric Diels–Alder reaction of cinnamates and cyclopentadiene (Fm: 9-fluoroenylmethyl).

While many other chiral Lewis acids have previously been developed and applied in enantioselective Diels–Alder reactions, unactivated cinnamates had long remained a very challenging substrate class. Our work is the first example of this transformation and the first asymmetric counteranion-directed catalytic Diels–Alder reaction.

B) 1,1,3,3-Tetratriflylpropene (TTP) in Brønsted and Lewis Acid Catalysis

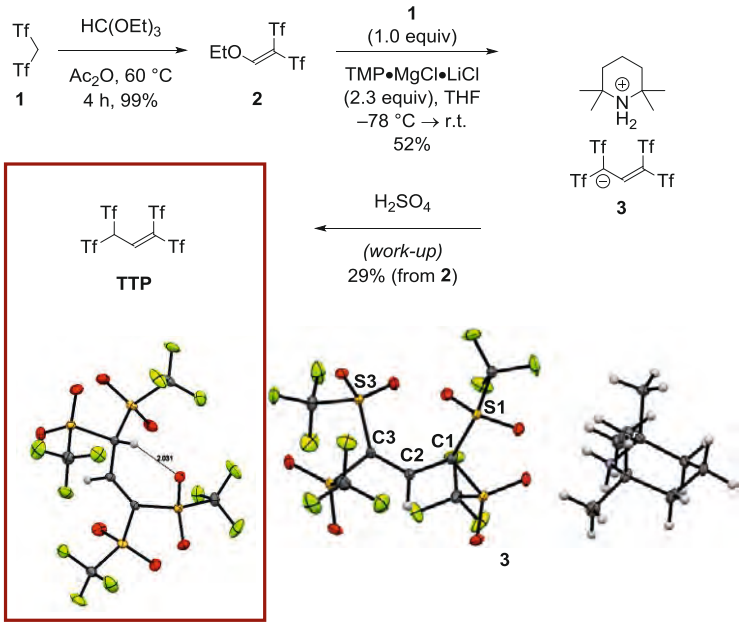
We also focused on the development of achiral, allylic C–H acids with increased acidity. Substituting the rather electron-rich binaphthyl backbone of chiral C–H acids with two triflyl groups was expected to lead to a dramatic increase in acidity as four

equally strong electron-withdrawing groups should provide a highly stabilized, symmetric anion. These considerations led to the design and development of 1,1,3,3-tetratriflylpropene (**TTP**, Scheme 4) whose activity was closely compared to other strong, structurally related organic Brønsted and Lewis acids.



Scheme 4. Design of tetratriflylpropene (**TTP**).

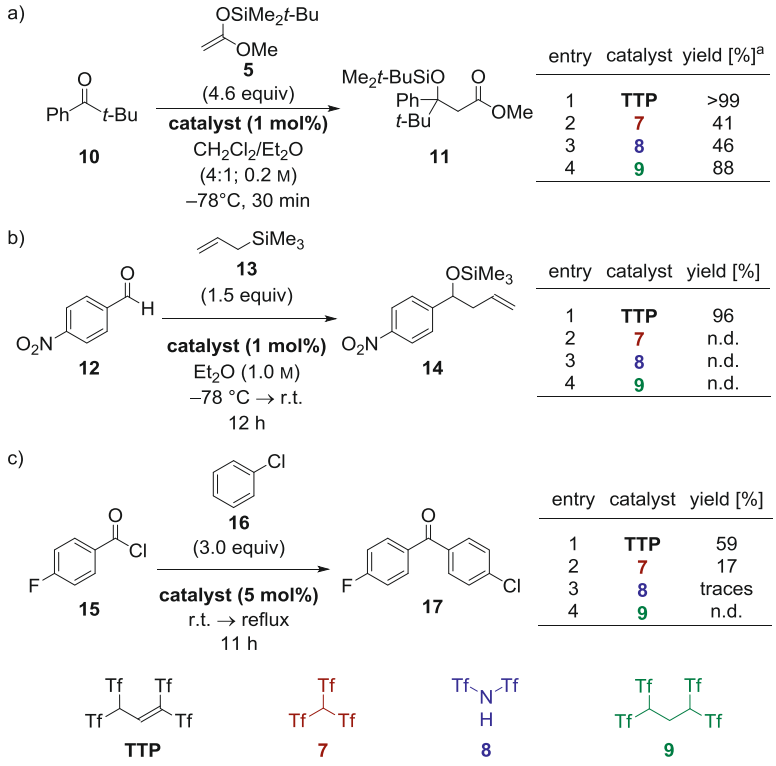
In analogy to our previous synthesis of chiral allyltetrasulfones, the novel, allylic C–H acid **TTP** can readily be obtained via a two-step synthesis (Scheme 5) starting from commercially available bistriflylmethane (**1**). Starting material **1** is first converted almost quantitatively to enol ether **2**, which is then treated with bistriflylmethane (**1**) and TMP base (= 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex solution) to give the TMP•TTP salt (**3**). Ammonium salt **3** can be either isolated or directly converted to **TTP** with an acidic work-up.



Scheme 5. Synthesis of **TTP** and X-ray analysis.

TTP was tested in a variety of synthetically relevant C–C bond forming reactions (Scheme 6) and compared to Tf_3CH (**7**), Tf_2NH (**8**), and diacid **9**. In the Mukaiyama aldol reaction of silyl ketene acetal **5** to the sterically demanding ketone **10**, **TTP** proved to be the most active catalyst, but **9** also showed a very promising activity (Scheme 6a). The Hosomi–Sakurai reaction of electronpoor *p*-nitrobenzaldehyde (**12**) with allylsilane **13** was chosen as another useful synthetic reaction (Scheme 6b). Due to the nitro group in the *para* position of **12** the Lewis basicity of the aldehyde is reduced rendering the commonly accepted activation mode via coordination of a Lewis acid to the oxygen's lone pair electron of **12** less favorable.

Surprisingly, only **TTP** gave the desired homoallylic silyl ether **14** in almost quantitative yields under these reaction conditions. Lastly, a Brønsted acid catalyzed Friedel–Crafts acylation reaction of electronpoor chlorobenzene **16** with benzoylchloride **15** was carried out for each catalyst (Scheme 6c). When **8** and **9** were employed, no desired product could be isolated. Carbon acid **7**, however, was able to give at least 17% of product while **TTP** gave, satisfyingly, 59% yield.



Scheme 6. Application of **TTP** and comparison with other catalysts. ([a]Triphenylmethane was added to reaction a) and the yield was determined by ^{1}H NMR analysis. n.d. = not detected.)

TTP hence looks very promising in Lewis and Brønsted acid catalyzed reactions. In comparison to the prominent, very active organic acids **7**, **8**, and **9**, **TTP** constantly showed the highest activity.

Future directions: We intend to continue with the exploration of new applications for the synthesized chiral and achiral C–H acids, the design of new motifs with confined structures and enhanced acidity, the measurement of pK_a values as well as computational and spectroscopical investigations to evaluate the activation mechanisms for Lewis acid catalysis. Further applications of **TTP** to synthetical useful reactions, which require strong Brønsted or Lewis acid activation, are currently investigated.

Publications resulting from this research area: 28

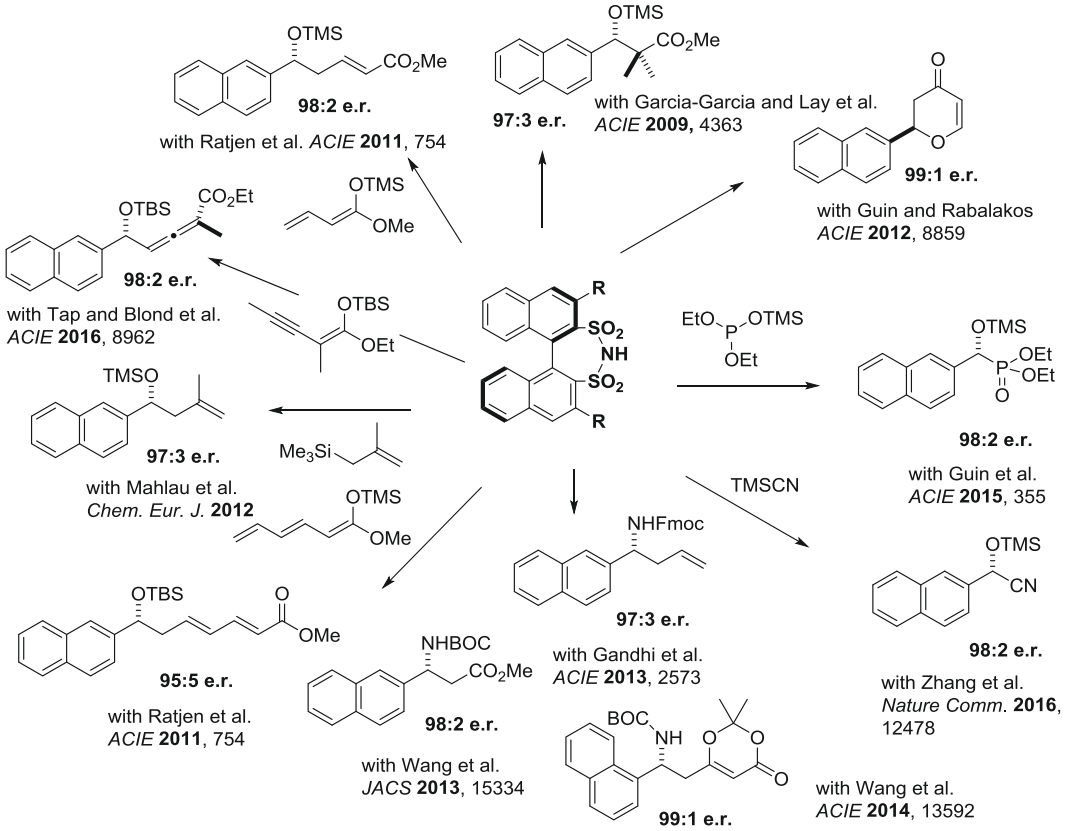
External funding: European Research Council Advanced Grants (HIPOCAT and CHAOS)

Cooperations: J. Lingnau, C. Farès (Mülheim/Ruhr, DE), I. Leito (University of Tartu, EE)

2.2.2 Research Area "Silylium ACDC" (B. List)

Involved: H. Y. Bae, A. Blond, T. Gatzenmeier, J. Guin, D. Höfler, P. S. J. Kaib, S. Lee, M. Leutzsch, R. Properzi, K. Rabalakos, L. Schreyer, A. Tap, M. van Gemmeren, V. Wakchaure, Q. Wang, Y. Xie, Z. Zhang

Objective: The field of Lewis acid organocatalysis has gained momentum in recent years as we expanded our asymmetric counteranion-directed catalysis (ACDC) concept to silylium-based Lewis acid catalysis (Scheme 1). Accordingly, in situ generated silylium ions, paired with an enantiopure counteranion, function as powerful and highly enantioselective Lewis acid catalysts. This strategy has proven to be successful in a variety of Mukaiyama-type Si-transfer reactions and also in non-Si-transfer reactions, such as the Diels–Alder reaction of cinnamates. Attractive features of silylium-based Lewis acid organocatalysis include the in situ regeneration of the catalyst ('self-healing') and relatively low catalyst loadings.

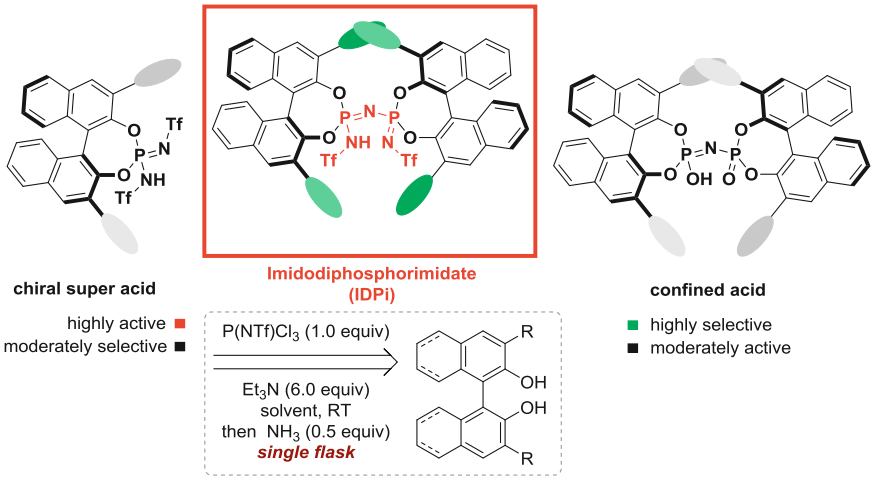


Scheme 1. Silylium-ACDC using chiral disulfonimide catalysts.

However, reactions of small aliphatic substrates that do not possess sterically demanding protecting groups, large aromatic surfaces, or bulky substituents, are still

rare. We therefore proposed the development of highly active “confined acid catalysts”, namely C_2-symmetric imidodiphosphorimidates (IDPi), possessing a sterically extremely demanding chiral microenvironment.

Results: IDPi acids, based on the interlocking of two identical BINOL subunits, were designed and prepared (Scheme 2).



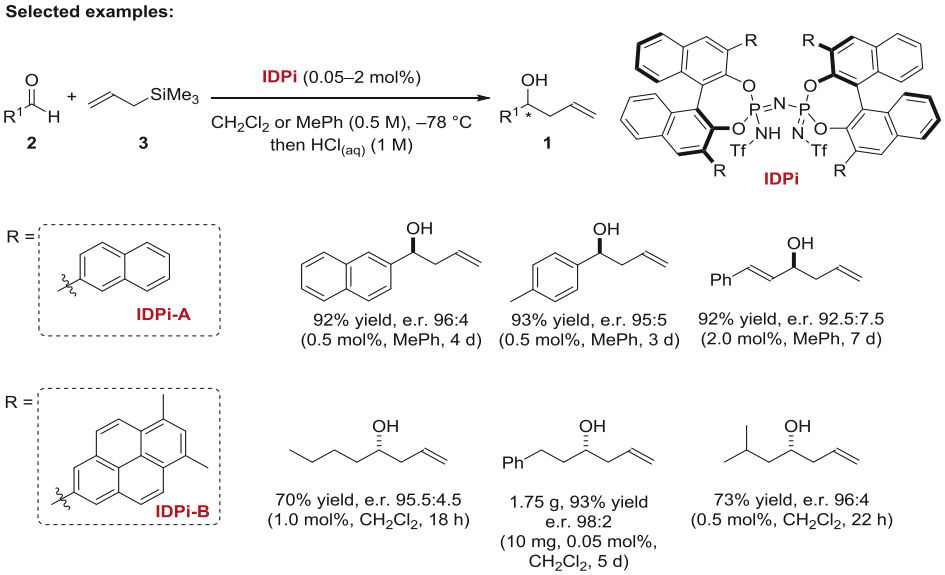
Scheme 2. Design of highly acidic sterically constrained imidodiphosphorimidate (IDPi) Brønsted acids, and its single flask synthetic procedure.

So far, IDPi acids are the most active and enantioselective catalysts ever made in this research group and currently help to solve some very challenging problems in asymmetric catalysis.

A) Hosomi–Sakurai Reaction

The enantioselective allylation of aldehydes to form homoallylic alcohols is one of the most frequently used carbon–carbon-bond forming reactions in chemical synthesis and, for several decades, has been a testing ground for new asymmetric methodology. However, a general and highly enantioselective catalytic addition of the inexpensive, non-toxic, air and moisture stable allyltrimethylsilane to aldehydes, the Hosomi–Sakurai reaction, has remained elusive. Due to the low nucleophilicity of this reagent (Mayr nucleophilicity: N = 1.6), its employment in asymmetric, catalytic addition reactions to aldehydes requires extremely reactive Lewis acids, and previously reported catalysts were found to be insufficiently active in this transformation. Imidodiphosphorimidates (IDPi) enable this allylation, converting various aldehydes with aromatic and aliphatic groups, at catalyst loadings ranging from 0.05 to 2.0 mol% with excellent enantioselectivities (Scheme 3). Our results show that confined

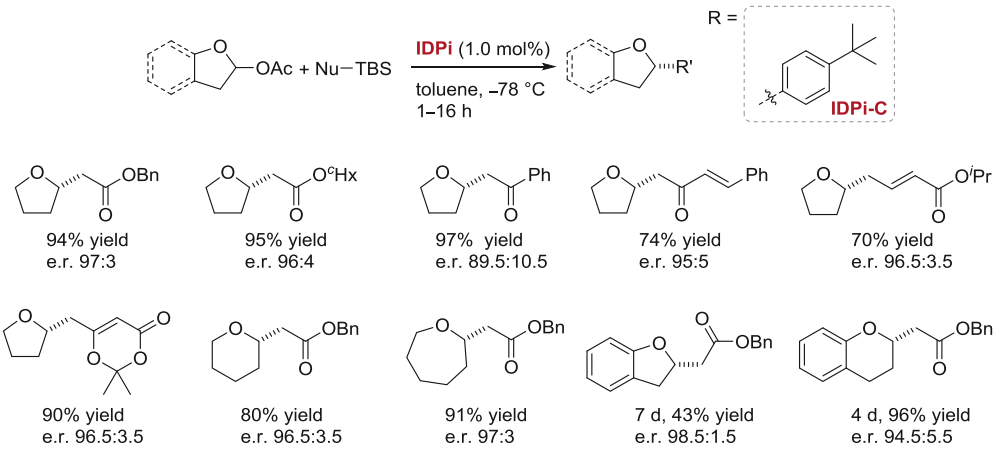
organocatalysts with extreme acidity and steric demand can overcome current synthetic limitations and solve a long standing problem in chemical synthesis.



Scheme 3. Synthetic applications of the Hosomi–Sakurai reaction.

B) Enantioselective Synthesis of *O*-Heterocycles

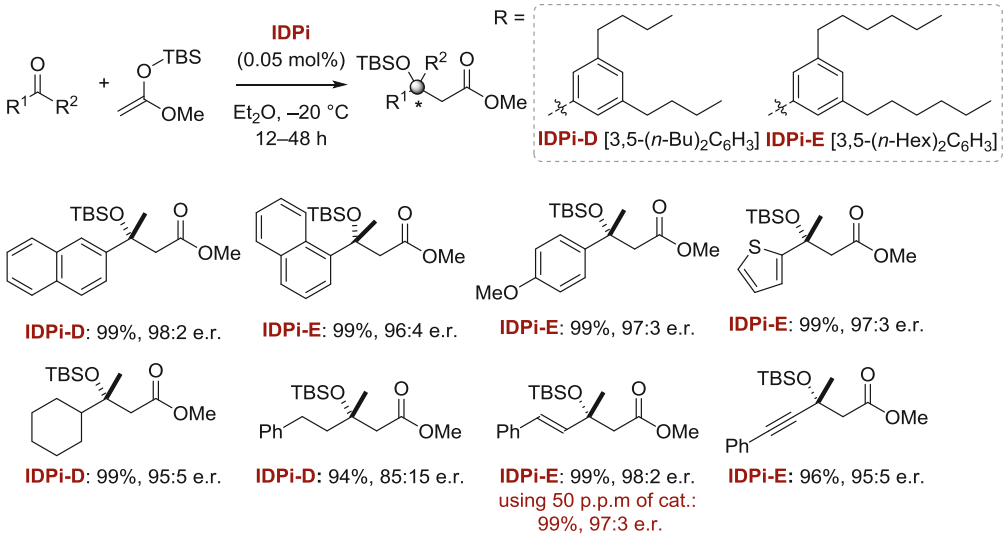
Oxygen containing heterocycles are essential building blocks for natural products, especially for carbohydrate chemistry. In spite of their frequent appearance, direct general methods to access these chemicals are quite limited. We extended our silylium-ACDC concept further to produce optically enriched heterocycles via unbiased oxocarbenium ion intermediates. The recently developed imidodiphosphorimidate catalyst proved to be an efficient catalytic system due to its high acidity as well as its extremely confined structure. As a result, five-, six-, and seven-membered *O*-heterocycles as well as a chromane and a dihydrobenzofuran were synthesized with moderate to high yields and high enantioselectivities (Scheme 4).



Scheme 4. Enantioselective synthesis of *O*-heterocycles.

C) Mukaiyama Aldol Reaction of Ketones

Despite numerous catalytic asymmetric Mukaiyama aldol reactions of silyl ketene acetals with aldehydes, Mukaiyama aldol reactions using ketones are quite rare. Ketones are not only less reactive than aldehydes, but the enantiofacial differentiation of two alkyl (aryl) groups in a ketone is also more challenging. For the preparation of enantiomerically enriched tertiary aldols, Lewis base and metal Lewis acid catalyzed methods have been reported, however, their substrate scope is limited and relatively high catalyst loadings (5–20 mol%) are required. We recently discovered that IDPi catalysts containing 3,5-(*n*-alkyl)$_2$-C$_6$H$_3$ groups, such as **IDPi-D** and **IDPi-E**, are remarkably efficient pre-catalysts for Mukaiyama aldol reactions of ketones with silyl ketene acetals. A variety of ketones with aromatic, heteroaromatic, secondary alkyl, or primary alkyl groups were subjected to this reaction. Surprisingly, the typical catalyst loading could be lowered to 0.05 mol%. In the presence of catalyst **IDPi-D** or **IDPi-E**, the ketones were converted to the desired chiral tertiary aldols in excellent enantiomeric ratio (up to 98:2) and with high chemical yields (up to 99%). Interestingly, the catalyst loading could be lowered to a part-per-million level (0.005 mol%: 50 p.p.m.), without erosion of enantioselectivity (99% yield, 97:3 e.r.; Scheme 5).



Scheme 5. Substrate scope of the catalytic Mukaiyama aldol reaction of ketones with silyl ketene acetal.

Future directions: Our rationally constructed, extremely active IDPi acid catalysts feature a highly tunable and sterically demanding active site and selectively process small and loosely bound substrates, promising high utility in various other challenging chemical reactions.

Publications resulting from this research area: 12, 16, 28, 34, 36, 38

External funding: European Research Council Advanced Grant (HIPOCAT), German Research Foundation: RESOLV Cluster of Excellence (fellowship to H.-Y. Bae)

Cooperations: M. Klußmann (Mülheim/Ruhr, DE)

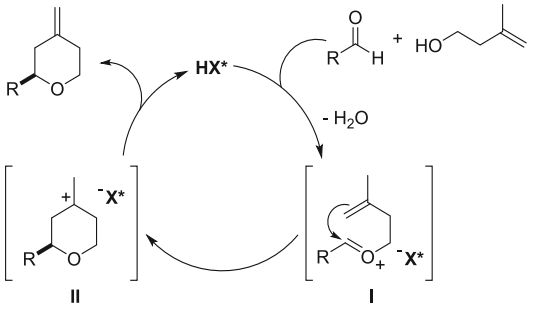
2.2.3 Research Area "Catalytic Asymmetric Reactions of Aldehydes with Olefins" (B. List)

Involved: M. W. Alachraf, N. Dupré, P. S. J. Kaib, M. Leutzsch, L. Liu, S. Prévost, A. Tap, G. C. Tsui, V. Wakchaure, Q. Wang, Y. Xie

Objective: The field of Brønsted acid organocatalysis has acquired wide popularity in recent years. However, typically used substrates such as imines are relatively basic and it is of high priority in our group to expand the scope of useful substrates to less basic but equally interesting substrates such as aldehydes, ketones, and olefins. The aim of this project was to investigate catalytic asymmetric reactions involving carbonyl electrophiles and alkenes as nucleophiles. Highly attractive examples include the Prins-, carbonyl ene-, and Torgov cyclization, and the hetero-Diels–Alder reaction of aldehydes with dienes.

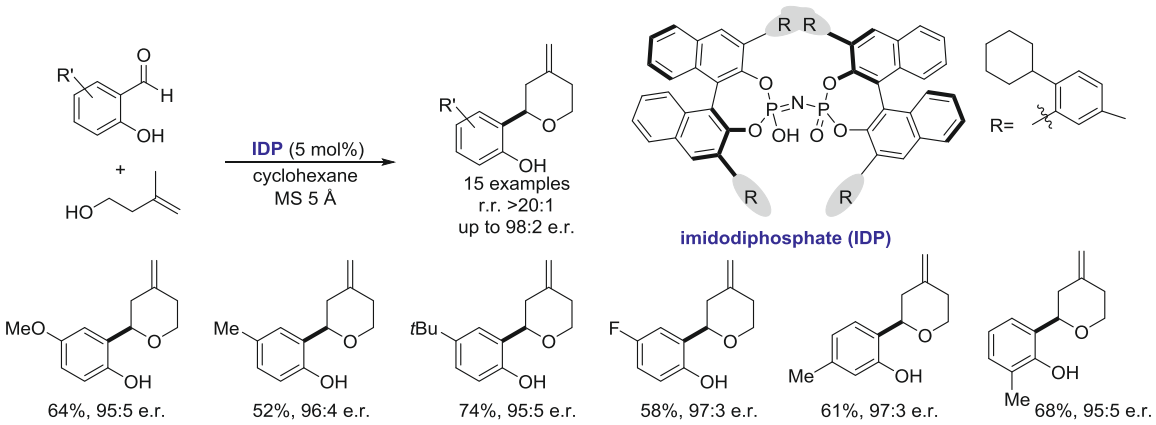
Results:

A) Catalytic Asymmetric Prins Cyclization



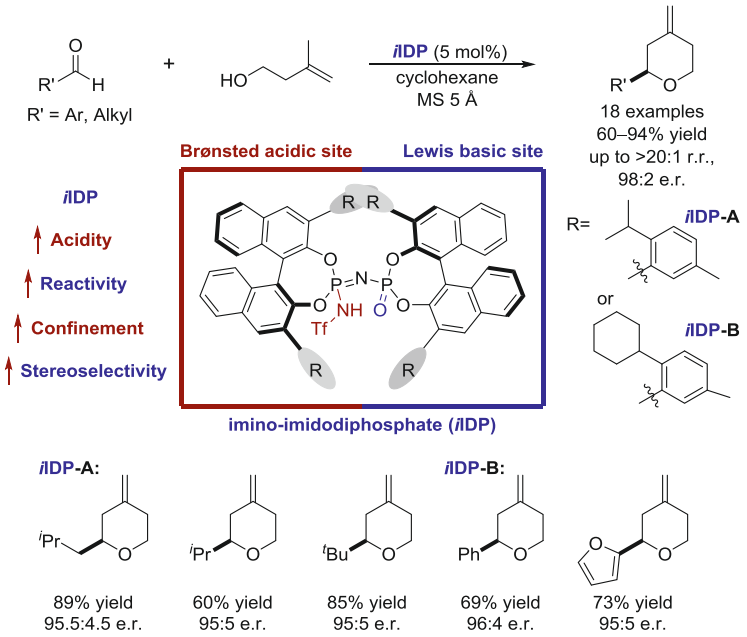
Scheme 1. Mechanistic cycle of the Prins cyclization.

Chiral functionalized tetrahydropyrans (THPs) are widely used as scaffolds in fragrances and pharmaceuticals, and are substructures in many natural products. The Prins cyclization between an aldehyde and a homoallylic alcohol is a particularly efficient approach to furnish THPs in which oxocarbenium ion **I** reacts intramolecularly with an alkene, creating a stereogenic center present in cation **II** (Scheme 1). We found that enantiodiscrimination can indeed be achieved with our confined imidodiphosphate (IDP) catalysts, which have previously demonstrated excellent enantiocontrol in asymmetric acetalization reactions. Nevertheless, activated substrates such as salicylaldehyde were required to afford functionalized 4-methylene tetrahydropyrans in excellent regio- and enantioselectivity (Scheme 2).



Scheme 2. Catalytic asymmetric Prins cyclization of salicylaldehydes.

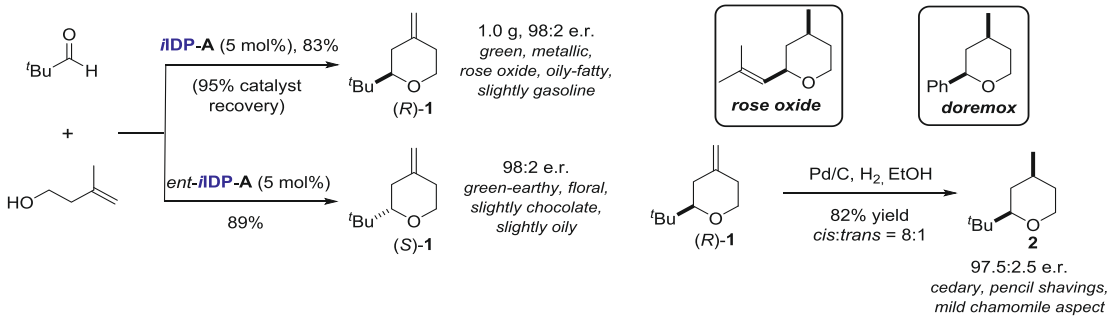
To promote asymmetric Prins cyclizations of unactivated aldehydes, we hypothesized that an approach towards acidifying our IDP catalysts may involve the replacement of an oxo-group with a stronger electron acceptor, such as a NSO_2CF_3 (NTf)-group. We envisioned that a confined imino-imidodi-phosphate (*i*IDP) structure would not only be more acidic than the parent IDP catalyst but also allows for the individual modulation of the acidic and basic component of the inherently bifunctional catalyst. Indeed, various linear, α- and β-branched aliphatic and aromatic aldehydes proved to be suitable substrates for *i*IDP catalysts, yielding excellent enantioselectivities and good yields under our optimized standard reaction conditions (Scheme 3).



Scheme 3. Catalytic asymmetric Prins cyclization using aliphatic and aromatic aldehydes.

Rose oxide and doremox can be obtained via hydrogenation of Prins THP products. (*R*)-**1** could be synthesized on a gram-scale while catalyst ***i*IDP-A** was recovered in 95% yield. For cyclic ether **1**, different scents of the corresponding enantiomers were revealed. (*S*)-**1** can be recognized by its floral and slightly chocolate bouquet.

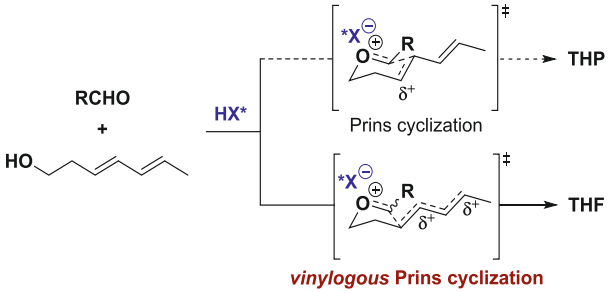
Hydrogenation of product **1** to saturated derivative **2** led to yet another scent, illustrating the fast and straightforward access to diverse scents using our methodology (Scheme 4).



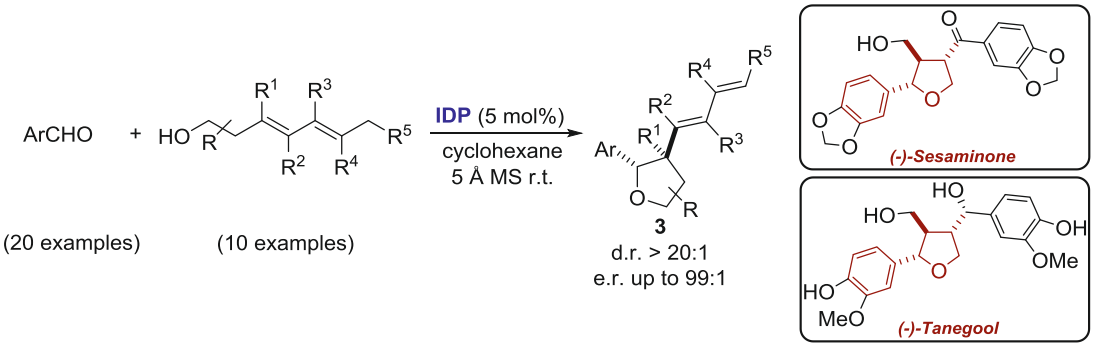
Scheme 4. Hydrogenation of Prins THP products.

B) Catalytic Asymmetric Vinylogous Prins Cyclization

Sporadic reports on the use of Prins cyclizations for the synthesis of tetrahydrofurans (THF) suffer from low diastereoselectivities and a catalytic asymmetric variant has been completely missing. Inspired by our successful previous THP syntheses, we designed a novel Prins cyclization in which a *dienyl* homoallylic alcohol is used instead of a homoallylic alcohol. We expected a vinylogous Prins cyclization to the corresponding THF product via a 5-endo-trig pathway to be preferred, as it would proceed via an allylic cation (Scheme 5).



Scheme 5. Prins cyclization vs. vinylogous Prins cyclization.

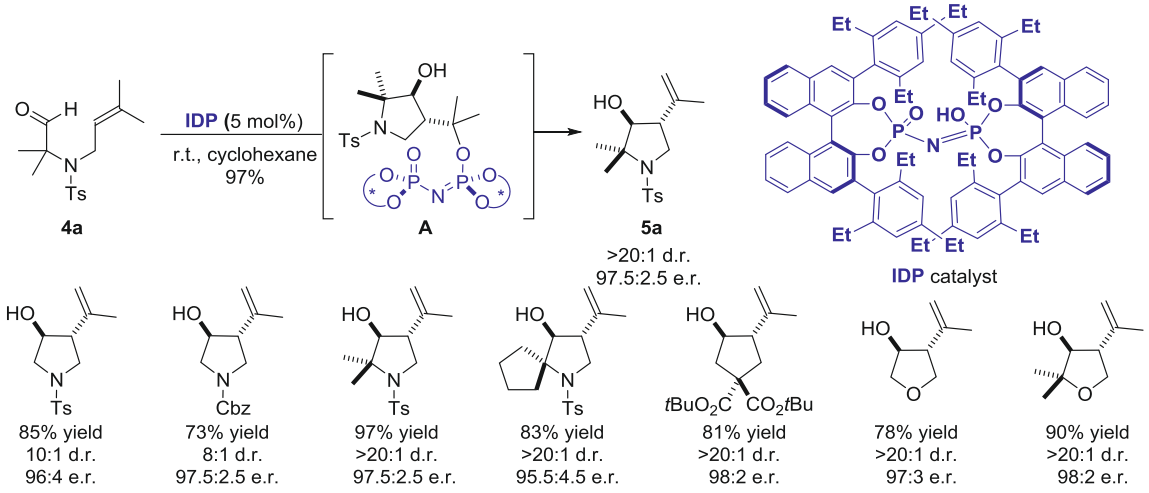


Scheme 6. Vinylogous Prins cyclization using aromatic and heteroaromatic aldehydes.

Under the optimized reaction conditions, various aromatic as well as heteroaromatic and even aliphatic aldehydes were investigated affording the product with good to excellent yield and selectivity. Dienyl alcohols with different substitution patterns were also well tolerated. Highly substituted THFs such as 2,3,4- or 2,3,5-trisubstitued THFs could be accessed by using enantiomerically enriched chiral dienyl alcohols. The stereochemical arrangement of the products matches that of the lignan natural products Sesaminone and Tanegool (Scheme 6).

C) Catalytic Asymmetric Carbonyl-Ene Reaction

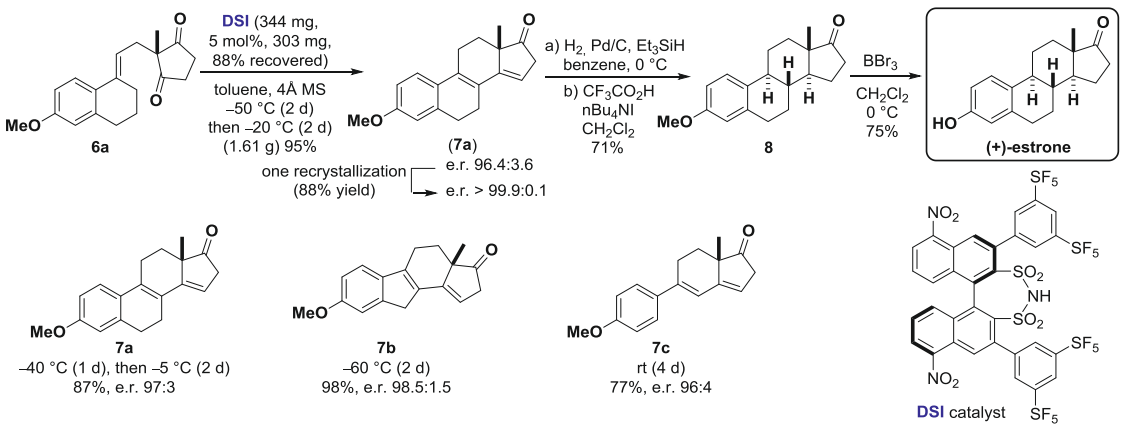
The carbonyl-ene reaction is arguably the most direct and atom economic carbon-carbon bond forming approach to homoallylic alcohols. Intramolecular carbonyl-ene cyclizations are frequently used, also in natural product synthesis and in an industrial route to menthol. Our laboratory has pursued an organocatalytic asymmetric intramolecular carbonyl-ene cyclization for several years. Various reported chiral Brønsted acids such as phosphoric acids, *N*-triflylphosphoramides and disulfonimides were investigated, but unfortunately, all of these acids proved to be active but poorly enantioselective. We now show that a confined imidodiphosphate catalyst (**IDP**), which has previously found utility in asymmetric acetalizations and sulfoxidations, can handle the asymmetric intramolecular carbonyl-ene cyclization. Diverse *trans*-3,4-disubstituted carbocyclic and heterocyclic five-membered rings were obtained in high yields and with good to excellent diastereo- and enantioselectivities (Scheme 7).



Scheme 7. Catalytic asymmetric carbonyl-ene reaction.

D) Catalytic Asymmetric Torgov Cyclization

The Torgov cyclization of **6a** gives diene **7a**, which can be readily transformed to racemic estrone, a female sex hormone. Despite previous efforts towards the development of an asymmetric version of this reaction, high selectivity and turnover numbers had not been achived. To solve this problem, we designed a new chiral disulfonimide (**DSI**) catalyst bearing nitro groups in the 5- and 5'-positions and a pentafluorothio moiety as a sterically bulkier and electronically more withdrawing alternative. With the optimized reaction conditions in hand, we also explored various other diketones. To illustrate the synthetic utility of this method, a gram scale Torgov cyclization and concise synthesis of (+)-estrone were realized. With slightly modified reaction conditions, product **7a** was obtained on gram scale with excellent yield and enantioselectivity. Most of catalyst **DSI** could also be recovered after the reaction. After recrystallization, diene **7a** was submitted to a two-step procedure to yield the fully reduced **8**, which, upon demethylation, gave enantiopure (+)-estrone. This (+)-estrone synthesis via a catalytic asymmetric Torgov reaction is the shortest route reported to date (Scheme 8).



Scheme 8. (+)-Estrone synthesis via catalytic asymmetric Torgov reaction.

Future directions: Further applications of our new Brønsted acid catalysts are currently in progress in our laboratory.

Publications resulting from this research area: 10, 21, 26, 37, 40

External funding: European Research Council Advanced Grant (HIPOCAT), Alexander von Humboldt Foundation (fellowship to Y. Xie and G. C. Tsui)

Cooperations: W. Thiel (Mülheim/Ruhr, DE), Givaudan (Dübendorf, CH)

2.2.4 Research Area “Enol Catalysis” (B. List)

Involved: G. Pupo, R. Properzi, G. A. Shevchenko

Objective: Having recently established a new organocatalytic activation mode for carboxylic acids via supramolecular hetereodimerization, we became interested in the activation of less-acidic ketones. Inspired by enzymatic enolizations, we envisioned that an interaction of the chiral phosphoric acid with the lone pair of the carbonyl and the α-proton would lead to the enolization of the ketone substrate. Furthermore, the resulting “chiral enol-phosphate complex” could possibly interact with an electrophile *via* hydrogen bonding thus resulting in an asymmetric α-functionalization reaction (Figure 1). Reminiscent of enamine catalysis, this design could however overcome some of its limitations. When α-branched ketones are employed as substrates, enamine catalysis, except in rare cases, suffers from the increased steric hindrance of the formed enamine intermediate and therefore, if at all, preferentially reacts via the kinetic enamine, restricting the access to quaternary stereocenters. We envisioned that by shifting to “enol catalysis”, we could form the corresponding thermodynamically more stable, higher substituted enol. This design would therefore allow a direct asymmetric access to quaternary and tetrasubstituted chiral centers.

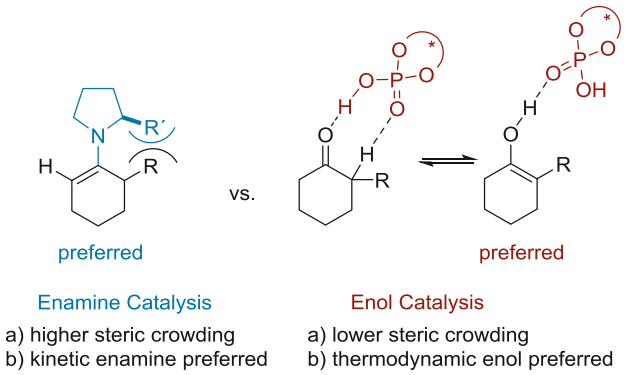
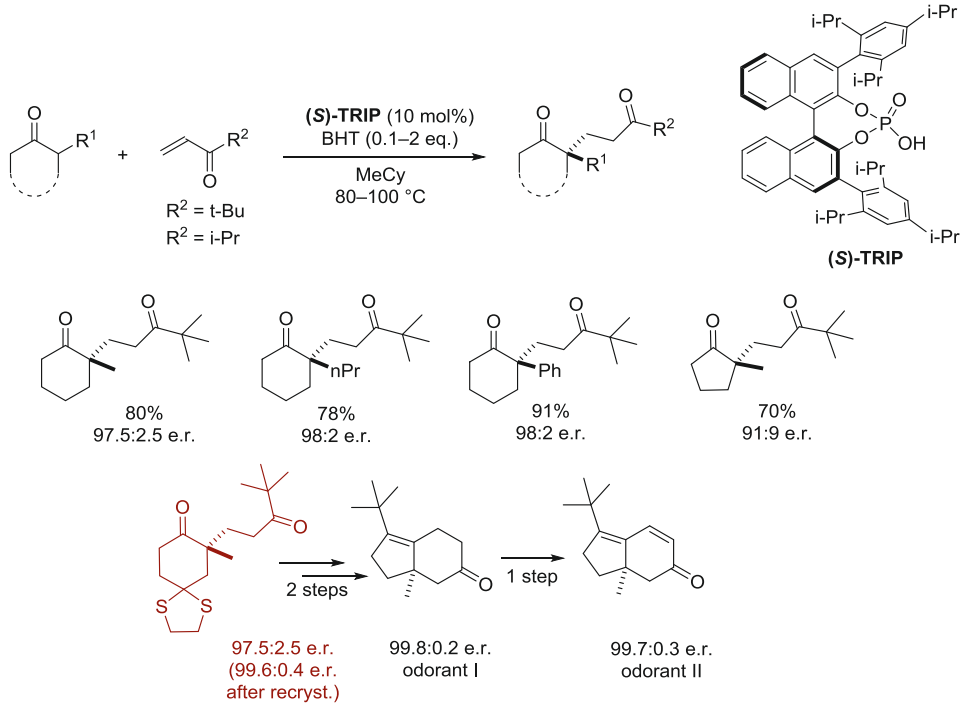


Fig. 1. Enamine vs. enol catalysis.

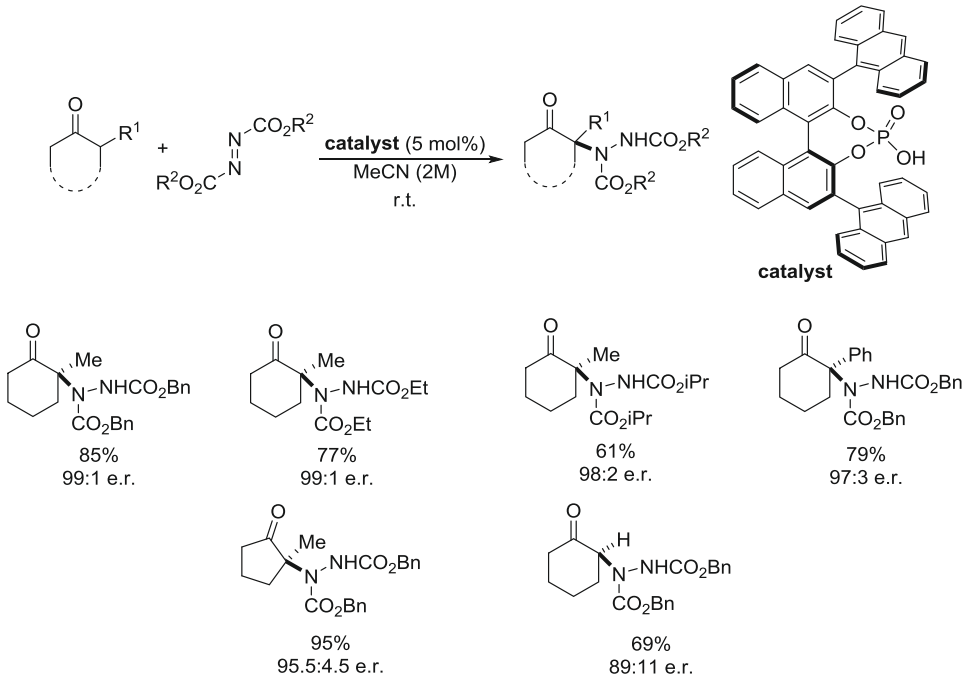
Results: In 2015 we successfully applied this concept to the Brønsted acid-catalyzed Michael addition of α-branched ketones to enones (Scheme 1). α-Alkyl as well as α-aryl substituted ketones were tolerated under the reaction conditions giving the desired products in good yields and excellent enantioselectivities (e.r. up to 98:2) thus underlining the broad applicability of enol catalysis. This novel methodology was then applied as the key step in the total synthesis of novel designer odorants.



Scheme 1. Brønsted acid-catalyzed Michael addition of α-branched ketones to enones.

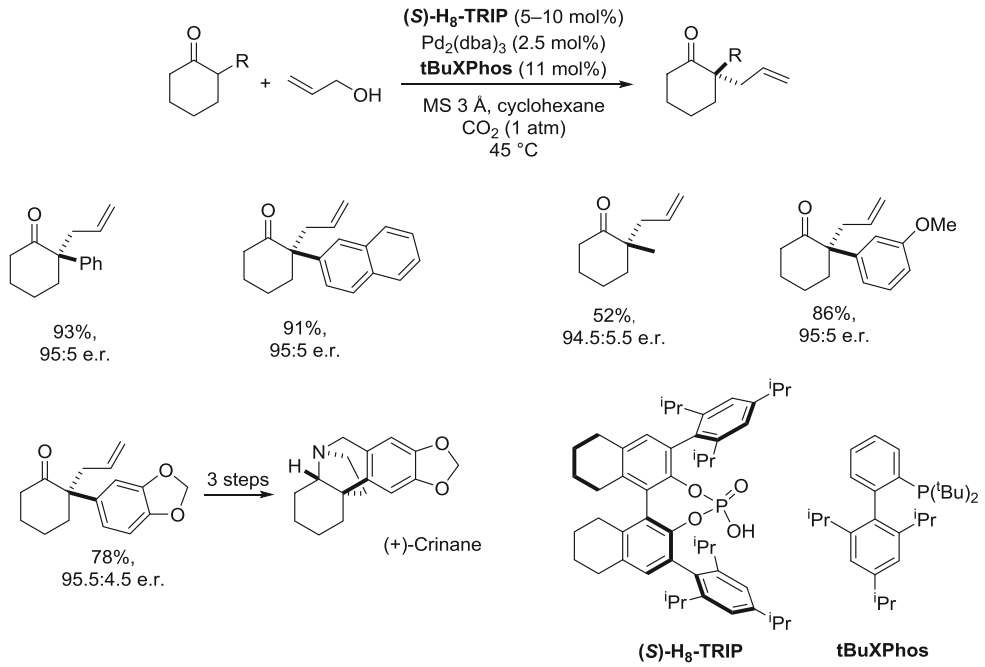
Following the initial results we focused on the exploration of enol catalysis as a generic activation mode. The α-amination of α-branched cyclic ketones (Scheme 2) attracted our attention since this methodology would allow a quick and elegant access to α-amino ketones and 1,2-aminoalcohols, motifs which can be found in numerous natural products and pharmaceuticals.

Gratifyingly, treating ketones with azodicarboxylates in the presence of a chiral phosphoric acid gave the desired products in high yields and excellent enantioselectivities (e.r. up to 99:1). Furthermore, enol catalysis proved to be a valuable tool for the synthesis of tertiary stereocenters as the corresponding product was obtained when cyclohexanone was used as substrate, albeit with slightly diminished enantioselectivity (89:11 e.r.). Interestingly, tetralone and indanone derived substrates resulted in lower yields and enantioselectivities.



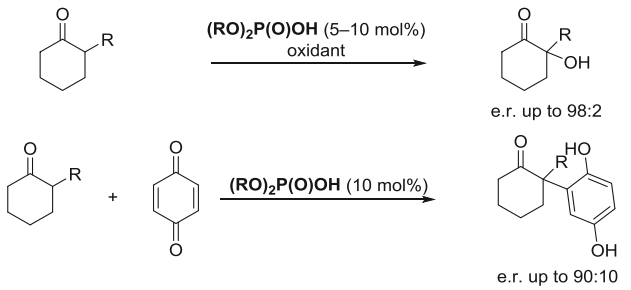
Scheme 2. α-Amination of α-branched cyclic ketones.

We then turned our attention towards the direct catalytic asymmetric α-allylation of α-branched ketones (Scheme 3). This fundamental transformation offers an efficient approach towards quaternary all-carbon stereocenters, which are common motifs in natural products and pharmaceuticals. Various indirect methods are known in the literature, but suffer from low atom-economy due to elaborate substrate preparation. We could overcome these drawbacks by using a combination of a Tsuji–Trost type activation of allylic carbonates and enol catalysis using (*S*)-H_8-TRIP as the chiral phosphoric acid. Later we could prove that even allylic alcohol, upon in situ activation by CO_2, was a suitable electrophile giving the desired products in high yields and excellent regio- and enantioselectivities. One of the key features of the protocol is that it only generates water as by-product. This methodology was applied as the asymmetric key step in the so far shortest formal total synthesis of Ameryllidaceae alkaloid (+)-crinane.



Scheme 3. Direct catalytic asymmetric α-allylation of α-branched ketones.

Future directions: Current efforts in our group focus on further exploring enol catalysis. Recently great progress was achieved in the asymmetric α-hydroxylation of α-branched ketones as well as in the direct α-arylation using benzoquinone as electrophile (Scheme 4).



Scheme 4. Asymmetric α-hydroxylation and direct α-arylation of α-branched ketones

Publications: 17, 20, 32

External funding: Fonds der Chemischen Industrie (fellowship to G. Pupo), "Sustainable Chemical Synthesis" program (fellowship to G. Shevchenko)

Cooperations: Givaudan (Dübendorf, CH)

2.2.5 Research Area "Catalytic Asymmetric Imine Reductions" (B. List)

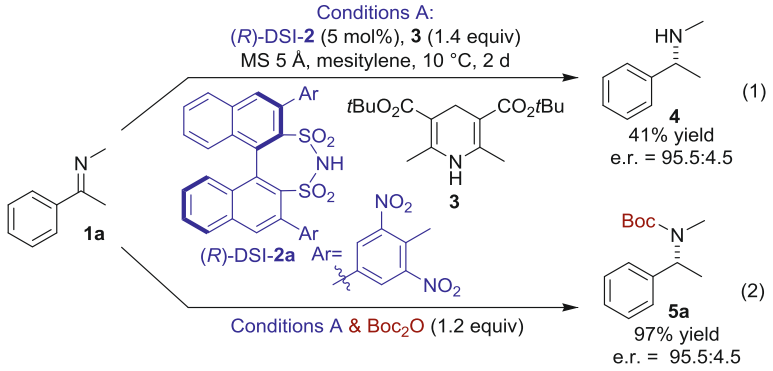
Involved: P. S. J. Kaib, M. Leutzsch, V. N. Wakchaure

Objective: Enantiomerically pure amines, in particular α-chiral amines, represent a privileged pharmacophore that can be found in a vast number of pharmaceutical and agrochemical substances. Catalytic asymmetric imine reductions and reductive aminations of carbonyl compounds are efficient approaches for the construction of optically pure amines. A few years ago, our group developed a Brønsted acid catalyzed asymmetric imine reduction and reductive amination of ketones that make use of Hantzsch esters as hydrogen source. Despite these advances, however, such reductions have been limited to *N*-aryl imines. *N*-Alkyl imines are highly attractive substrates for asymmetric reductions since they would directly furnish the *N*-alkyl amine pharmacophore. Chiral phosphoric acids typically fail in the corresponding Hantzsch ester mediated imine reductions and alternative approaches have only rarely been investigated and remain a major challenge. The aim of this project was to develop a simple, efficient and highly enantioselective methodology for the synthesis of α-chiral *N*-alkyl amines. Furthermore, this methodology should be expanded to an even more challenging reduction of *N*-H imines.

Results:

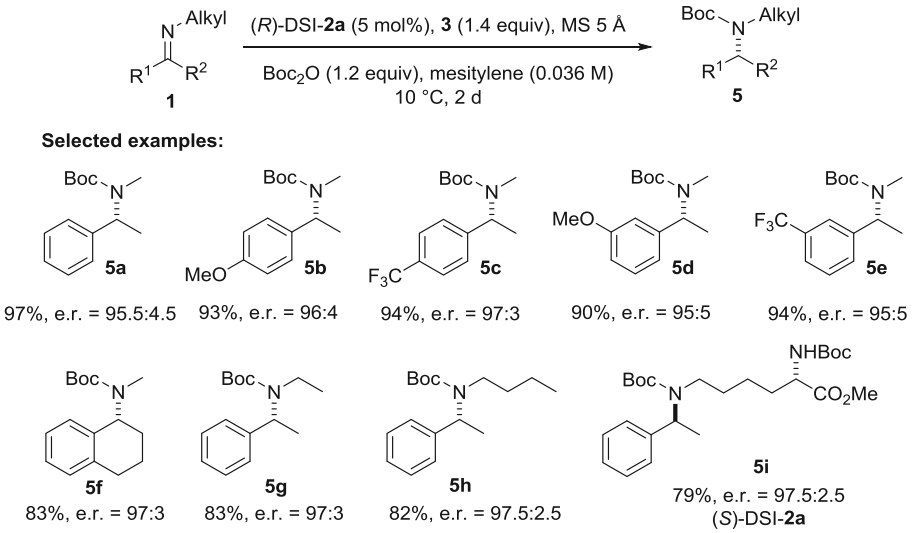
A) Disulfonimide-Catalyzed Asymmetric Reduction of *N*-Alkyl Imines

At the outset of our work, we hypothesized that the high basicity of the desired *N*-alkyl amine products may make the use of stronger Brønsted acid catalysts necessary for the Hantzsch ester mediated reduction of *N*-alkyl imines to achieve high turnover and enantioselectivity. Indeed, our chiral disulfonimide DSI-**2a** catalyzed the transformation more rapidly than the alternative phosphoric acid-based catalysts and also afforded amine **4** with higher enantioselectivity. However, the reaction was still rather sluggish and the product was isolated in only 41% yield (Scheme 1, eq 1). We speculated that the poor isolated yield was still due to catalyst deactivation through salt formation with highly basic amine **4**. It has previously been reported that related product inhibitions can be eliminated by in situ protection. Encouraged by these reports, we investigated the effect of running the reaction in the presence of di-*tert*-butyl dicarbonate (Boc_2O). Remarkably, we found that full conversion to the desired *N*-Boc-protected product **5a** in 97% yield with an identical e.r. of 95.5:4.5 was observed under these conditions (Scheme 1, eq 2).



Scheme 1. Reaction conditions for the disulfonimide-catalyzed asymmetric reduction of *N*-alkyl imines.

With the optimized conditions, a variety of *N*-alkyl imines were efficiently reduced in the presence of (*R*)-DSI-**2a** (5.0 mol%) to afford the corresponding Boc-protected *N*-methyl amines with high yields and enantioselectivity (Scheme 2). Additionally, the method tolerates a large variety of alkyl amines, thus illustrating potential for a general reductive cross-coupling of ketones with diverse amines; it was applied in the synthesis of the pharmaceuticals (*S*)-Rivastigmine, NPS *R*-568 Hydrochloride, and (*R*)-Fendiline.

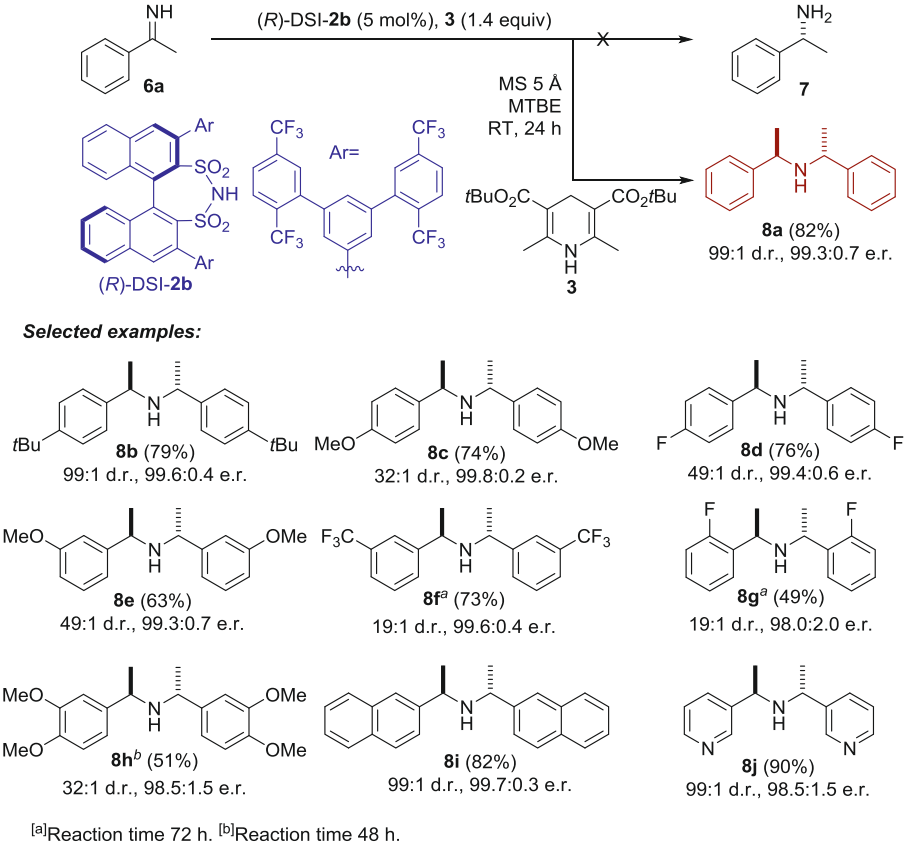


Scheme 2. Scope of the asymmetric reduction of *N*-alkyl imines.

B) Disulfonimide-Catalyzed Asymmetric Reduction of *N*-H Imines: Synthesis of C_2-Symmetric Amines

Subsequently, we became interested in extending our methodology to include the equally attractive and challenging *unsubstituted N*-H imines. We initially hoped that this process could provide direct access to enantioenriched primary amines (Scheme 3). Reductions of this type have rarely been studied and remain a major challenge. Surprisingly, when investigating the reduction of imine **6a** using Hantzsch ester **3** in the

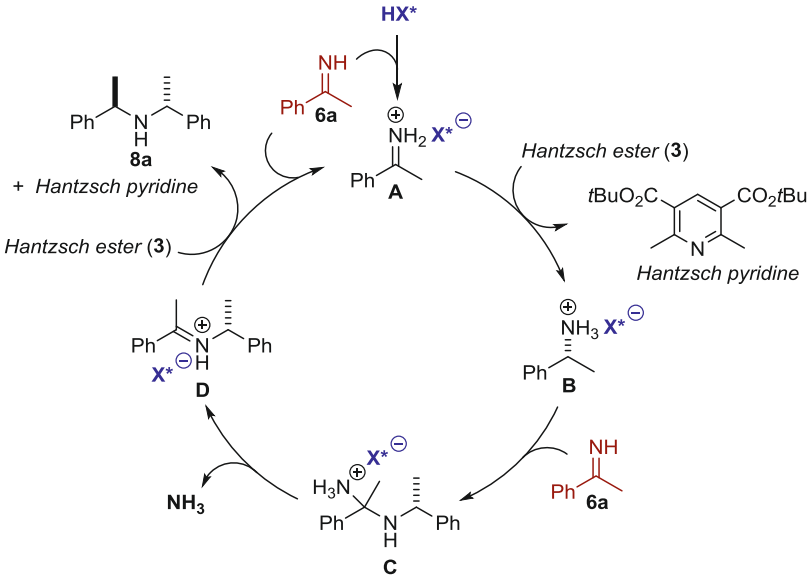
presence of DSI-**2b**, we found that instead of primary amine **7**, the corresponding C_2-symmetric secondary amine **8a** was obtained with outstanding diastereoselectivity and enantioselectivity (Scheme 3). This product has previously been reported as a by-product in a chemoenzymatic dynamic kinetic resolution of racemic primary amine **7**. However, to the best of our knowledge, such an asymmetric reductive condensation of *N*-H imines has previously been unknown. Encouraged by our initial observation and in consideration of the various applications of C_2-symmetric secondary amines, we have developed an asymmetric Brønsted acid catalyzed reductive condensation of *N*-H imines. A variety of *N*-H imines efficiently underwent the reductive condensation in the presence of disulfonimide **2b** (5.0 mol%) to afford the corresponding C_2-symmetric secondary amines in good yields and with outstanding diastereoselectivity and enantioselectivity (Scheme 3).



Scheme 3. Scope of the asymmetric reductive condensation of *N*-H imines.

We currently envision a catalytic cycle that is initiated by protonation of imine **6a** from chiral DSI-**2b** (Scheme 4). The resulting iminium ion pair **A** undergoes reaction with Hantzsch dihydropyridine **3** to give enantiomerically enriched primary amine salt **B** and the corresponding Hantzsch pyridine. Subsequently, amine **B** undergoes a

transimination with substrate **1a**, first to produce aminal **C**, which then liberates ammonia to form secondary iminium ion pair **D**. Finally, a second reduction of intermediate **D** provides diastereo- and enantioenriched secondary amine product **8a**. It is noteworthy that we observed a slight kinetic resolution in the reduction of iminium ion pair **D**, further enhancing the enantiomeric ratio of our C_2-symmetric secondary amine products. Perhaps this explains the superb enantioselectivities observed.



Scheme 4. Catalytic cycle.

Future directions: The focus in the future will be directed towards the development of stronger Brønsted acid catalysts to broaden the substrate scope.

Publications resulting from this research area: 25, 39

External funding: European Research Council Advanced Grant (HIPOCAT)

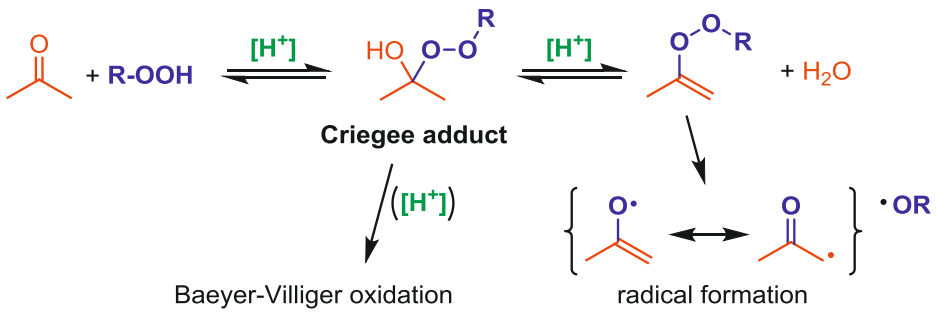
Cooperations: none

2.2.6 Research Area "Alkenyl Peroxide Chemistry" (M. Klußmann)

Involved: E. Böß, A.-E. Bosnidou, J. Demaerel, H. Engler, M. Hasenbeck, S. Karanestora, B. Schweitzer-Chaput, R. Verschueren

Objective: In previous mechanistic studies, we had discovered that the combination of ketones, hydroperoxides or hydrogen peroxide and acid generates radicals. Further studies led us to postulate the formation of highly reactive alkenyl peroxides as intermediates, which rapidly decay by homolytic O–O bond cleavage. We sought to investigate the underlying mechanisms, their importance for peroxide chemistry, as well as potential applications in synthesis.

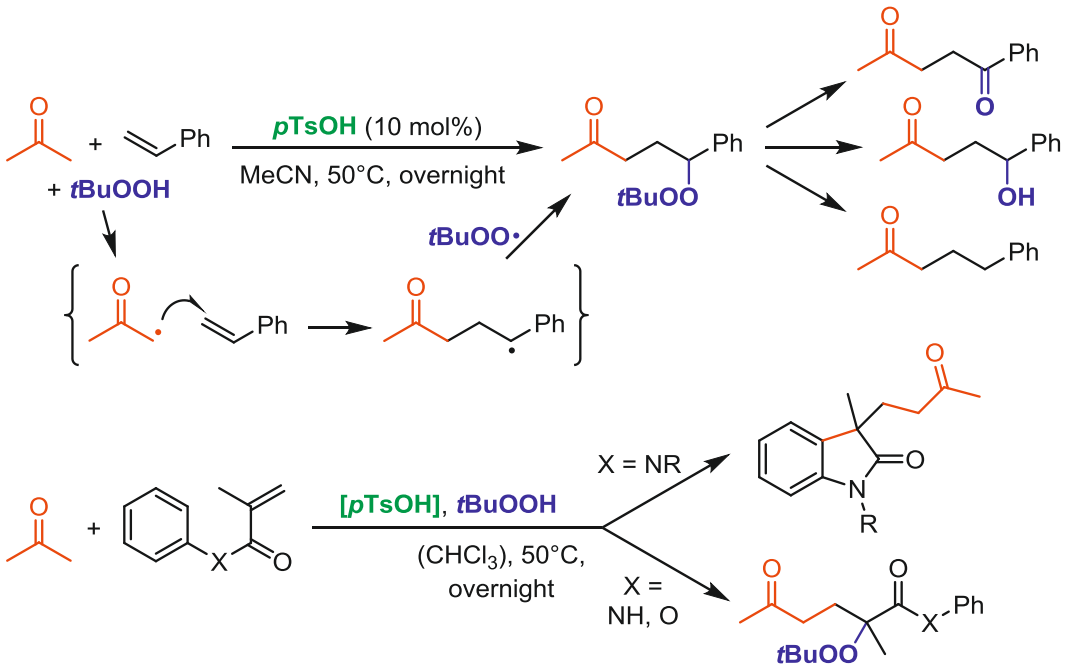
Results: Alkenyl peroxides are a special class of peroxides that are characterized by a significantly weaker O–O bond dissociation energy compared to other peroxides, resulting in homolytic decay at probably ambient temperature or below for most structures. An oxyl and a resonance-stabilized β-oxo-alkyl (or oxyallyl) radical are formed. Reports on this substance class were nearly exclusively limited to theoretical studies of atmospheric chemistry. Our studies revealed that alkenyl peroxides can be easily formed in solution by an acid-catalyzed condensation reaction between ketones and hydroperoxides or hydrogen peroxide. In a very small number of previous publications, this phenomenon was indicated, but our group was the first to rationalize the mechanism.



The mechanistic proposal shown above for the generation of alkenyl peroxides in solution has also implications for the Baeyer–Villiger oxidation of ketones, which shares a common intermediate, the so-called Criegee adduct. Our studies pointed out that the problems associated with the use of hydrogen peroxide as oxidant in Baeyer–Villiger oxidations is due to a competitive formation of alkenyl peroxides, which

generate undesired byproducts. Alkyl hydroperoxides favour alkenyl peroxide formation, while peracids favour rearrangement of the Baeyer–Villiger oxidation.

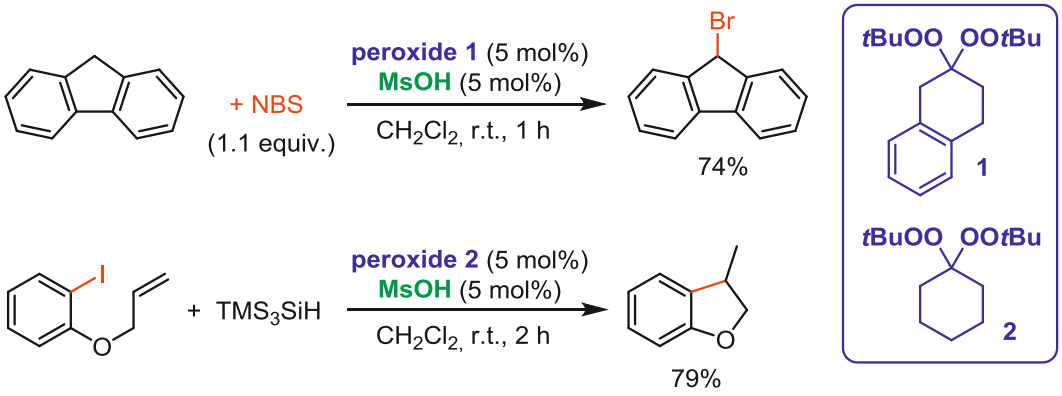
For organic synthesis, alkenyl peroxides offer a simple means to generate radicals from ketones, which is otherwise often limited to more activated 1,3-dicarbonyl compounds. We could form a number of radical addition products of various ketones to styrene derivatives, isolating γ-peroxyketones. These compounds can be easily transformed into synthetically interesting building blocks like 1,4-diketones or homo-aldol products. Addition reactions to *N*-aryl-*N*-alkyl methacrylamides led to radical cascade reactions generating ketone-functionalized oxindoles.



If a large excess of olefins is used, polymerization reactions can be conducted. In collaboration with the group of Prof. Junkers in Belgium, our method was applied to room-temperature radical RAFT polymerizations.

In addition, we found that alkenyl peroxides can be formed somewhat faster by treatment of geminal bisperoxides with acid, compared with the method described above. The radicals so generated can be used to initiate a variety of radical cascade reactions, so that the combination of geminal bisperoxides and acid is effectively a way of generating radical initiators *in situ* at temperatures as low as −20 °C. Given that the initiation rate can be fine-tuned by the peroxide structure and the amount and nature of

the acid, and that geminal bisperoxides are relatively stable, cheap and commercially available compounds, this method might be useful for a wide range of applications.



Future directions: develop new synthetic applications of alkenyl peroxides as precursors of ketone-radicals, develop novel ways of alkenyl peroxide generation, increase the rate of radical generation for low-temperature initiation of chain reactions.

Publications resulting from this research area: 43, 46, 48, 49, 51, 53

External funding: Deutsche Forschungsgemeinschaft (Heisenberg Scholarship to M. Klußmann)

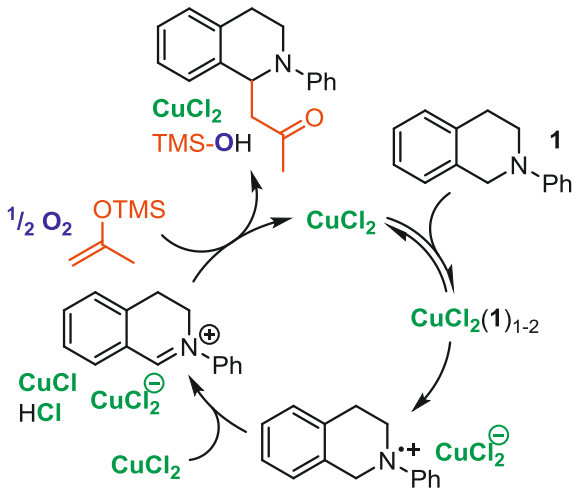
Cooperations: T. Kurtén (Helsinki, FI); T. Junkers (Hasselt, BE)

2.2.7 Research Area "Catalytic Oxidative Reactions and Mechanistic Studies" (M. Klußmann)

Involved: E. Böß, N. Gulzar, K. Jones, M. Scott, A. Sud, H.-L. Yue

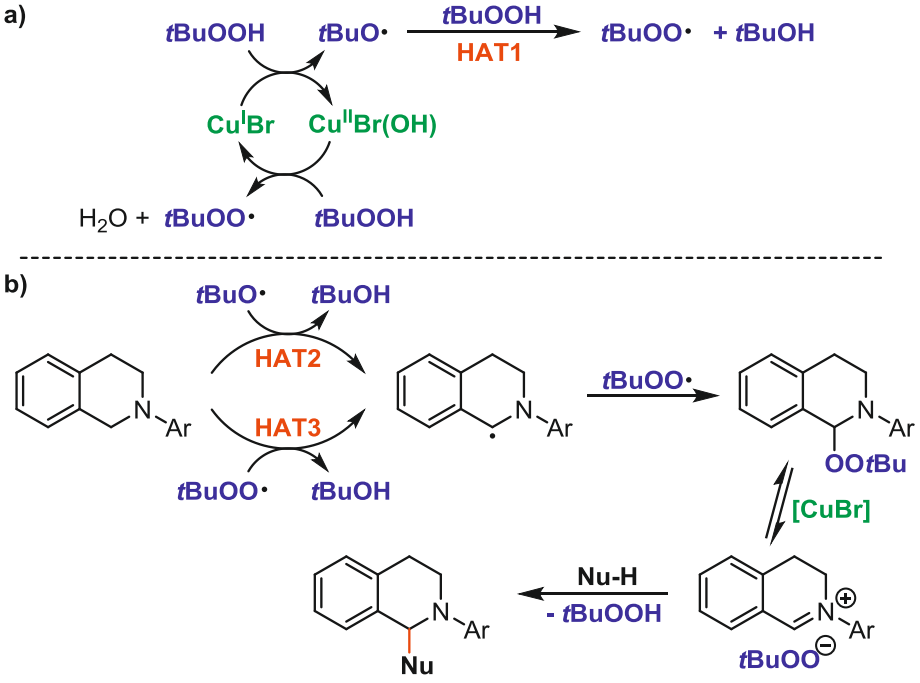
Objective: Our group has a strong interest in detailed mechanistic studies, as these provide inspirations for the development of new synthetic methodology, improve the general understanding of chemical reactivities, and thus also have a direct impact on teaching. Kinetics play a central role in our investigations of reaction mechanisms and we often collaborate with other research groups to tackle a complex mechanistic problem. The findings from recent studies involving peroxide-mediated C–H functionalization reactions go hand in hand with applications in synthesis.

Results: Our group had previously developed oxidative coupling reactions for the formation of C–C bonds from C–H bonds, in particular methods for the functionalization of *N*-aryl tetrahydroisoquinolines. Such reactions gained a lot of attention after the group of C.-J. Li had reported Cu-catalyzed functionalization reactions using *tert*-butyl hydroperoxide (*t*BuOOH) as oxidant. We had reported a related method with a very broad substrate scope using elemental oxygen as the oxidant and we were the first to provide detailed mechanistic studies for this type of reaction. We have studied the kinetics of our oxygen-mediated reaction in detail, which helped to clarify differences in the substrate scope between this and the *t*BuOOH-mediated reaction by Li.

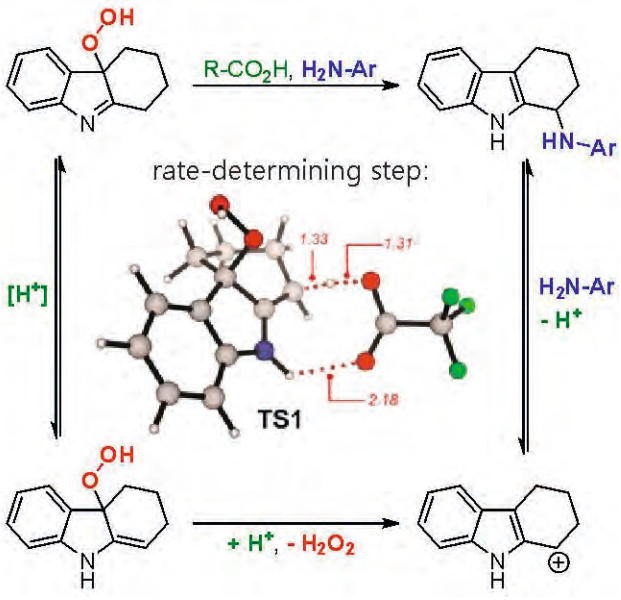


Our mechanistic proposal for the latter method by the group of C.-J. Li was recently challenged by a study from the group of Michael P. Doyle. We had suggested hydrogen atom transfer (HAT) from the amine to intermediate oxyl and peroxyl radicals (formed by Cu-catalysis from *t*BuOOH) as key step, which was dismissed by Doyle's report suggesting electron transfer. In a collaborative effort utilizing different kinetic and computational investigations, we could find strong support for a mechanism via HAT

and also uncovered a competitive system of three different HAT reactions that leads to significant differences in kinetic isotope effects, depending on reaction conditions.



The formation of peroxides as reactive intermediates in C–H functionalization reactions, as in the mechanism shown above, has inspired us to develop this as a general strategy. Especially if the C–H functionalization via Intermediate PeroxideS (CHIPS) could be mediated by the use of elemental oxygen, such reactions could be conducted in a rather sustainable manner. We had thus developed an aerobic method for the functionalization of tetrahydro-carbazol derivatives using visible light, a sensitizer and a Brønsted acid catalyst, which could be used for the synthesis of antiviral compounds. The reaction involved an interesting shift during the substitution of the hydroperoxide group. The mechanism of this reaction was



investigated using kinetic and computational methods, and an acid-catalyzed imine-enamine tautomerization was revealed as the rate controlling step.

An extension of this strategy to other substrate classes is ongoing. In addition, we have developed an oxygenative thiol-ene reaction using *t*BuOOH as oxidant which was inspired by our recent investigations of Brønsted acid catalysis and radical reactions. Finally, we have investigated kinetic aspects of an asymmetric Brønsted acid catalyzed reaction in a collaborative effort together with the group of Prof. Benjamin List.

Future directions: Investigate other amines and amides in oxidative coupling reactions of increased synthetic interest, extend the concept of CHIPS to other substrate classes.

Publications resulting from this research area: 36, 42, 44, 45, 47, 50, 52

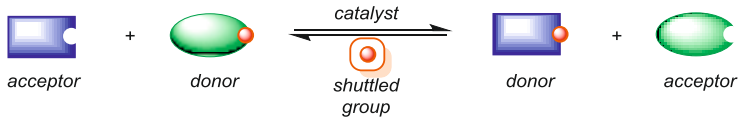
External funding: Deutsche Forschungsgemeinschaft (Heisenberg Scholarship to M. Klußmann); Alexander von Humboldt-Stiftung (stipend to K. Jones); Chinese Scholarship Council (stipend to H.-L. Yue)

Cooperations: M. Bietti (Rome, IT); M. Breugst (Köln, DE); B. List, W. Thiel (Mülheim/Ruhr, DE)

2.2.8 Research Area "Shuttle Catalysis" (B. Morandi)

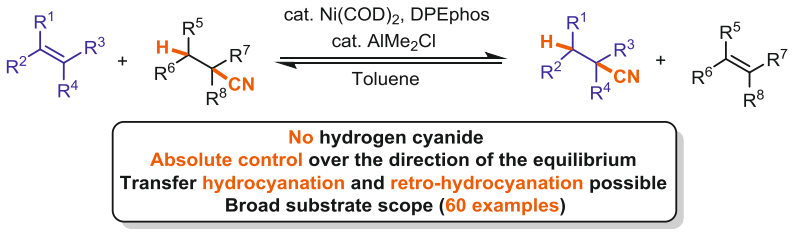
Involved: X. Fang, P. Yu, Y. Lee, B. Cacherat, Z. Lian, G. Prina Cerai, B. N. Bhawal, E. Wöstefeld

Objective: Catalytic reversible reactions, such as alkene metathesis and transfer hydrogenation, have had an auspicious impact on the molecular sciences. We are currently developing "shuttle catalysis" reactions that parallel the mechanism of transfer hydrogenation through the reversible transfer of chemical moieties beyond H_2 (Scheme 1), to address synthetically relevant challenges in catalysis and provide new disconnections for synthetic chemists.



Scheme 1. Schematic representation of the shuttle catalysis concept.

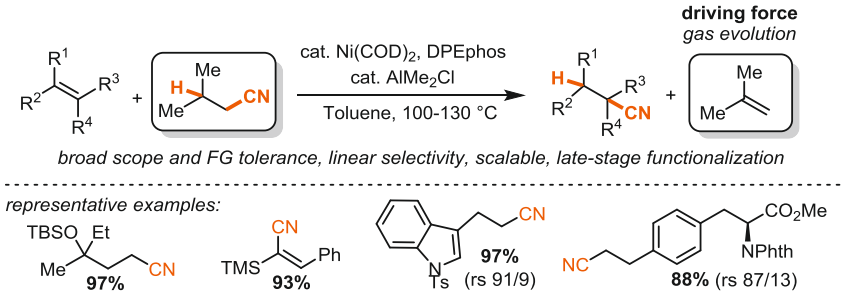
Results: At the outset of our investigations, we targeted the development of a catalytic reversible hydrofunctionalization reaction of alkenes. We selected the hydrocyanation reaction because alkenes and nitriles are very useful synthetic intermediates with complementary reactivity profiles. Furthermore, the hydrocyanation of alkenes has been underexploited in routine laboratory-scale synthesis because traditional approaches rely on the use of volatile and highly toxic hydrogen cyanide (HCN). Additionally, the reverse retro-hydrocyanation is thermodynamically disfavored and has not been realized experimentally. To address these challenges, we have reported a Ni-catalyzed transfer hydrocyanation reaction that efficiently interconverts alkenes and nitriles (Scheme 2).



Scheme 2. Our recently developed transfer hydrocyanation.

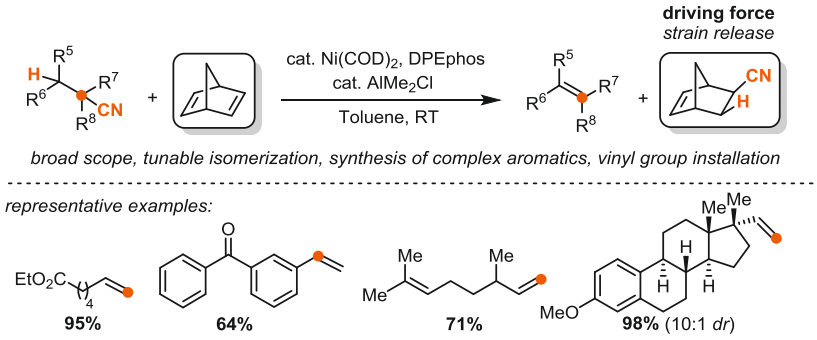
This strategy circumvents the need to employ the highly toxic and volatile reagent hydrogen cyanide, and thus provides a safer approach to hydrocyanation reactions when

compared to traditional approaches. This reaction is also a rare example of transfer functionalization wherein the direction of the equilibrium can be fully controlled using simple driving forces, such as strain release or gas extrusion, to undergo either the forward or reverse reaction with a broad set of structurally different substrates. The forward functionalization reaction can be favored using a sacrificial donor molecule, isovaleronitrile, which is transformed into isobutene, a volatile compound that can escape the reaction mixture thus driving the reaction process to completion (Scheme 3). The method tolerates a broad scope of functional groups, as demonstrated in the late-stage transfer hydrocyanation of bioactive starting materials.



Scheme 3. Forward transfer hydrocyanation of alkenes.

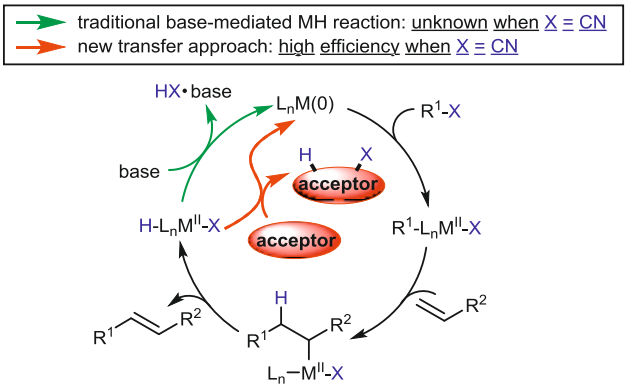
The reverse process, retro-hydrocyanation, can be performed when sacrificial norbornadiene is used to drive the reaction to completion through ring strain release (Scheme 4). Retro-hydrocyanation enables the use of the nitrile group as a removable activating group for the construction of C–C bonds, and this strategy was used both in the synthesis of complex aromatic products and the stereoselective installation of a quaternary vinyl group.



Scheme 4. Retro-hydrocyanation of nitriles.

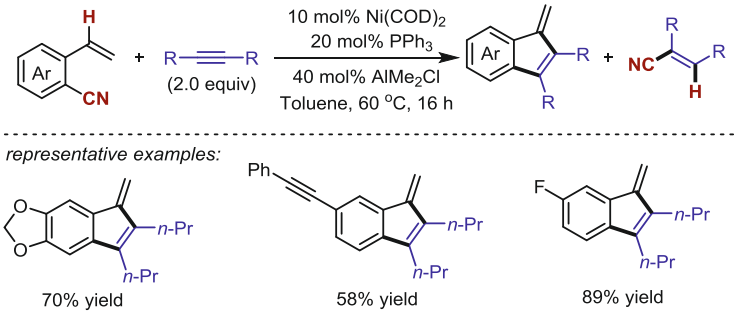
In more recent results, we demonstrated that the transfer hydrocyanation can also be used as a turnover-enabling step in unprecedented cross-coupling reactions (Scheme 5). Using this strategy, we could unlock the Mizoroki–Heck (MH) reaction of aryl cyanide

electrophiles, a process that is difficult to perform under the traditional, basic conditions. Our approach makes use of a key transfer hydrocyanation step instead of a base to regenerate the active Ni(0) species under base-free conditions. This was critical for the success of this reaction because the activation of the C–CN bond usually requires a Lewis-acid that is poorly compatible with the use of base.



Scheme 5. Comparison of classical MH mechanism with the new approach involving transfer hydrocyanation as a turnover-enabling step.

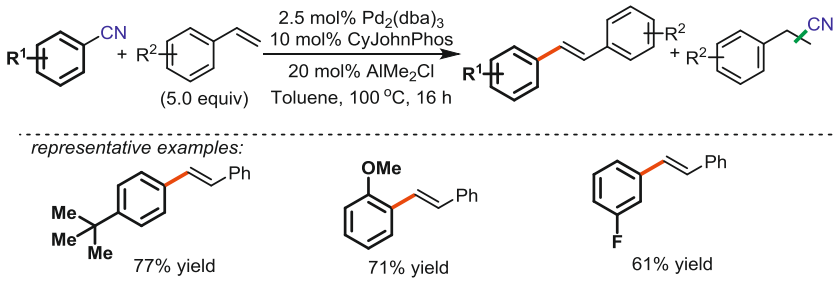
Using this strategy, we could develop two novel Mizoroki–Heck-type reactions of aryl cyanides. Initially, a cascade carbonickelation/MH reaction of 2-cyanostyrenes was achieved using a key alkyne transfer hydrocyanation step (Scheme 6). This reaction led to the facile preparation of benzofulvenes that are useful molecules for synthesis. Labelling studies confirmed that a transfer hydrocyanation of the alkyne took place.



Scheme 6. Cascade carbonickelation of alkynes/MH reaction of 2-cyanostyrenes.

In further work, we targeted the intermolecular MH reaction of arylcyanides and styrenes, a reaction not previously reported in literature (Scheme 7). Following the same concept, the use of an excess of styrene as both cross-coupling partner and HCN acceptor led to the isolation of the MH product in good yields. Overall, this unusual application of the transfer hydrofunctionalization concept is a useful complement to the

use of classical aryl halide electrophiles and demonstrates the potential of reversible transfer reactions to unlock unprecedented reactivity beyond alkene functionalization.



Scheme 7. MH reaction of aryl cyanides.

Finally, in a recently invited perspective article, we have coined the term shuttle catalysis to describe isodesmic reactions, such as our transfer hydrocyanation protocol, which enable the reversible transfer of a reactive intermediate or small molecule between two substrates. In this article we used the "shuttle catalysis" umbrella to link previously isolated examples of transfer reactions from the literature, with the hope of stimulating further research in this exciting area.

Future directions: We are currently exploring the possibility to discover several new transformations following the shuttle catalysis principle, most notably alkene functionalization and carbonylation reactions, as well as novel metathesis reactions.

Publications resulting from this research area: 59, 63-65

External funding: LG Chemicals (stipend to Y. Lee); China Scholarship Council (stipend to P. Yu); Carlsberg Foundation (postdoc fellowship to Z. Lian); The Leverhulme Trust (postdoc fellowship to B. N. Bhawal)

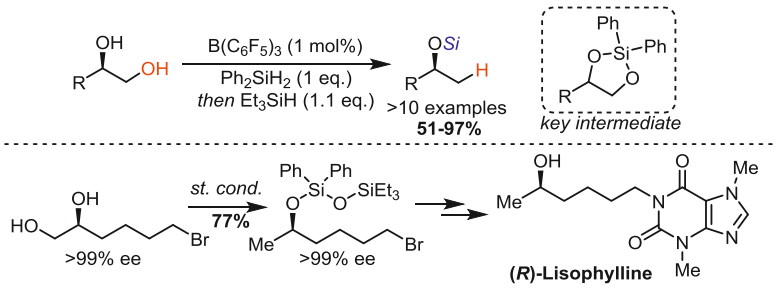
Cooperations: none

2.2.9 Research Area "C–O Bond Activation" (B. Morandi)

Involved: N. Drosos, R. Ramírez-Contreras, G. Prina Cerai, E. Özkal, B. Cacherat, S. Willems, B. N. Bhawal, S. Spandick

Objectives: The alcohol group is one of the most widespread functional groups in organic synthesis. Additionnally, alcohols are ubiquitous in renewable feedstocks, such as carbohydrate derivatives. Therefore, methods for the transformation and functionalization of alcohols are in high demand in synthesis. The research area "C–O bond activation" targets the development of novel transformations employing alcohol derivatives as starting materials, with a particular emphasis on the selective functionalization of polyol derivatives.

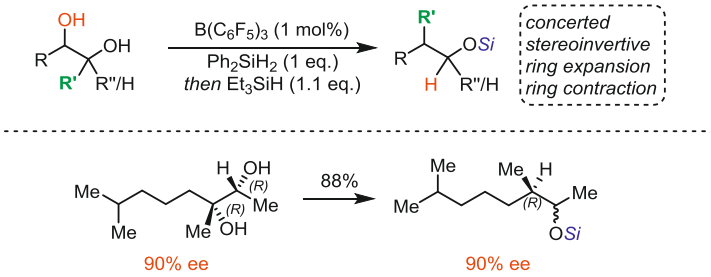
Results: A challenge in polyol chemistry is the selective deoxygenation of a specific hydroxyl group. In this context, we became interested in developing a regioselective deoxygenation of terminal diols because this motif is commonly encountered in renewable feedstocks and synthetic intermediates. We developed a selective deoxygenation of 1,2-terminal diols at the primary position using a simple, commercially available boron catalyst and silane reagents (Scheme 1). A key feature of the reaction is the formation of a cyclic intermediate that enhances the rate of the first deoxygenation step and prevents overreduction. Using this strategy, we could deoxygenate a wide range of substrates and even access a highly enantioenriched 2-alkanol product that was subsequently used in the enantioselective synthesis of an anti-inflammatory drug.



Scheme 1. Selective deoxygenation of diols at the primary position.

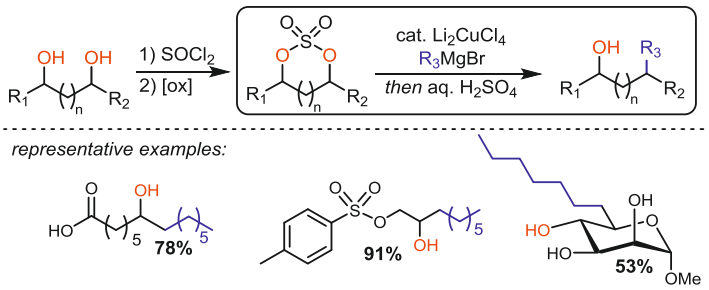
In more recent, unpublished work, we have been able to develop the first example of a reductive pinacol-type rearrangement that can efficiently transform unactivated internal diols (Scheme 2). The reaction is stereospecific and provides novel retrosynthetic

disconnections for the construction of α-substituted alcohols. We are currently exploring the scope of this transformation.



Scheme 2. Catalytic reductive pinacol-type rearrangement of unactivated diols.

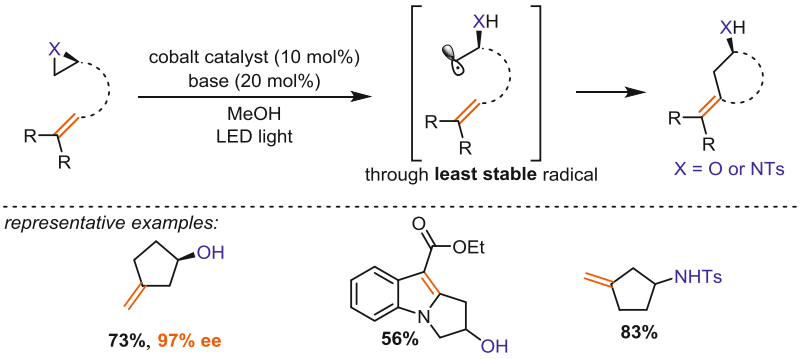
Inspired by the enhanced reactivity of cyclic intermediates in C–O bond reduction, we reasoned that this effect could be harnessed in mechanistically distinct C–O bond cleavage reactions. We thus explored the possibility of using cyclic sulfates, an easily accessible class of electrophiles derived from simple diols, in carbon–carbon bond forming reactions. We have developed a Cu-catalyzed Kumada-type coupling of cyclic sulfates that enables the synthesis of a wide range of functionalized alcohol products in high regio- and chemoselectivity (Scheme 3). The activating effect of the cyclic intermediate is demonstrated by the chemoselective coupling of the cyclic sulfate in the presence of a chemically related tosylate group. Beyond providing a powerful new tool for the construction of functionalized alcohols, this work might encourage the design of new catalytic methods that employ diol-derived cyclic sulfates as electrophiles.



Scheme 3. Copper-catalyzed Kumada-type coupling of cyclic sulfates.

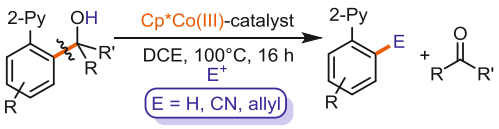
Combining our interest in alkene and C–O bond functionalization, we have developed a Co-catalyzed cross-coupling reaction between epoxides/aziridines and alkenes (Scheme 4). Key to the development of this reaction was the observation that the alkoxide base, generated through S_N2-type epoxide opening by a Co(I)-species, is sufficiently basic to turnover the Co(III)–H species formed at the end of the catalytic cycle. This led to the

development of a fully atom-economical MH-type reaction of epoxides and aziridines, providing a straightforward access to homoallylic alcohols and amines.



Scheme 4. Cobalt-catalyzed cross-coupling between epoxides/aziridines and unsaturated bonds.

Finally, we have also pursued a complementary approach to the functionalization of alcohols that proceeds through the β-alkyl cleavage of C–C bonds. This type of carbon–carbon bond activation usually relies on the use of expensive noble metals such as Pd and Rh. We recently reported the first example of a catalytic C–C bond activation reaction under cobalt catalysis (Scheme 5). A cationic Cp*Co(III) complex could efficiently cleave an arylmethanol starting material using a pyridyl directing group with subsequent trapping of the Co-alkyl intermediate by a suitable electrophile. This new reactivity of cobalt complexes bodes well for the development of sustainable Co-catalyzed C–C bond activation reactions.



Scheme 5. Cobalt-catalyzed functionalized of unactivated C–C bonds.

Future directions: We are currently exploring the application of our boron-catalyzed reaction to the deoxygenation of sugar derivatives. We are also trying to expand the cross-coupling chemistry of cycling sulfates and related alcohol-derived electrophiles to the use of milder coupling partners under Pd and Ni-catalysis, with the goal of developing selective approaches to the functionalization of aliphatic alcohol derivatives.

Publications resulting from this research area: 56, 57, 60-62

External funding: The Leverhulme Trust (postdoc fellowship to B. N. Bhawal)

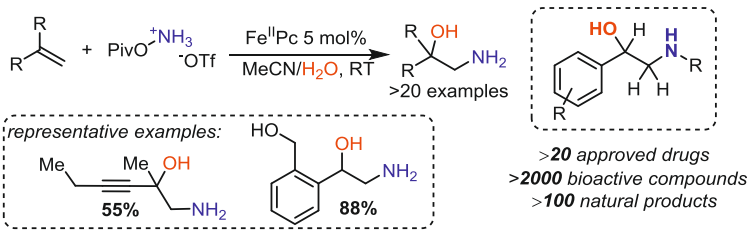
Cooperations: W. Thiel (Mülheim/Ruhr, DE)

2.2.10 Research Area "Direct Catalytic Synthesis of Unprotected Amines" (B. Morandi)

Involved: L. Legnani, G. Prina Cerai

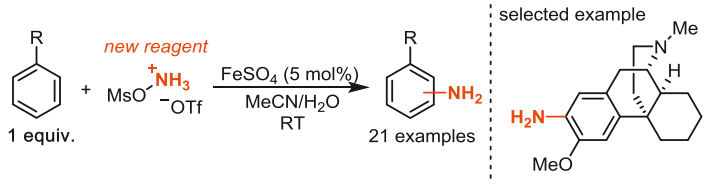
Objectives: The formation of C–N bonds is one of the major challenges in the preparation of bioactive molecules. The direct catalytic amination of hydrocarbons is an attractive approach to address this challenge and has been the subject of intense research efforts. However, most of the methods developed thus far lead to the installation of a protected form of the versatile primary amine group, requiring additional and often challenging protecting group manipulations. In contrast, the research program "Direct Catalytic Synthesis of Unprotected Amines" circumvents the protecting group limitation by enabling a direct access to the desired primary amine. Besides its synthetic potential, this project also addresses a fundamental challenge in catalysis, namely the synthesis of unprotected functionalized molecules that are prone to deactivating coordination of metal catalysts.

Results: Amino alcohols are among the most common bioactive compounds and their synthesis has attracted significant attention. The aminohydroxylation of alkenes is a powerful reaction for the direct preparation of these nitrogen-containing products. However, the conventional methods are limited by the necessity to introduce a protected version of the amino and/or hydroxyl group for efficient reactivity. Since these protecting groups (such as Ts for the amino group) usually need to be cleaved prior to subsequent synthetic steps, we reasoned that a method providing direct access to the free NH_2-group would streamline the preparation of medicinally relevant nitrogen compounds. We have thus developed a Fe-catalyzed preparation of unprotected amino alcohols from alkenes that relies on the use of an easily accessible hydroxylamine-derived reagent (Scheme 1).



Scheme 1. Iron-catalyzed aminohydroxylation of alkenes.

The transformation is particularly effective for the preparation of 2-amino-1-phenylethanols, a structural motif present in over 2000 bioactive compounds and 20 approved drugs, and the utility of the method was demonstrated in the preparation of bioactive compounds. Recently, we could extend the use of a closely related catalytic system and reagent to the direct, innate amination of aromatic substrates (Scheme 2). This novel transformation is operationally simple and can facilitate the amination of a wide range of substrates, including complex bioactive compounds. More importantly, this work is a very rare example of a direct C–H amination reaction leading to the formation of the versatile primary aniline.



Scheme 2. Iron-catalyzed direct C–H amination for the synthesis of primary anilines.

Future directions: We are actively exploring the development of other aminofunctionalization reactions of olefins using the reagents developed in our laboratory. Due to the versatility of nitrogen-centered radicals in hydrogen-atom transfer reactions, we are also planning to explore the use of our catalytic system in aliphatic C–H bond activation. Finally, we are planning to do mechanistic studies to unravel the nature of the aminating species (whether free radical or iron mediated) to provide a foundation for the development of more active systems.

Publications resulting from this research area: 58, 66

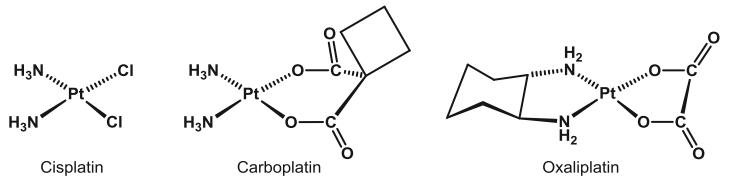
External funding: Fonds der chemischen Industrie (Sachkostenzuschuss)

Cooperations: W. Thiel (Mülheim/Ruhr, DE), J. Bode (Zürich, CH)

2.2.11 Research Area "Bispidine Analogs of Cisplatin, Carboplatin, and Oxaliplatin" (K.-R. Pörschke)

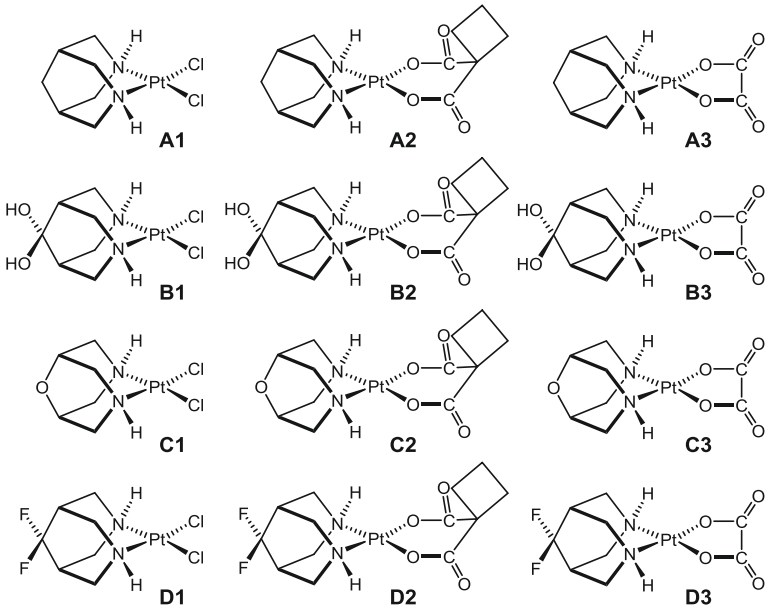
Involved: D. Pollak, R. Mitra, R. Goddard

Objective: Cisplatin, carboplatin, and oxaliplatin represent worldwide clinically administered anticancer drugs. However, there are many problems associated with the



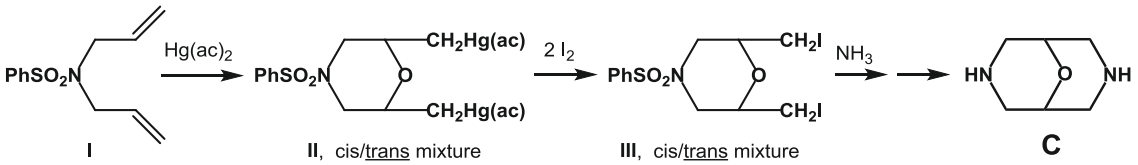
therapy, in particular inherent and acquired platinum resistance, which calls for continued research efforts in this area. Bispidine (3,7-diazabicyclo[3.3.1]nonane) and its congeners represent a limiting case of SAR (structure activity relationships).

In previous work we have synthesized and characterized two series of complexes **A1–A3** and **B1–B3**, in which **A** represents parent bispidine, $C_7H_{12}(NH)_2$, and **B** bispidin-9,9-diol, $(HO)_2C_7H_{10}(NH)_2$. For systematics, we have retained the anions chloride (**1**), 1,1-cyclobutanedicarboxylate (cbdca) (**2**), and oxalate (**3**) in all studies. Compounds **A1–A3** and **B1–B3** displayed cytotoxic potency toward the ovarian cancer cell line A2780 and its Pt resistant subline A2780 CisR similar to that of the standard drugs.

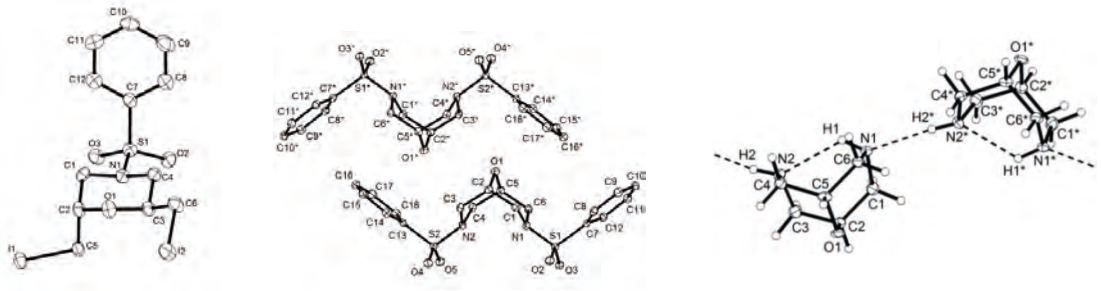


We have now studied complexes **C1–C3** and **D1–D3** in which **C** represents 9-oxa-bispidine, $OC_6H_{10}(NH)_2$, and **D** represents 9,9-difluorobispidine, $F_2C_7H_{10}(NH)_2$.

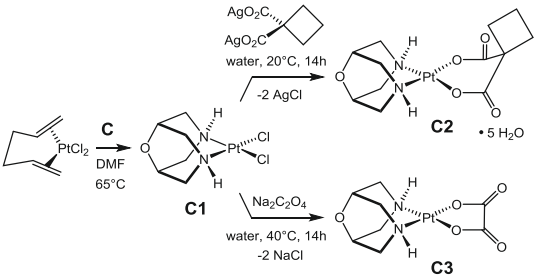
Results: Revisiting the literature synthesis of 9-oxabispidine (**C**), we encountered a series of unexpected problems. These were solved by analyzing **cis/trans-III**, replacing pyridine with THF as a solvent to avoid an unrecognized solute **V**·½**py**, and altering the work-up.

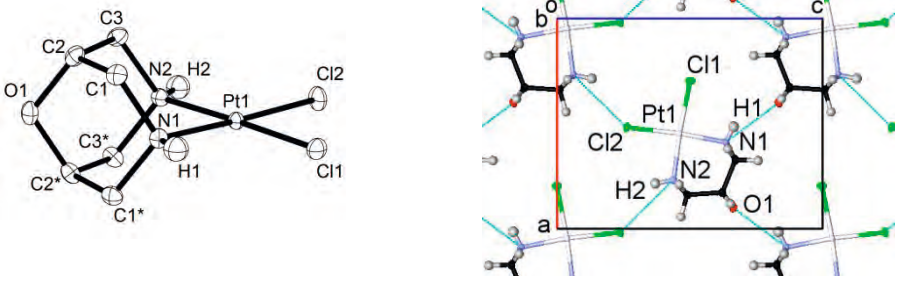


We have characterized two key species (**trans-III** and **V**·½**py**) and also the highly hygroscopic bispidine **C** by X-ray structure analysis.



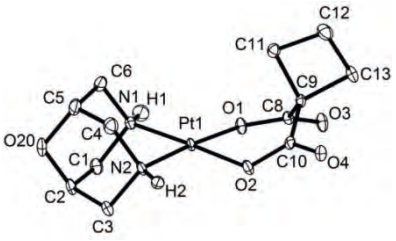
Synthesis of **C1–C3** proceeded on routes we had established before. The dichloride **C1** (crystals were from DMF) is virtually insoluble in most solvents including water. In the crystal, the molecules form a planar 2D network of hydrogen bonds which are strong enough to resist cleavage by water.

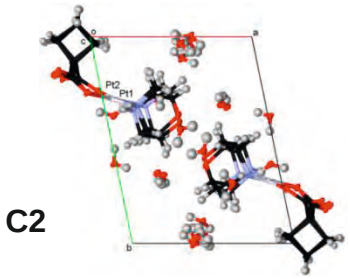




C1

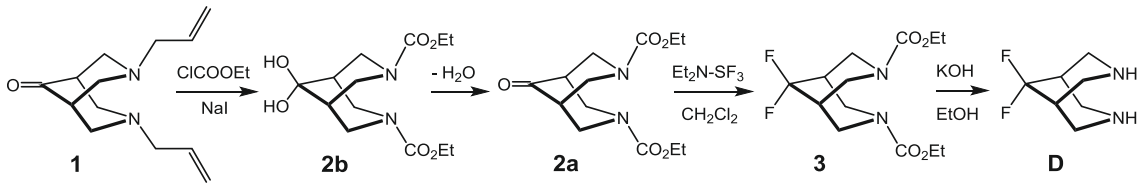
In contrast, the Pt–cbdca complex **C2** forms a pentahydrate, and all individual complex molecules are fully encapsulated by water.



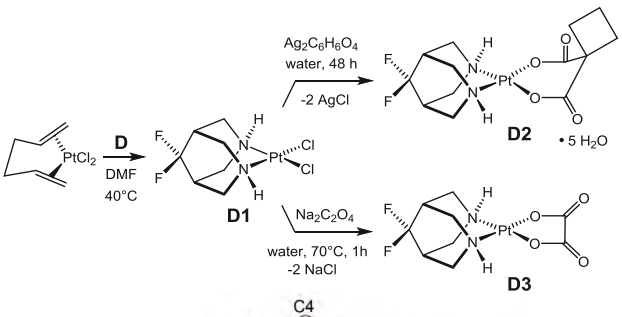


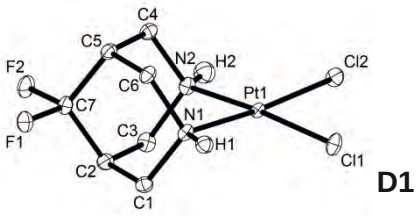
C2

Synthesis of the new 9,9-difluorbispidine (**D**) started from **1** (below) which represents an isolable intermediate of the synthesis of parent **A**. We found that protection of the amino functions as carbamates allowed for a clean reaction, but the ketone had intermediately been converted into the 9,9-diol **2b**. After dehydration of **2b**, ketone **2a** was successfully 9,9-difluorinated by standard techniques to afford **3** which, after deprotection, gave **D**.



The melting points of **A** (198 °C) and **D** (227 °C) are high, in agreement with the presence of a plastically crystalline phase. All isolated bispidines (**A**, **C**, **D**) sublime. Reaction of **D** with (1,5-hexadiene)-$PtCl_2$ affords **D1**, from which **D2** and **D3** are accessible. **D1** crystallizes from water without hydrate formation (in contrast to parent **A1**) and forms a dimer (in contrast to the 2D polymer **C1**). The Pt–cbdca derivative **D2** forms a pentahydrate from water and the structure is isomorphous to those of **A2** and **C2**; thus, 9,9-difluorination does not repel the water surroundings.





D1

Although the complexes of parent **A** show anticancer potency on the μM concentration range, potency of the **B–D** complexes is lower. This is explained by an increased bond polarization of the bispidine skeletons due to the strongly electronegative O or F atoms.

It remains to be determined how lipophilic, but less electronegative substituents such as C or Si at 9-position will alter the anticancer properties of the compounds.

Future directions: No further studies are scheduled due to termination of the group.

Publications resulting from this research area: 68, 71, 73

External funding: none

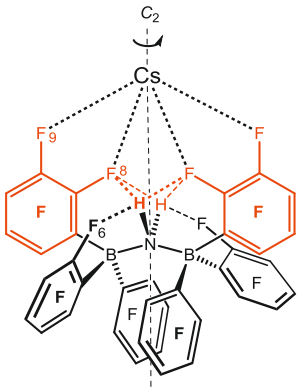
Cooperation: M. Kassack, A. Hamacher (Düsseldorf, DE)

2.2.12 Research Area "FAB Processes for Cesium and Rubidium Exploitation and Radiocesium Separation and Decontamination" (K.-R. Pörschke)

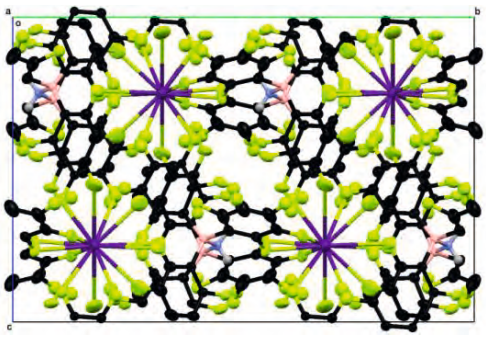
Involved: D. Pollak, R. Goddard

Objective: By serendipity we have discovered a process which might revolutionize the current exploitation of cesium and rubidium, as well as separation of radiocesium for various purposes and radiocesium decontamination.

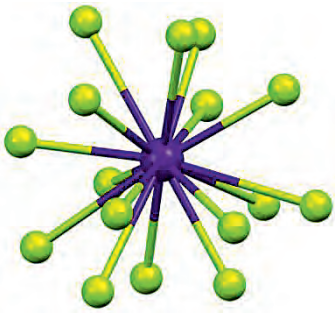
Results: Our interest in weakly coordinating anions (WCAs) has led us to synthesize the new cesium salt, $Cs[H_2NB_2(C_6F_5)_6]$ (**1**). We noticed that **1** is insoluble in water and that it is instantaneously formed by mixing any aqueous solution containing Cs^+ with virtually any source of the $[H_2NB_2(C_6F_5)_6]^-$ anion. The reaction is 100% specific for Cs^+, since only in this case $[H_2NB_2(C_6F_5)_6]^-$ changes its usual asymmetric conformation to an "inverse C_2 symmetric" conformation to form a specific 3D lattice. The X-ray structure of **1** reveals that in the crystal 16 F atoms of five $[H_2NB_2(C_6F_5)_6]^-$ anions surround the Cs^+ cation, which corresponds to a record-setting Werner coordination number of CN = 16 for any ligand element, including hydrogen.



Conformation of **1**



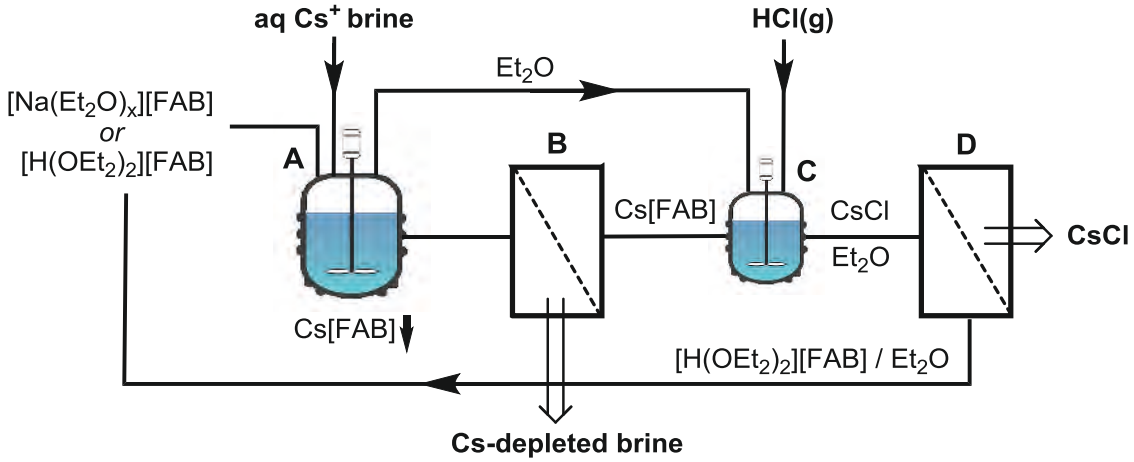
Unit cell of **1**



CsF_{16} coordination in **1**

In the CsF_{16} structure of **1** the largest and least electrophilic monoatomic cation is combined with a (per**f**luoro**a**ryl)**b**orate (FAB) WCA of extremely low basicity, paired with high hydrophobicity. The low electrophilicity entails a low solvation enthalpy of Cs^+, and so the perfectly fitting WCA can compete with the water at Cs^+ on electrostatic grounds. Because of the weak and long $Cs^+\cdots F$ coordination bonds the coordination sphere is large; thus, many F atoms can interact with Cs^+. The high number of cation–anion interactions stabilizes the given 3D network.

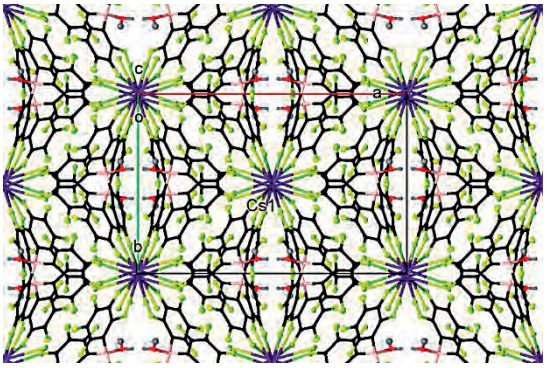
The polymeric **1** precipitates or can be extracted quantitatively from water or acidic solutions containing Cs^+ in concentrations as low as a few ppm. Remarkably, once **1** is isolated from water, it can be cleaved, e.g., by HCl gas in diethyl ether to quantitatively precipitate pure CsCl, with recovery of the FAB WCA in the form of $[H(OEt_2)_2]^+[H_2NB_2(C_6F_5)_6]^-$ (**2**). Feeding **2** back to an aqueous Cs^+ brine and evaporating the organic solvent allows for a cyclic process in which Cs^+ is 100% selectively and quantitatively extracted from any aqueous or acidic Cs^+ solution and "catalytically" converted into, e.g., pure CsCl without formation of byproducts. The following scheme gives a flowchart for the process.



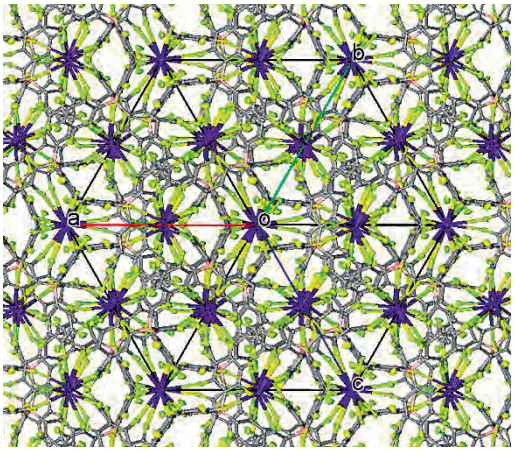
"FAB process" for the exploitation of cesium-containing mineral brines (FAB = **f**luoro**a**ryl**b**orate anion)

In mixer **A** the aqueous or acidic Cs^+ brine is treated with starting Na[FAB] dissolved in some ether (Et_2O or MTBE); the ethereal solvent is distilled off and Cs[FAB] precipitates quantitatively. In separator **B** the precipitated Cs[FAB] is isolated (by filtration or centrifuge) and dried (airstream); the Cs^+-depleted brine is discharged for other uses. In the small mixer **C** the isolated Cs[FAB] is redissolved in the ether distilled from **A**, and the concentrated solution is treated with HCl gas to precipitate CsCl. The product slurry is transferred to separator **D** for isolation of pure CsCl; the ether filtrate containing pure $[H(OEt_2)_2][FAB]$ (or MTBE solvate) is fed back to mixer **A**. Thus, besides the recycled stocks of Na[FAB] reagent and ether solvent, the only reagents which are consumed are the extracted Cs^+ and the equimolar amount of HCl gas. In addition to gaseous HCl, the process is expected to work equally well with other non-aqueous acids such as HBr, H_2SO_4, RCOOH etc. to afford the corresponding Cs salts.

In a similar process, extraction of Cs^+ might occur with $B(C_6F_5)_3$ in aqueous or acidic solutions. $B(C_6F_5)_3$ forms adducts with water such as $(C_6F_5)_3B(OH_2)_x$ (**3**) which in the presence of Cs^+ dimerize to give likewise insoluble $Cs[H(HO)_2B_2(C_6F_5)_6]$ (**4**). The lattice of **4** consists of 2D layers with Cs^+ being only 12-coordinate. For the binding in both 1 and 4 it is decisive that a dinuclear anion of type $[(C6F5)3B(\mu\text{-}X)B(C_6F_5)_3]^-$ is given, featuring a pair of coplanar C_6F_5 groups, one from each $B(C_6F_5)_3$ group. Primary coordination of Cs^+ occurs by two sets of vicinal F atoms of the coplanar C_6F_5 groups, giving rise to a tetradentate chelation by the anion (see drawing of **1**, above).



A quite different situation is given for the anion $[B(C_6F_5)_4]^-$. While the parent $[B(C_6H_5)_4]^-$ forms solvent-free and isomorphous complexes $M[B(C_6H_5)_4]$ with all alkali metals by coordination via the phenyl 6e-donors, this is impossible for the $[B(C_6F_5)_4]^-$ anion. Here, only $Rb[B(C_6F_5)_4]$ and $Cs[B(C_6F_5)_4]$ (and also $Tl[B(C_6F_5)_4]$) form isomorphous 3D networks, giving rise to water-insoluble solids, whereas the lighter alkali metals are increasingly well solvated by water and hence more soluble. Thus, only $Rb[B(C_6F_5)_4]$ and $Cs[B(C_6F_5)_4]$ precipitate from an aqueous solution containing all alkali metals. Worthy of note, these complexes represent the first examples of CN = 15 for any donor atom other than H.



For selective separation of rubidium, a tandem process can be envisaged, in which in the first step Cs^+ is separated by the $[H_2NB_2(C_6F_5)_6]^-$ or $[H(HO)_2B_2(C_6F_5)_6]^-$ anions. In the second step, the solution is treated with $Li[B(C_6F_5)_4]$ to selectively and nearly quantitatively precipitate $Rb[B(C_6F_5)_4]$. Reaction of the latter with an anhydrous acid in ethereal solution affords precipitation of, e.g., pure RbCl together with the recycled anion. By a tandem set-up of two cycles of the given flowchart, the first cycle with $[H_2NB_2(C_6F_5)_6]^-$ or $[H(HO)_2B_2(C_6F_5)_6]^-$ as an extracting anion for Cs^+ and the second with $[B(C_6F_5)_4]^-$ for extracting Rb^+, any brine containing, inter alia, Cs^+ and Rb^+ (but free from Tl^+) may be exploited for these elements in a cyclic process, allowing

selective and quantitative isolation of pure salts CsX and RbX. We suggest the term "FAB process" for referring to the Cs^+ and Rb^+ extraction by fluoroarylborate anions.

There are numerous applications conceivable for the FAB process, notably for Cs:

(a) Exploitation of Cs and Rb minerals. The FAB process avoids the otherwise numerous recrystallizations, handlings of large volumes, and environmental problems associated with current industrial processing of Cs and (less important) Rb.

(b) Environmental issues. Viewing current cesium production, full removal of Cs^+ is a pressing problem because of environmental reasons. Using FAB reagents as an additive to a final settling basin for the brine will allow quantitative sedimentation of Cs[FAB] and Rb[FAB] and full exploitation of the contained Cs and Rb.

(c) $^{135/137}$Cs Fission Product Extraction (FPEX). Nuclear fuel reprocessing occurs by the PUREX and UREX processes. In the joined FPEX process, $^{135/137}Cs^+$ is currently extracted by **c**hlorinated **c**obalt bis(**d**icarbollide), $[CCD]^-$. Cs[FAB] extraction appears superior to current Cs[CCD] extraction, since the FAB reagents are more readily available, more selective, and only a single separation step is necessary, which simplifies the process, reduces costs and waste, and allows for saver execution.

(d) ^{137}Cs technical and radiopharmaceutical applications. The FAB process should allow ready preparation of pure ^{137}Cs[FAB] and other ^{137}CsX radioisotope compounds by the modified FPEX process (see c) and easier handling of the compounds. Typical commercial applications for ^{137}CsX compounds are, inter alia, sewage sludge sterilization, furnace lining controlling, and cancer afterloading therapy.

(e) ^{131}Cs radiopharmaceuticals. ^{131}Cs ($t_{½}$ = 9.7 d) is used for cancer seed implantation (brachytherapy). For this purpose, ^{131}Cs is prepared by treating an aqueous $^{130}Ba^{2+}$ solution with neutrons to afford ^{131}Ba, which transforms into ^{131}Cs. The (slowly formed) ^{131}Cs must be continuously removed to avoid further neutron capture to give ^{132}Cs. Precipitating $^{131}Cs^+$ with [FAB]– in aqueous solution is expected to allow for fast, quantitative, and continuous separation of pure ^{131}Cs[FAB] from $^{130/131}Ba^{2+}$.

(f) $^{135/137}$Cs decontamination. Waste waters from nuclear plants or discharges form nuclear plant accidents containing $^{135/137}$Cs loadings can be reprocessed, with Cs[FAB]

separation being effective down to the ppm level. $^{135/137}$Cs decontamination of humans or mammals is also conceivable, challenging the current Prussian blue therapy.

Future directions: No further studies are projected due to termination of the group.

Publications resulting from this research area: 72, two patent applications

External funding: none

Cooperations: none

2.2.13 Publications 2014-2016 from the Department of Homogeneous Catalysis

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(4) Martínez Cuezva, A.; Zumbansen, K.; Döhring, A.; van Gemmeren, M.; List, B. *Synlett* **2014**, *25*, 932-934.

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(9) List, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 8528-8530.

(10) Prévost, S.; Dupré, N.; Leutzsch, M.; Wang, Q.; Wakchaure, V.; List, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 8770-8773.

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(20) Shevchenko, G.; Pupo, G.; List, B. *Synlett* **2015**, *26*, 1413-1416.
(21) Tsui, C.; Liu, L.; List, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 7703-7706.
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(23) James, T.; van Gemmeren, M.; List, B. *Chem. Rev.* **2015**, *115*, 9388-9409.
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2.3 Department of Heterogeneous Catalysis

Director:
Ferdi Schüth (born 1960)

Further group leaders:

Frank Marlow (born 1960)

Gonzalo Prieto (born 1981)
group leader since 2015

Wolfgang Schmidt (born 1962)

Harun Tüysüz (born 1978)

Claudia Weidenthaler (born in 1965)

Curriculum Vitae: Ferdi Schüth

1960	Born in Allagen (now Warstein), Germany
1978-84	Chemistry studies at the Westfälische Wilhelms-Universität Münster, Diploma October 1984
1983-88	Law Studies at the Westfälische Wilhelms-Universität Münster, First State Examination February 1989
1984-88	Doctoral studies in the group of E. Wicke, Institute of Physical Chemistry, Münster, Dr. rer. nat. June 1988
1988-89	Post-doc at the Department of Chemical Engineering and Materials Science, University of Minnesota, USA, L. D. Schmidt
1989-95	Wissenschaftlicher Assistent (Assistant Professor) at the Institute of Inorganic and Analytical Chemistry of the Universität Mainz, K. Unger, Habilitation February 1995
1993	Visiting Assistant Professor at the Department of Chemistry, University of California at Santa Barbara, USA, G. D. Stucky
1995-98	Full Professor of Inorganic Chemistry at the Johann-Wolfgang-Goethe Universtität Frankfurt
1998-	Scientific Member of the Max Planck Society and Director at the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr

Awards and Honors

1989	Award for outstanding Ph.D. thesis
1991	Boehringer-Ingelheim Research Award
2001	Award des Stifterverbandes für die Deutsche Wissenschaft
2003	Gottfried Wilhelm Leibniz Award of the Deutsche Forschungsgemeinschaft
2007	Honorary Professor of Dalian University of Technology, China
2008	Elected member of German Academy of Science Leopoldina
2009	Guest Professor Beijing University, China
2009	European Research Council Advanced Grant
2010	Heisenberg-Medaille of the Alexander von Humboldt Foundation
2010	Elected member of the Nordrhein-Westfälische Akademie der Wissenschaften und der Künste
2010	Nominated for the Deutscher Zukunftspreis 2010
2011	Ruhrpreis für Wissenschaft und Kunst (Ruhr Award for Science and Arts)

2011	Wöhler-Award for resource-saving processes
2011	Hamburger Wissenschaftspreis (Hamburg Award for Science)
2012	Wilhelm-Klemm-Preis of the GDCh
2013	Chemical-Engineering-Medal of the ETH Zürich
2014	Carl Friedrich von Weizsäcker-Award
2016	Honorary doctorate of TU Munich

Other Activities / Committees (only current)

1996-	Member of the Editorial Board, *Microporous Materials*
1998-	Member of the Editorial Board, *Advanced Materials*
2000-	Member of the Dechema Board of Governors
2003-	Member of the Editorial Board "QSAR-Combinatorial Science"
2005-	Chairman of the Investment Committee "Life Science, Materials and Energy" of the German High-Tech Fund
2005-	Member of the Editorial Advisory Board, *Chemical Engineering & Technology*
2006-	Editor, *Chemistry of Materials*
2006-	Member of the Advisory Board, *Chemistry–An Asian Journal*
2007-	Member of the Editorial Board, *Advances in Catalysis*
2007-	Member of the Hochschulrat, University Duisburg-Essen
2009-	Vice-Chairman of Dechema
2010-	Member of the Trustees of the Federal Institute of Materials Testing and Research (BAM)
2011-	Member of the Board of Trustees of the Award "Otto-Bayer-Preis"
2012-	Member of the selection committee of the "Deutscher Zukunftspreis" (Future Award of the German President)
2013-	Chairman of the selection committee of the "Deutscher Zukunftspreis"
2014-	Vice President of the Max-Planck-Society in Munich
2016-	Chairman of the Scientific Commission of Lower Saxony

Department of Heterogeneous Catalysis

The situation in the department in the reporting period was strongly affected by the election of Ferdi Schüth to the office of vice president of the Max-Planck-Society. While this is technically an honorary position – only the office of president is a full-time position in the MPS – it requires in fact approximately 75 % of the time. The group of the department head was consequently downsized to some extent, and each new Ph.D. student of Ferdi Schüth is assigned to a group leader as second supervisor. Nevertheless, the office requires substantial periods of absence which reduces the possibility of personal interactions with the members of the department. However, due to the fact that the group and the department was always organized in a rather independent manner, relying strongly on interactions between the members, and the quality of the senior scientists in the department, the overall performance currently does not seem to have substantially suffered. Also efforts to secure third-party funding have been taken over to a large extent by the group leaders, so that also here the decreasing time resources of the department head are essentially compensated.

As in previous reporting periods, the department of Heterogeneous Catalysis has seen change in the personnel situation over the last three years, not only on the level of post-docs and Ph.D. students, where it is natural, but also on the level of the group leaders. The positions of some of the group leaders are non-permanent, so that they contribute to the scientific profile of the Institute for limited periods only, and then find new challenges at other institutions. This allows to bring in new ideas with new scientists from outside of the institute. Continuity of the work, on the other hand, is ascertained by the director of the department (F. Schüth) and few senior scientists on permanent positions (F. Marlow, W. Schmidt, C. Weidenthaler, M. Felderhoff). Compared to the other departments of the Institute, the number of senior scientists is somewhat higher, which is due to the fact, that this is the only department focused on solids, which requires to maintain a range of different expertise specifically for the department alone.

During the reporting period, Roberto Rinaldi, who had pursued a vigorous research program in biomass conversion, left the institute for a faculty position at Imperial College. Part of the research activities in this field will be continued in the Schüth group, especially those on sugar and on bio-oil conversion, while the activities in lignin conversion are to a large extent discontinued, since they will be a major thrust of the Rinaldi group in London. Part of the members of Rinaldi-group stayed at the Institute in order to finish their projects, the last students and post-docs left the department early in 2017.

The successor of Roberto Rinaldi as group leader is Gonzalo Prieto. He had joined the institute as post-doc coming from the group of Krijn de Jong, and due to the excellent performance was promoted to a group leader position in 2015, initially financed by a Humboldt-Fellowship, followed by a Marie-Curie Fellowship and now on a senior scientist position of the Institute. Gonzalo Prieto has initiated a strong research program on the conversion of small molecules in energy relevant reactions, supplemented by the knowledge-based synthesis of structured catalysts and their analysis by advanced electron microscopy techniques.

In addition to the move of Roberto Rinaldi to Imperial College, also several other scientists were promoted to faculty positions at leading institutions. Ryan Wang, who was a post-doc in the department, accepted an offer to join the faculty of University College London, and Dong Gu and Guanghui Wang received offers for professor positions at the Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Science and the Wuhan University in China, respectively.

The research activities of the department continue to be centered on the synthesis of nanostructured catalysts and their use in different catalytic reactions, most of these reactions being relevant in energy conversion processes. The different groups of the department work together on different aspects of this overall thrust, to a large extent in joint projects. The group of Ferdi Schüth is focused on the synthesis of nanostructured catalysts based on polymeric supports, in which the distribution of the active material is controlled on the level of nanometers. The materials are applied as sinter-stable electrocatalysts or in biomass conversion reactions. In addition, the group pursues research on unusual catalytic problems, i.e. in methane activation in oleum to result in methylbisulfate, or in the conversion of acetylene to value-added products. The group is also interested in the fundamentals of solids formation, where there is a close interaction with the group of Wolfgang Schmidt, whose activities are directed to the use of zeolites in different applications and to the understanding of zeolite formation on the molecular level. The formation of materials on the atomic scale can only be studied by a coordinated effort, bringing together complementary experimental techniques, which are ideally used in-situ. Here the group of Claudia Weidenthaler is instrumental in developing new in-situ X-ray diffraction methods for use in the department. The thrust of the group is on the methodologies, but the examples to which the methods are applied are those which are relevant also for the other groups of the department. A prominent example for this interaction is the joint BMBF-funded project which Claudia Weidenthaler has won together with Michael Felderhoff. In this project, novel approaches towards hydrogen

storage in complex hydrides are studied, and the in-situ analysis of the hydrogen adsorption/desorption processes are instrumental for the knowledge-based improvement of the systems. Hydrogen storage is one aspect of the research of Michael Felderhoff, but the complex hydrides can also be used for heat storage at different temperature levels. Heat storage is an important element in coupling the different sectors in our energy system, and thus a substantial fraction of the activities of the Felderhoff-group are directed at the practical implementation of hydrides as heat storage materials. The research focus of the Prieto group has already been described above: his team controls the active metal distribution in nanostructured materials in order to create the optimum catalyst for specific reactions, and these catalysts are then used for energy relevant reactions involving small molecules, such as in the coupling of hydrocracking/Fischer-Tropsch reactions. Harun Tüysüz and even more so Frank Marlow complement the activities of the department in using nanostructured materials for catalysis, but also especially for use in solar cells and in photo- and electrochemical reactions, where the use of such well-defined materials and careful analysis helps in understanding the fundamentals of these important application fields of nanostructured materials. Highlights of the research activities of the different groups are given further down in this book in the reports on the different research activities.

The analytical capabilities of the department were substantially extended by the acquisition of the new STEM Hitachi HD-2700 with a point-to-point resolution of 0.4 nm, but more importantly EDX analytical capabilities at a resolution of a few nm, depending on the sample. A joint Ph.D. student of Christian Lehmann and Ferdi Schüth is exploring the limits of the possibilities which this new instrument brings.

As can clearly be seen from the list of publications, there are many joint activities within the department and within the Institute. Beyond this, the department is linked to other groups world-wide in various ways, be it by joint projects, such as the Cascatbel EU-project or a project funded by the ministry of economy with five partners from academia and industry, by exchange visits of students and post-docs with many laboratories world-wide, including UC London, DTU Lyngby, or University of Wisconsin, or with guest professorships or named lectures, such as at Dalian University of Technology, UC Berkeley or Shandong University. On the German level, the involvement of the department in two Clusters of Excellence (CoE), funded in the framework of the German Excellence Initiative, should be mentioned. One of these clusters in centered at RWTH Aachen, with a focus on fuels from biomass (Roberto Rinaldi and Ferdi Schüth), the second one is located at Bochum University and is directed towards the understanding

of solvation effects (Harun Tüysüz and Ferdi Schüth). Bilateral cooperations were also important in advancing the research activities of the department, which include the one with Osamu Terasaki (Stockholm and KAIST), Brad Chmelka (UCSB), Ryan Wang (UC London), and Soren Kegnaes (DTU Lyngby), amongst others. The department members are also active in teaching in the neighbouring universities, where Ferdi Schüth, Frank Marlow, Gonzalo Prieto, Harun Tüysüz, and Claudia Weidenthaler teach a number of different classes.

The research activities of the members of the department have also been acknowledged by a number of awards and academic distinctions, such as the Habilitation of Claudia Weidenthaler (2015) and Harun Tüysüz (2016), the Carl-Friederich-von-Weizsäcker Preis of the German Academy of Science, an honorary doctorate of TU München and the Mutterthies Lecture of UC Berkeley for Ferdi Schüth, guest professorships for Claudia Weidenthaler and Wolfgang Schmidt at Shandong University, or the Jochen-Block award of the German Catalysis Society for Harun Tüysüz. Moreover, Wolfgang Schmidt is editor-in-chief of Microporous and Mesoporous Materials, the key journal for porous materials research, and Ferdi Schüth is editor of Chemistry of Materials.

Also the third party funding activities were substantial. During the reporting period, Ferdi Schüth completed his ERC Advanced Grant project, Roberto Rinaldi the AvH Sofja Kovalevskaja Award. Moreover, several DFG-projects, BMBF, BMWi, AIF, and industry projects were pursued during the reporting period; in addition, a number of Alexander-von-Humboldt fellows were active in the department. This helps to expand the scope of the activities which would be somewhat more limited if only the Institute resources were available.

2.3.1 Research Area "High Surface Area Materials" (F. Schüth)

Involved: P. Bazula, A. Pommerin, H. Bongard, M. Dierks, J. Engelhardt, D. Gu, I. Lim, V. Nese, A. Padovani, C. Pichler, F. Richter, B. Spliethoff, F. Wang, G. H. Wang, B. Zibrowius

Objective: The synthesis and study of high surface area and porous materials is a research theme which is pursued in the group for more than 20 year. The focus of the development is on oxides and carbons, and this research area has strong overlap with the other fields of research of the group, since many of the materials produced later find applications in catalysis or other fields. Templating, be it hard or soft templating, is the main method for the production of this class of solids, but the work is not restricted to it, but also relies on other methods, if they appear suitable. Also the group of Wolfgang Schmidt and Harun Tüysüz are active in the development of porous solids for specific applications, and there is fruitful collaboration between the different groups in the department, resulting sometimes in joint publications, but each group also pursues its individual research topics.

Results: The most spectacular success during the reporting period was certainly the development of the surface casting method for the synthesis of high surface area and ordered porous oxides[22]. Surface casting, i.e. the coating of a template with a very thin layer of another material with subsequent removal of the mold has so far only been successful in the case of carbon by a method developed by Ryong Ryoo in 2001, which could thus be obtained in the form of the hexagonal array structure of carbon tubes called CMK-5. In spite of many attempts, this method could not be extended to compositions other than carbons. Analysis of the synthesis process pointed towards insufficient interaction between the mold oxide and the material to be cast, resulting in the formation of particles in the pores instead of a surface coating. The lack of silanols on the surface of the template silica was identified as the reason for this insufficient interaction. Based on this, a mild, non-thermal template removal/surface activation process, relying on treatment with HNO_3/H_2O_2 at 80°C, was found to be suitable to induce selective surface coating of the silica template with a broad range of different materials. Using these templates, zirconia and iron oxide could be produced with a structure similar to CMK-5, although not quite as perfect. Various oxides could be obtained from mesocellular foams in a foam-like structure themselves. Important for practical applications,

amorphous, high surface area silica gels could also be used as molds, resulting in very high surface area oxides. Several examples are shown in Fig. 1. Irrespective of the template used, the typical surface areas of the surface cast oxides exceed those of oxides obtained by hard templating by a factor of two to three, and surface areas on the order of 300-400 m^2/g are regularly achieved even for high density oxides, such as zirconia. Incidentally, the functionalization of the silica surface also improves the casting of polymers, and thus, CMK-5 with very high structural perfection can be obtained.

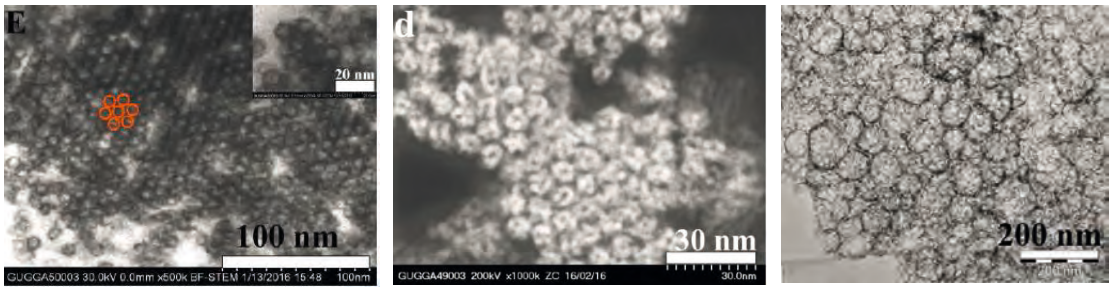


Fig. 1: TEM images of different surface cast oxides. Tubular ZrO_2 with a surface area of approximately 380 m^2/g (left); tubular Fe_2O_3 with a surface area of approximately 300 m^2/g (middle); mesocelluar TiO_2 with a surface area of approximately 250 m^2/g (right).

The oxides produced by the surface casting process consist of very small, connected oxide nanoparticles, which, based on TEM and XRD observations have sizes on the order of only a few nanometers, depending on thermal treatment temperatures. Also, the crystalline structure is sometimes unusual: zirconia is obtained as the cubic polymorph, which typically requires high temperature treatment. Whether this is due to residual silicon in the framework or the small primary particle sizes is currently unclear. The materials produced by the surface casting process are currently studied for different applications.

The nanocasting approach has also been used in its more conventional form of bulk casting for the synthesis of different oxides for specific catalytic applications. Casting of different cobalt-based materials with controlled doping has been used to identify the active sites in such catalysts for low temperature CO-oxidation[27]. In these studies, also materials consisting predominantly of Co^{2+} were found to be highly active, but surface oxidation of cobalt in octahedral sites was found to be responsible for high activity. If only tetrahedral cobalt sites were exposed to the surface, oxidation was found to be more difficult so that the resulting catalysts only showed moderate CO-oxidation activity. Similarly, a series of different manganese oxide based catalysts were produced by nanocasting[51]. Onto these solids, gold nanoparticles, produced by colloidal deposition,

were placed and the resulting catalysts were studied again in CO-oxidation. The catalysts produced are the most active ones so far reported in literature for this reaction, and surprisingly, it was not Mn_2O_3, which so far was assumed to be the best support material, but the MnO_2 based system.

Nanocasting is also of high relevance in the production of systems for electrochemical applications. Nanocast carbon, loaded with Co_3O_4 at high loading levels was found to be an excellent electrode for lithium ion batteries[31], and the nanocasting synthesis of antimony-tin-oxide is currently used for the production of stable electrodes for the oxygen evolution reaction in the framework of MaxNet Energy.

While most of the synthetic activities directed at the production of high surface area materials rely on nanocasting and soft templating, another method recently implemented in cooperation with Duisburg-Essen University was found to be well suited for the high volume production of acidic high surface area carbon materials, i.e. pyrolysis in a continuous process[40]. Nebulizing a solution of sucrose and sulfuric acid directly led to the formation of acidic carbon materials after passing the aerosol through an oven at temperatures between 400 and 800°C with a residence time of 2 seconds. If salts were added to the solution, salt templating led to the development of a pronounced mesopore system, and materials with surface areas of around 500 m^2/g and acid site concentrations close to 2 mmol/g were obtained. The performance of the catalysts in fructose dehydration and inulin hydrolysis was comparable to commercial sulfonated resin catalysts, but the carbons have higher thermal stability and are easy to produce. Fig. 2 shows a TEM of a product synthesized in the presence of salt, where the mesopores are clearly visible, and the performance of different catalysts, including reference systems, in inulin hydrolysis.

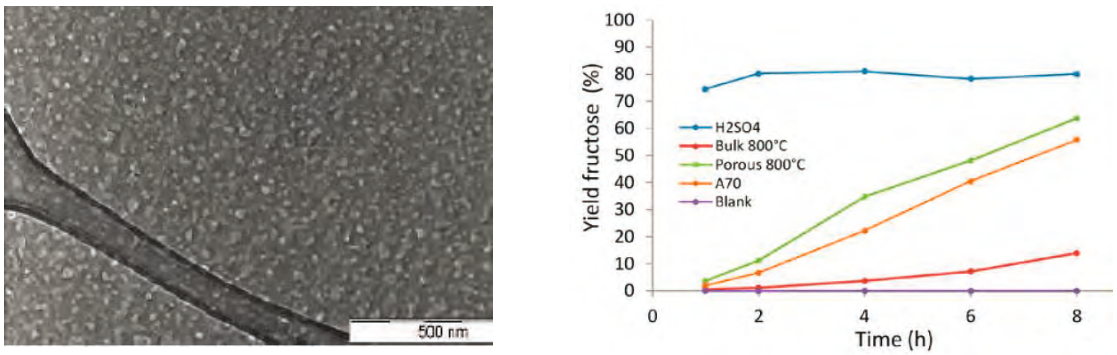


Fig. 2: TEM image of a sulfonated carbon obtained by spray pyrolysis. The white features are the pores created by salt templating (left); catalytic performance of such carbons in the hydrolysis of inulin, together with performance of reference catalysts; bulk 800°C is a catalyst obtained by pyrolysis at 800°C without salt, porous 800°C is the material pyrolized in presence of salt under otherwise identical conditions, A70 is Amberlyst A70, which was the most active one among three tested Amberlyst types (right).

In this research area also other high surface area materials, such as polymers, carbides, and oxides, were developed. Most syntheses relied on templating approaches, but also hydrothermal methods were used, as in the case of manganese oxides. Most of the resulting solids were used in biomass conversion reactions, such as for the hydrodeoxygenation of bio-oils, and they will therefore be discussed in the description of that research field.

Future directions: Work on high surface area materials belongs to the core activities of the department and has a cross-sectional quality, since many of the developed materials are used in other projects, either directly as catalysts, as catalyst supports for specific reactions or as starting materials for the preparation of nanoengineered materials. Therefore, work in this research area will continue in the future at least at the level as in the reporting period. In the last report, a shift away from ordered mesoporous materials was expected, since this field appeared to have reached a high level of maturity. However, with the successful development of the surface casting approach the research has taken a new turn, and therefore, surface casting will be an important research topic for the next years. The other systems will be continually developed further and used more as routine tools for the production of catalysts for specific applications.

Publications resulting from this research area: 9, 10, 19, 25, 26, 27, 28, 31, 33, 40, 44, 45, 49, 51, 52

External Funding: ERC, IMPRS SURMAT, EU Cascatbel

Cooperations: A. Fürstner, C. Lehmann, W. Schmidt, H. Tüysüz, C. Weidenthaler (Mülheim); W. Lubitz (Mülheim); A.H. Lu, W.C. Li (Dalian, CN); D.Y. Zhao (Shanghai, CN), D. Serrano (Madrid, ES), A. Lappas (Thessaloniki, GR); O. Terasaki (Stockholm, SE)

2.3.2 Research Area "Nanoengineered Catalysts" (F. Schüth)

Involved: H. Bongard, N. Duyckaerts, D. C. Galeano-Nunez, D. Gu, D. Jalalpoor, J. Knossalla, S. Mezzavilla, C. Ochoa, B. Passas-Lagos, N. Pfänder, B. Spliethoff, A. C. Swertz, T. Trotus, J. vom Stein, G.H. Wang, F. Wang

Objective: The structuring of solid catalysts on the scale of nanometers and below is a continuing theme in the research of the department. If catalysts are synthesized in a controlled manner on this scale, they can be tuned towards specific applications. This research area thus tries to develop new and improve known methods for the nanostructuring of solid catalysts on the one hand, and on the other hand to apply the resulting catalysts for specific reactions. The synthetic approaches rely on a number of different methods, including nanocasting, colloidal deposition, and sol-gel chemistry. The synthetic work is complemented by different analytical methods, most notably and importantly electron microscopy.

Results: The development of nanoengineered catalysts was pursued predominantly in two different directions, i.e. the synthesis of hollow graphitic shell-based electrocatalysts, and different types of supported catalysts on the basis of polymers of the resorcinol-formaldehyde type and carbons derived from these polymers. Some other systems were studied as well, such as gold on manganese oxides which were synthesized by colloidal deposition. However, these systems will not be treated here in detail, since related systems have been the subject of extensive descriptions in previous reports.

The previous work on platinum-based fuel cell catalysts has been extended to different kinds of alloy catalysts[3,56]. In addition, the approach which had been used for the synthesis of the first generation of hollow shells is not suitable for the production of higher amounts. These, however, had been requested by several industrial companies who were interested in testing the catalysts in single cell measurements. Therefore, the synthesis was modified in order to provide scalable production routes[30,38,50]. Moreover, non-hollow reference catalysts have been synthesized in order to elucidate the origin of the good performance of the fuel cell catalysts.

Alloying of platinum is known to result in improved electrocatalytic performance. However, the production of alloys typically requires high temperature treatment which leads to growth of particles, with corresponding loss in electrocatalytic activity. This

growth can be prevented by the “confined space alloying” approach, which was developed on the basis of the hollow graphitic spheres[3]. The alloying in the approximately 5 nm sized void in the shells of the hollow shell material restricts the growth of the forming alloy particles, so that the particle sizes remain around 4-5 nm. This in turn results in highly active electrocatalysts with approximately 2.5 times higher specific activity as the pure platinum catalyst (Fig. 1). A similar material, also with improved activity as compared to pure platinum, was obtained with platinum-cobalt alloys. The materials have extensively been studied with respect to structure, and especially concerning the leaching behavior under different aging conditions.

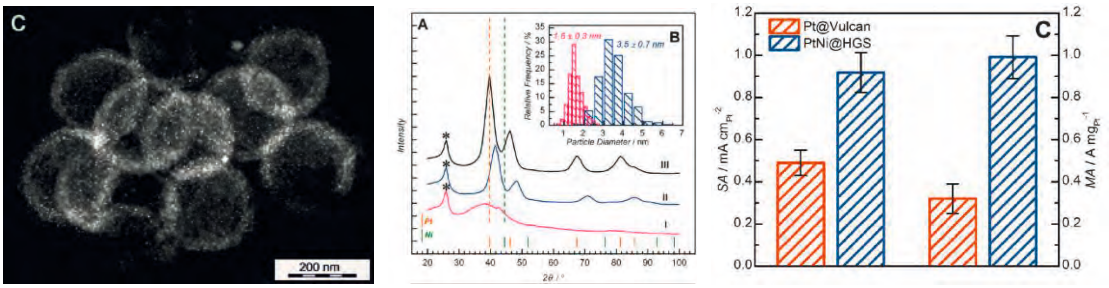


Fig. 1: PtNi loaded hollow graphitic spheres (left); XRD patterns of PtNi loaded hollow graphitic spheres (middle) after reduction (I), after high temperature treatment (II) and Pt/HGS for comparison (III). Area and weight normalized activity of Pt/Vulcan and PtNi/HGS (right).

The catalysts require several hundred redox cycles in order to remove the carbon layer formed during high temperature treatment. This is impractical in real fuel cell applications. Thus, alternatives have been investigated and finally, ozone treatment has been identified as a viable pathway[38]. Also the synthesis of the hollow shell substrate has been simplified, both by continuous synthesis in a tubular reactor and by a one-step synthesis of the solid core and the hollow shell[50]. Interestingly, a material in form of a solid sphere with otherwise identical textural properties performs equally well in rotating disc electrode measurements, but is inferior in single cell experiments. This implies either different mass transfer properties or different penetration by the Nafion ionomer.

The precursor for the hollow sphere materials is a polymer which is infiltrated into the pores of a silica hard template. Under suitable conditions, polymers can also be obtained with highly defined porosity and mesostructured in the absence of hard templates, but using surfactants instead. Resorcinol-formaldehyde-based resins have been developed as a highly versatile platform for the synthesis of different nanostructured catalysts, which are highly active and selective for different reactions. Conceptually, the resins are synthesized from precursors which contain ion exchange groups. The ion exchange sites can be used to anchor metal precursors in the polymer, and these precursors are con-

verted to metals, alloys, or oxides in a subsequent thermal treatment step. Examples for precursors with ion exchange groups are 2,4-dihydroxybenzoic acid or 3-aminophenol. The crosslinking in these resins occurs between the hydroxygroups and the formaldehyde, while the carboxylic acid or amine functionality provide the ion exchange functionality. These polymers have proven to be highly suitable for the synthesis of different catalytic materials. Various metals and metal alloys could be deposited in this way in the form of very highly dispersed nanoparticles in these resins and the carbons obtained after thermal treatment; with a somewhat modified synthesis protocol, also highly dispersed oxide nanoparticles were accessible. PtCo catalysts obtained via this pathway were very active for the hydrogenolysis/hydrogenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran[12], materials with smaller PtCo nanoparticles with sizes around 1.5 nm were highly interesting systems for the hydrogenation of the phenolic groups in bio-oils[22], and Co_3O_4 nanoparticles synthesized on such polymers (Fig. 2) were very active and selective (S typically exceeding 95 %) in the selective transfer hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols[42].

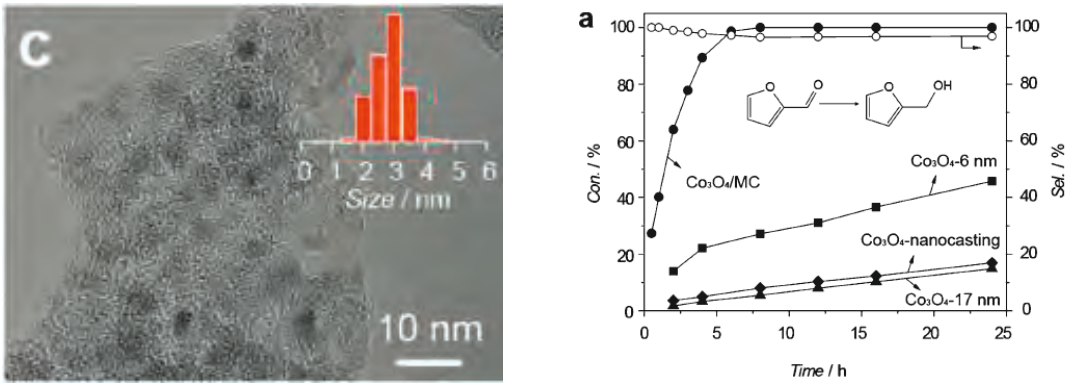


Fig. 2: Co_3O_4 nanoparticles on carbon obtained via an aminophenol-formaldehyde resin with particle size distribution as inset (left). Conversion (filled symbols) and selectivity (open symbols) in the transfer hydrogenation of furfural with isopropanol over different catalysts (right).

Future directions: The development in the field of nanoengineering of solid catalysts has been rapid and is expected to continue this way also in the next years. The work in this field will thus remain at approximately the same level, and for both classes of catalysts described in more detail in this section, possible commercialization will be explored. Thus, in addition to studies broadening the range of materials and reactions, concepts for upscaling will become more important.

Publications resulting from this research area: 1, 3, 4, 6, 14, 17, 20, 30, 34, 36-38, 41, 42, 45, 46, 50, 53, 56

External Funding: BMWI, CoE TMFB

Cooperations: C. Lehmann, W. Schmidt, H. Tüysüz, C. Weidenthaler (Mülheim); K. Mayrhofer (Düsseldorf, DE); V. Peinecke (Duisburg, DE); O. Terasaki (Stockholm, SE); R. Schlögl (Berlin, DE); H. Wiggers (Duisburg, DE)

2.3.3 Research area “Novel Catalytic Concepts” (F. Schüth)

Involved: M. Bilke, R. Eckert, A. Grünert, S. Immohr, W. Kersten, H. Schreyer, M. Soorholtz, M. Thomas, T. Trotus, D. Wendt, T. Zimmermann

Objective: This research area is composed of projects of a highly exploratory, but at the same time very exciting nature, where typically only one or two students or post-docs work on a given topic. Unusual reactions or unusual approaches are studied in this research area in an exploratory approach in order to assess, whether more intensive efforts are justified in the future. Topics covered in the research area include catalytic methane activation in oleum, acetylene conversion, mechanocatalytic reactions, and the synthesis of oligomethyleneethers.

Results: The study of mechanocatalytic reactions originates in the work on complex hydrides, was then extended to mechanocatalytic depolymerization of biomass, and finally to mechanocatalyzed gas-phase reactions. The mechanocatalytic depolymerization of biomass is by now well established and also used by several other groups world-wide. The focus of the current work in this field is the understanding of the mechanocatalytic reaction. Here a cooperation with the group of Harald Fuchs (Münster), who is an expert in in-situ scanning probe microscopies has been initiated. The current hypothesis concerning the mechanism of the mechanocatalytic depolymerization of cellulose is the concerted action of a proton and mechanical force, leading to a favorable deformation of the molecule. This is being simulated on a surface by depositing cellobiose, coadsorbing an acid, and then pressing on the molecule with the tip of an atomic force microscope to induce the reaction. This is a very high risk project, but first, preliminary results suggest that p-toluenesulfonic acid around cellobiose on a surface form specific structures (Fig. 1).

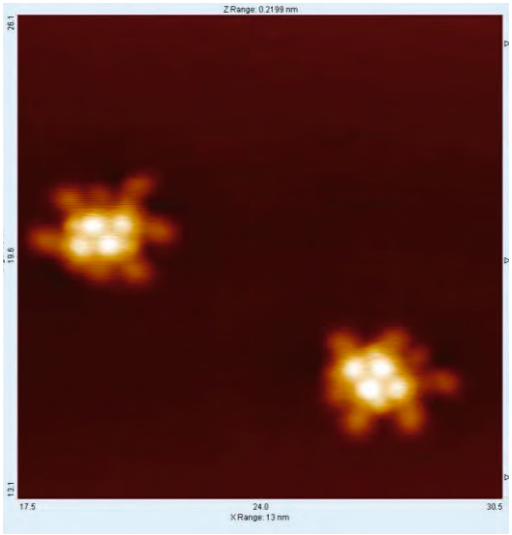


Fig. 1: STM images of cellobiose coadsorbed with p-TSA on Ag(111). Structures typical for certain deposition conditions and possibly cellobiose surrounded by p-TSA molecules (ccoperation H. Fuchs).

For the mechanocatalytic gas-phase reactions, rate increase by three orders of magnitude had been reported for CO-oxidation during in situ milling in a planetary ball mill. These studies have been extended to the preferential oxidation of CO in hydrogen [22]. Surprisingly, for this reaction the selectivity and activity increased with decreasing temperature, and at -40°C 81 % CO conversion at 95 % selectivity were achieved for the standard conditions for this reaction, which is attributed to slower healing of high activity defects at low temperature. For this reaction, the rate increase by ball milling amounts to approximately four orders of magnitude.

The catalytic chemistry of acetylene has been rather neglected over the past decades, in spite of many advances in catalysis in general[18]. Since acetylene could become an interesting feedstock in the future again, a program exploring acetylene chemistry has been initiated. A fully remote controlled, automated flow system has been constructed which allows safe handling of acetylene up to pressures of 30 bar, allowing both batch and continuous reactions. The work is of a highly exploratory nature, and several different reaction pathways starting from acetylene have been explored. The attempts were successful in acetylene-ethylene cross-metathesis to result in butadiene over known metathesis catalysts, which was the first reaction of this kind[35]. However activities are too low for practical applications. Solid catalysts suffer from very rapid deactivation in acetylene streams, which is mostly due to oligomer or carbon formation. However, one class of catalysts, copper on zeolites, and especially copper on zeolite Y, is a highly interesting system for the dimerization of acetylene to result in a high yield of C_4-products. Considering the possible shortage of these fractions due to the lighter feeds used in steam crackers, this could become an interesting development line also for industrial implementation.

Methane activation with a solid version of the Periana-catalyst had already been described in previous reports. Intensive efforts, involving several cooperation partners, have revealed a comprehensive picture of the structure of the solid: it is indeed to a large fraction a solid analogue of the molecular catalyst[54]. While this is highly interesting, the work on related solids,

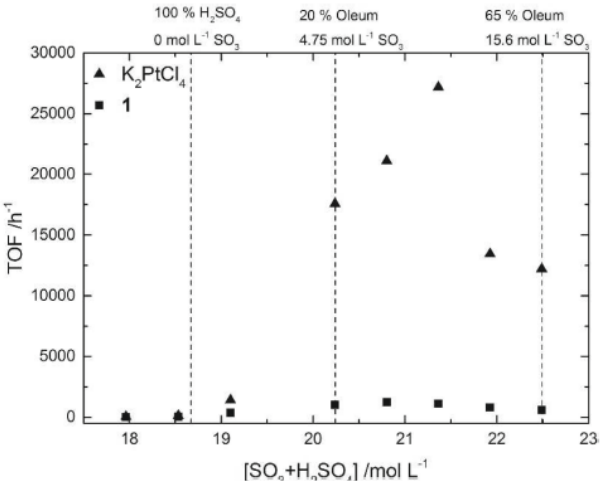


Fig. 2: TOF for methane oxidation in dependence of oleum concentration over K_2PtCl_4 (triangles) and the Periana catalyst $Pt(bpym)Cl_2$ (squares).

in which leaching of active species was observed, led to a spectacular result: It was found that under the right conditions (low concentration of the catalyst, high concentration of SO_3 in the oleum) the catalyst is more than three orders of magnitude more active than reported in the literature, at turnover frequencies close to 30.000 h^{-1} (Fig. 2)[43]. This brings the activity of this catalyst into the same domain as those realized in big commercial processes, such as the Cativa-process or hydroformylation. Also productivities (0.5 kg methanol per liter and hour) are in a range where commercial processes operate. This does, however, not mean that commercial implementation is imminent: the separation of the methylbisulfate from the reaction medium is difficult and costly, and current efforts are directed towards the solution of this problem.

A final project in this research area is directed at the synthesis of oligomethyleneethers (OMEs). These compounds are ideal Diesel-fuel additives, and due to their combustion properties and their higher boiling point superior to dimethylether. Direct synthesis processes from syngas are thermodynamically unfavorable, so that the reaction between methanol and formaldehyde or related compounds is the method of choice. However, this reaction is currently only carried out under batch conditions, which is not optimal. Efforts are therefore directed at the direct synthesis in the gas phase using water-free formaldehyde over different catalysts. This project, however, is still in an early phase.

Future directions: The very nature of the projects in this research area makes it difficult to exactly predict their course. For the mechanocatalytic reactions, the atomic probe microscopy studies to elucidate the fundamental principles of these reactions appears promising, but the interpretation is a substantial challenge which probably also requires support from theory. The formation of C_4 compounds from acetylene is still in an early phase and thus needs to be further studied, moreover, reactions of supported ionic liquid catalysts appear to be promising. Methane activation requires progress in product separation, which will be attempted by formation of compounds which are easier to separate. Finally, the work on OME synthesis is at its beginning, so that initially exploration of catalysts and reaction conditions is on the agenda.

Publications resulting from this research area: 18, 35, 43, 52, 54

External Funding: Industry

Cooperations: M. Antonietti (Golm, DE); B.F. Chmelka (Santa Barbara, US); J. Maier (Stuttgart, DE); H. Fuchs (Münster, DE)

2.3.4 Research area "Biomass Conversion" (F. Schüth)

Involved: G. Al Shaal, Z. Cao, M. Dierks, J. Engelhardt, J. Hilgert, M. Käldström, M. D. Kaufmann-Rechulski, N. Meine, V. Nese, A. Padovani, C. Pupovac, F. Richter, U. B. Richter, M. Ruby, L. Sahraoui, M. P. Tong, G. H. Wang

Objective: In the last report, biomass conversion was covered exclusively in the report of Roberto Rinaldi, although some of the research was a joint effort between the Schüth and the Rinaldi group. Some of the activities, especially those on lignin valorization, but also partly research on the conversion of other biomass components, moved with Roberto Rinaldi to Imperial College, but some of the activities are also being continued in the department at the Institute, and these activities will be covered here. The objective of this research is the valorization of biomass components, leveraging the catalysts and the concepts developed in the department in other research areas. Especially the possibilities of nanostructured catalysts shall be exploited, but here it is crucial to transfer the elaborate methods for nanostructuring to catalytic materials which are accessible at larger scale and at low cost, since the bulk type conversions and the prices associated with most routes are not compatible with expensive catalysts.

Results: The work on mechanocatalytic depolymerization of lignocellulose, which had been discovered in the previous reporting period, was continued with a focus on the processing and the scale-up of the procedure[16, 32]. The previous studies were all performed in laboratory planetary ball mills, where the energy required for mill operation exceeded the energy content of the products by a factor of approximately 50. In two different Simoloyer ball mills, the energy consumption was reduced to approximately 5 times the energy content of the products for the 100 g scale, and at the kg-scale, the milling energy and the energy content of the products was at the same level. This trend is promising with respect to a possible commercial application of the process.

Along the sugar route, the conversion of glucose to 5-hydroxymethylfurfural (HMF) and then further to 2,5-dimethylfuran (DMF) or other value-added products, such as 2,5-furandicarboxylic acid were and still are in the center of the attention[22]. Although the publication only appeared in this reporting period, in the last report the carbon-supported PtCo catalysts for the almost quantitative conversion of HMF to DMF had already been described. On paper, this would allow an overall yield of more than 75 %

of a fuel molecule (DMF) from cellulose. However, the three steps of the reaction – mechanocatalytic depolymerization of cellulose, conversion of celloligomers to HMF and hydrogenation of HMF to DMF – proceed at different conditions in different solvents. Work was thus directed to adjust the conditions of the different reactions to each other. A highly interesting development in this connection is the conversion of fructose to HMF in a reaction which is not acid/base catalyzed[48]. Based on reports in which ionic liquids had been described as suitable catalysts, with the anion being the active species, such systems were heterogenized in form of a polymer. In alcoholic solution, compatible with the hydrogenation of HMF, fructose could be converted to HMF at more than 70 % yield. More importantly, the majority of the original products are acetals from the reaction of the product with the solvent alcohol, which can be recovered. These studies are being continued in order to develop a coherent and simple process from cellulose to DMF. Parallel to these efforts, also the direct synthesis of other valuable products from HMF is explored. Particularly successful were attempts to synthesize furandicarboxylic acid. With ruthenium supported on modified porous silica, full conversion and 97% selectivity to FDCA can be achieved under optimized conditions[22].

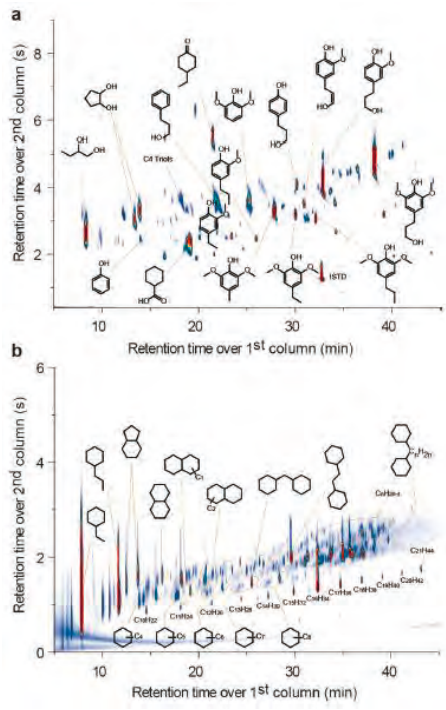


Fig. 1: GC x GC traces of non-pyrolytic bio-oil (top) and the same oil after HDO over PtCo on ordered mesoporous carbon (bottom). After HDO, only aliphatic compounds without oxygen are detected.

Alternative to the depolymerization/sugar conversion-route, the group is also active in the upgrading of bio-oil in the framework of an EU-sponsored project. Bio-oil is a very complex mixture of many highly oxygenated compounds. In order to stabilize it and allow further processing, deoxygenation is crucial. In the framework of the project, the department has the task to develop nanostructured, cheap catalysts for catalytic pyrolysis and for hydrodeoxygenation (HDO) of the bio-oils. For catalytic pyrolysis, hydrothermally synthesized high surface area manganese oxides are amongst the most promising catalysts, resulting in substantial deoxygenation already in the pyrolysis step. These catalysts have been selected for pilot plant pyrolysis experiments which will take place at CPERI/CERTH at Thessaloniki, Greece.

In the HDO, PtCo alloys supported on ordered mesoporous carbons are great catalysts, resulting in deep hydrogenation, so that complete deoxygenation and the production of fully aliphatic hydrocarbon mixtures is possible (Fig. 1)[41]. However, for bio-oil conversion reactions, PtCo catalysts are too expensive, and thus alternatives were explored. Based on the early notion of M. Boudart, that carbides, nitrides, or phosphides of the middle transition metals resemble noble metal catalysts in several of their properties, several such compounds, synthesized by different pathways, were explored as catalysts for these reactions. Nickel phosphide and molybdenum carbide based systems were identified as the most promising systems. With the different catalysts, the selectivity to different product ranges can be controlled: nickel phosphide catalysts result in predominantly aliphatic compounds, while molybdenum carbide favors the formation of aromatic compounds (at even somewhat higher temperatures). Both systems were considered as sufficiently interesting to scale-up the synthesis for pilot plant experiments.

Future directions: Work on biomass conversion will somewhat decrease in importance over the next years. This is partly due to the move of Roberto Rinaldi to Imperial College, partly also due to the completion of the ERC project, in which polymeric catalysts were investigated for biomass conversion. However, studies of conversion reactions via both the sugar route and the bio-oil route will be continued, because biomass conversion is an interesting application field for the nanostructured catalysts which are developed in any case.

Publications resulting from this research area: 2, 5, 7, 12, 13, 15, 16, 32, 41, 47, 48

External Funding: ERC, EU Cascatbel, CoE TMFB

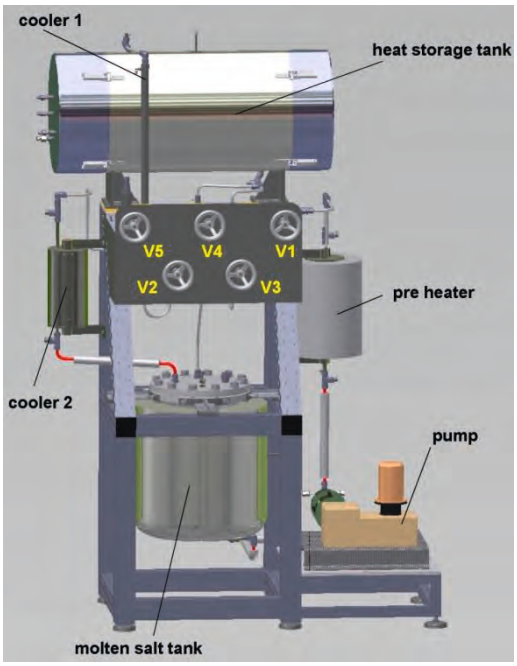
Cooperations: R. Rinaldi (Mülheim, London, UK); C. Fares, W. Schmidt, W. Thiel, C. Weidenthaler (Mülheim); R. Palkovits (Aachen, DE); D. Serrano (Madrid, ES); A. Lappas (Thessaloniki, GR); O. Terasaki (Stockholm, SE)

2.3.5 Research Area "Hydrides for Hydrogen and Energy Storage" (M. Felderhoff)

Involved: R. Albert, Z. Cao, A. Dwivedi, O. Kirschmann, D. Krech, M. Ley, K. Peinecke, M. Meggouh, R. Moury, P. Unkel, C. Weidenthaler, B. Zibrowius

Objective: Aluminium and magnesium based hydrides were intensively studied, both for their structural properties and as potential hydrogen and heat storage materials. Although they are presently not practical for mobile systems, they can be used for stationary fuel cell applications. The activities with these compounds have been focused in order to demonstrate the practicability of these materials for heat and hydrogen storage with fuel cell systems and to explore and characterize new compounds of aluminium based hydrides as possible hydrogen storage materials.

Results: Power-to-heat is one important component future energy systems, but efficient heat storage systems are missing. In the past MgH_2 and Mg_2FeH_6 were extensively characterized at lab scale size as heat storage materials. According to the following equation the material Mg_2FeH_6 can reversibly store heat combined with the uptake and release of hydrogen[70, 71].



Demonstration unit for thermochemical heat storage
Mg_2FeH_6, T_{max} = 550°C, molten salt for heat transfer

$$Mg2FeH6 + Q \rightleftharpoons 2\,Mg + Fe + 3\,H_2Mg_2FeH_6$$

shows exceptional stability over thousands of heat storage and heat relase cycles. The worldwide first demonstration unit with Mg_2FeH_6 as heat storage material for temperatures up to 550 °C (5 kg Mg_2FeH_6) was built up. In order to reach these high temperatures we used molten salts as heat transfer medium, because thermo oils are not stable under these conditions. After first successful operation of the system, technical optimization and long term experiments are in progress.

Aminoalane (NH_3-AlH_3) and substituted compounds are possible, but not examined materials for hydrogen. A broad screening of these materials was started in order to understand

the chemical behavior and to characterize these materials structurally and physically. For dimethylaminoalane $(NMe_2\text{-}AlH_2)_3$ a plastic crystalline phase has been discovered at T > 332 K. Interestingly, this plastic crystalline phase can be described as an A15 phase, which is normally observed only for micellar systems and for several intermetallic compounds. To the best of our knowledge this study was the first one that reported on an A15 phase for a simple metal organic compound. This plastic crystalline state of $(NMe_2\text{-}AlH_2)_3$ seems to be interesting as ion conductive material for battery applications [66, 69].

While $LiAlH_4$, $NaAlH_4$, and $KAlH_4$ were extensively studied for hydrogen storage applications over the last 15 years, only little information is available about the homologues $RbAlH_4$ and $CsAlH_4$. For both compounds a new direct synthesis method, starting from Rb or Cs and Al-metal under H_2-pressure was developed. A new tetragonal phase of $CsAlH_4$ was discovered and the phase transition from the tetragonal to orthorhombic phase and vice versa was in situ observed with X-ray diffraction. The temperature and the kinetics of this phase transition can be influenced through the addition of $TiCl_3$, which is often used as a catalyst for the decomposition and hydrogenation of complex aluminium hydrides. Nevertheless this effect is not completely understood and more investigations are in progress [57, 61].

Future directions: The size of demonstration projects for heat storage with Mg-based compounds in the temperature range of 400 °C (several hundred kg of heat storage material) will be increased. Use of complex hydrides for heat and hydrogen storage in combination with HT-PEM fuel cell systems for the optimization of the fuel cell performance will be demonstrated, and the properties of unstable hydrides (animoalanes, metal hydrides) in combination with high pressure hydrogen gas systems will be explored, in order to develop new solutions for hydrogen storage for fuel cell automotive systems.

Publications resulting from this research area: 57-72.

External funding: IMPRS SurMat, BMBF, AiF, Energieforschung NRW, CSC China (stipend to C. Zhijie), DAAD (stipend to A. Dwivedi), CDZ (travel stipend to M. Felderhoff)

Cooperations: F. Mertens (Freiberg, DE); D. Bathen, S. Peil (Duisburg, DE), M. Fichtner, A. Leon (Karlsruhe, DE), M. Zhu, L. Ouyang (Guangzhou, CN)

2.3.6 Research Area "Nanostructures and Optical Materials" (F. Marlow)

Involved: S. Abdellativ, J. Akilavasan, A. Hullermann, G. Mane, L. Messmer, M. Muldarisnur, D. Naumann, M. Rehosek, P. Sharifi, Y. Xiong

Objective: Novel functional materials consist of a hierarchy of building blocks which have to be assembled by precise and tunable methods. In this research area we investigate fundamental aspects of processing steps and nanostructure building block formation, and the tuning of optical and photocatalytic properties of materials, and their system integration.

Results:

Opals. Photonic crystals (PhCs) are highly ordered nanostructures with at least one length scales in the order of the wavelength of light. They have specific effects on electromagnetic fields. The self-assembly of these materials especially of artificial opals was investigated in our group. The improvement and understanding of one of the best-defined opal fabrication methods (capillary deposition method) was the focus of the research. Opal films fabricated by this method can be understood as intergrowth structures of two different fcc lattices, each of them interrupted by stacking faults. We found out that the fcc-fcc twinning leads to relatively big domains which are not limiting to potential applications. The mean free path for photon can reach about 100 µm which is the largest value published in literature.

The detailed understanding of the opal self-assembly process was the main focus of our research during the last years. The opal formation can be divided into two temporal phases: the wet assembly and the drying. Both are of relevance for the quality of the opals. We have followed these two temporal phases by optical spectroscopy in-situ. In the second phase, a counter-intuitive surprising process ("v-event") was discovered. In addition, the significant rearrangement processes during and after water extinction have been

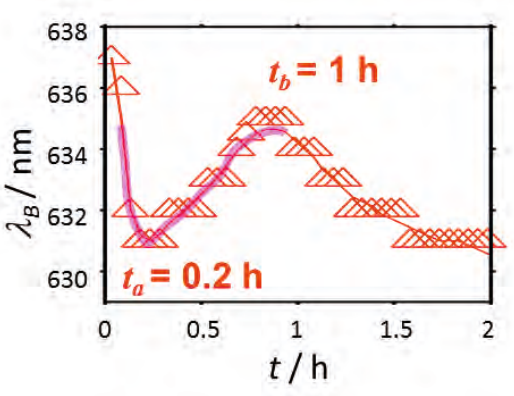


Fig. 1: The v-event in opal formation. The Bragg-peak position shifts during the drying process mainly due to shrinking. The general red shift is interrupted for a short period after about 15 min due to nanostructure dewetting. From: Marlow et al. *Angew. Chem.* **2014**.

studied in detail. Optical microscopy, electron microscopy, optical spectroscopy, and neutron scattering have been used for opal film characterization.

DSSC mechanisms and modeling. Dye-sensitized solar cells (DSSCs) are a promising type of alternative solar cells. After 20 years of continuous research, but slow progress with these cells, the interest has increased in the last years again. Therefore, we have developed techniques for the reliable fabrication, characterization, and description of these solar cells. Besides the use of modified semiconductor electrodes, an improved understanding of the charge transport mechanisms in these solar cells turned out to be crucial. Our measurements have shown clear inconsistencies for the current standard model of the DSSC mechanism. The development of a new basic understanding is the current project in this field.

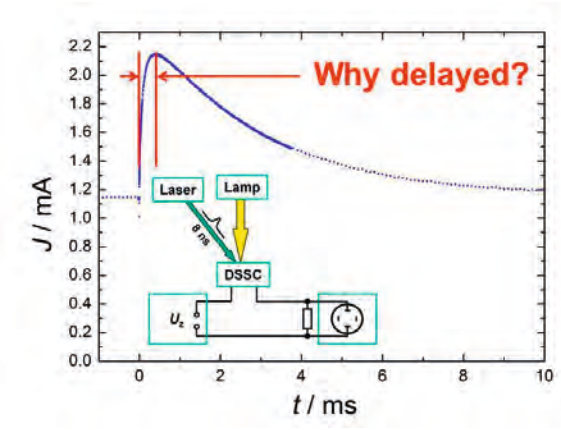


Fig. 2: One of the unsolved problems in DSSC research. Transients after short pulse laser excitation show a delay which is not explained by the current standard model. From: Marlow et al. *Adv. Mater*. **2015**.

Furthermore, we work on numerical DSSC modeling based on trustworthy input data. Especially, the applied porous semiconductor has unknown scattering properties and refractive indices. Recently, we succeeded in their determination. Besides the optimization of the cells, this enables a better interpretation of optical spectroscopy data obtained for DSSCs.

New photocatalytic reaction systems. DSSCs are quite complex, but highly efficient photoelectrochemical systems. They can give a number of inspirations for more efficient photocatalytic reaction systems as well. Most, if not all heterogeneous photocatalytic systems currently studied suffer under inefficient use of visible photons, strong electron-hole recombination, and unfavorable mutual influence of electron and hole reactions. Therefore, we developed a new concept applying sensitized semiconductors at liquid-liquid interfaces. This could solve the three mentioned photocatalytic problems: sensitizer molecules can enhance the visible light absorption, electron-hole recombination can be suppressed by band bending techniques, and the two different photochemical reactions are located in two different media. The realization of this concept requires many partial steps. Currently, we develop an appropriate measurement setup and study the transport of charges through liquid-liquid interfaces.

Janus-Particles. For efficient catalytic and photocatalytic processes at interfaces as e.g. described above, one needs stable incorporation of solid particles into these interfaces. Janus particles are known since long to have interesting and stable incorporation behavior. However, their synthesis is up to now fragile, not well tunable, and not well up-scalable. Therefore, we have studied two synthesis pathways in detail and extended them for our purpose. The Feyen pathway developed by Schüth et al. was extended to a photo-catalytically interesting system by site-selective TiO_2 coating. The wax-masking pathway (Granick et al.) was successfully up-scaled and is now our most promising basis for further interface incorporation investigations.

Future directions: The activities in the DSSC field will be continued. The understanding of the working mechanism of DSSCs is regarded as a crucial issue which is not satisfactory in the literature up to now. We will work on a modified mechanistic DSSC model. Novel DSSC-inspired photocatalysts will be another long-term topic of our research.

Publications resulting from this research area: 73-77

External funding: IMPRS SurMat, Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft.

Cooperations: A. Khalil (Cairo, EG), C. Chan (Tempe, US), N. Benson (Duisburg, DE), H. Wiggers (Duisburg, DE), H. Tüysüz (Mülheim/Ruhr, DE), P. Schulze (Mülheim/Ruhr, DE)

2.3.7 Research Area "Novel Processes and Catalysts for Selective *syngas* Conversion" (G. Prieto)

Involved: N. Duyckaerts, J. Kim, T. Haak, A. Rocha-Vogel.

Objective: Valorization of delocalized, petroleum-alternative feedstocks, such as associated- and shale-gas gas or lignocellulosic biomass, into liquid fuels and platform chemicals, e.g. via *syngas* (H_2+CO+(CO_2)), is hampered by their envisaged small scale and corresponding economy-of-scale penalties. Process intensification is thus an enabling prerequisite for such approaches. In particular, the integration of two catalytic functions in a single reactor, to effect sequential reactions in tandem, gains increasing interest as intensification strategy. The overriding goal of this research area is to gain fundamental insight into, and purpose-design innovative solids catalysts for, tandem catalytic processes for selective *syngas* conversion.

Results: The research has focused initially on the single-step conversion of *syngas* into liquid hydrocarbons via the one-pot integration of the Fischer-Tropsch (FT) and hydrocracking reactions. Our investigations on the processing of model FT hydrocarbon feedstocks on a Pt/H-ZSM-5 bifunctional hydrocracking catalyst revealed the impact of the gas atmosphere on the reaction pathway for paraffin and α-olefin primary FT products [52]. Unlike under standard hydrocracking conditions (H_2 atmosphere), the presence of *syngas*, which mimics the conditions encountered in the tandem process, results in severe poisoning of the platinum (de)hydrogenation functionality by strong CO adsorption, which causes a notable divergence in the reaction pathway for each type of FT product. Under these conditions, particularly α-olefin primary FT products are notably more reactive, as they by-pass the dehydrogenative activation step required for paraffins, contribute to moderate the undesired secondary cracking, likely via an enhanced competitive adsorption on the acid sites, and undergo oligomerization reactions, bringing about an extra, acid-catalyzed chain-growth mechanism which adds to restricting the overall yield to undesired light (C_{4-}) hydrocarbon products. Our results highlight the significance of the nature of the FT primary products exchanged by the tandem catalysts for the overall efficiency, thus pointing to it as a major design variable.

Under relevant reaction conditions, pore mass transport phenomena can notably affect, and therefore serve as lever on, the primary FT product pattern. In this respect, we have developed a research platform to design FT supported cobalt-based catalysts with be-

spoke multimodal porosities. Our synthesis efforts rely on the combination of soft- and hard-templating routes with structural diagnostics obtained, a.o., by tomographic FIB-SEM imaging (Figure 1a). On the other hand, catalytic experiments have revealed a striking impact of porosity on the primary FT product pattern. As a showcase, Co/Al_2O_3 catalysts featuring a trimodal macro-macro-mesoporous topology lead to up to an order of magnitude higher olefinicity of the FT products compared to conventional mesoporous counterparts, due to the notably shorter effective (mesopore) transport distances for most primary α-olefin products, which limits their secondary processing into paraffin products via chain-reinsertion and hydrogenation reactions on the cobalt sites. These results are currently being valorized to optimize the overall efficiency of a tandem process for the single-step production of wax-free liquid hydrocarbons, by independently engineering the chemical and spatial intimacies between the integrated Fischer-Tropsch and hydrocracking catalysts.

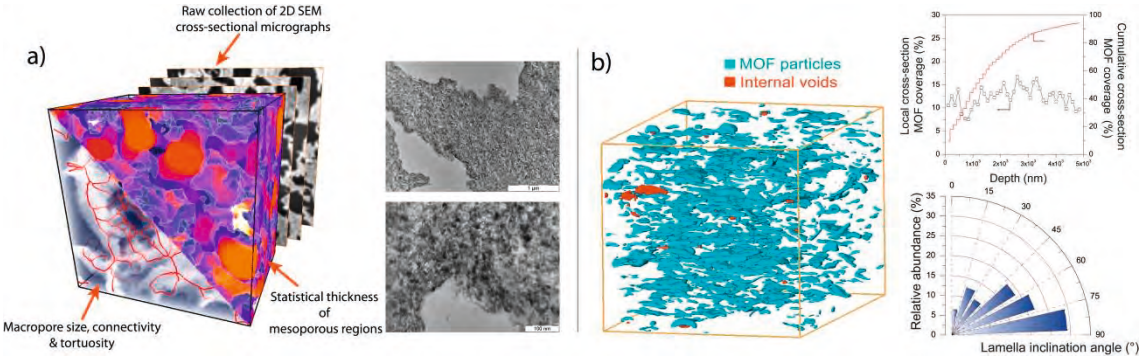


Fig. 1: a) Schematic representation of the 3D macroporosity quantification in multimodally porous Co/Al_2O_3 Fischer-Tropsch catalysts by FIB-SEM tomography (left), and TEM images showing the confinement of cobalt nanoparticles within the mesopores (right); b) Segmented FIB-SEM tomogram (left) and quantification of the permeation cross-section coverage and MOF lamellae orientation (right) for a composite membrane bearing lamellae Cu-BDC MOF nanocrystals within a polyimide matrix[80].

The 3D microstructural quantification platform developed in the framework of this research area has also been leveraged in a spin-off project, in cooperation with researchers at ITQ (CSIC, Spain) and TU Delft (The Netherlands), to assist the fundamental understanding and development of novel MOF(metal-organic-framework)-polymer composites for gas-selective membrane applications (Figure 1b) [80].

Future directions: We aim to extend the implications of our recent findings to develop other catalysts and (tandem) processes for the selective conversion of *syngas* into relevant platform chemicals, such as long-chain olefins and oxygenates.

Publications resulting from this research area: 21, 29, 36, 45, 52, 78-82

External funding: European Research Commission (individual FP7 Marie Curie Actions grant to G. Prieto); Fonds der Chemischen Industrie (funding for consumable costs to G. Prieto).

Cooperations: A. Lorke (Duisburg, Essen, DE); N. Fischer (Cape Town, ZA); F. Llabrés and A. Corma (Valencia, ES); F. Kapteijn and J. Gascon (Delft, NL)

2.3.8 Research Area "Formation of Nanoporous Silicates" (W. Schmidt)

Involved: M. Castro, I. Lim, H. Bongard

Objective: Nanoporous silicates are essential components of many solid state catalysts. Their porosity, high internal surface area, and broad range of functionality make them highly valuable in heterogeneous catalysis. Synthesis of nanoporous silicates has seen tremendous progress in the last decades. However, the very basic formation processes on molecular level are often barely understood. Consequently, zeolite nucleation and crystallization are currently subjects of widespread investigation. Unravelling processes involved in the formation of nanoporous silicates is subject of this research area.

Results: In the last three years we focused preferentially on the formation of zeolite beta starting from molecular precursors [44,83]. In collaboration with laboratories in Versailles, Leuven and Lund the entire formation of the zeolite starting from clear solutions and ending in the crystalline zeolite was unrevealed by using complementary analysis methods including small angle X-ray scattering (SAXS), X-ray diffraction (XRD), mass spectrometry (MS), liquid state nuclear magnetic resonance spectroscopy (^{29}Si, ^{27}Al, ^{13}C, ^{1}H, ^{14}N NMR), transmission electron microscopy at cryogenic temperature (cryo-TEM), and scanning electron microscopy (SEM). We conclusively showed that formation of zeolite beta from clear solutions starts by formation of loose aggregates of oligomeric silicate species (Figure 1). These nanoaggregates (or primary nanoparticles) contained not only different oligomeric silicate species but also all aluminum present in the solution as well as tetraethylammonium cations, the structure directing agent that triggers the formation of zeolite beta. The compounds within these aggregates readily exchange with those in the surrounding solution. At higher silicate concentration, the nanoaggregates get transformed into secondary nanoparticles via silicate condensation and motional freedom of the individual compounds gets significantly restricted. At low silicate concentration, silicate condensation and formation of nanoparticles proceed only at elevated temperature. Irrespective of the temperature at which the

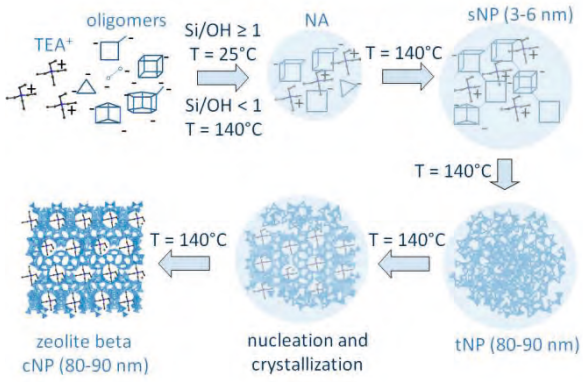


Fig. 1. Formation process of zeolite beta from clear solution [44].

secondary nanoparticles were formed, upon heating they grow to form much larger but still amorphous tertiary nanoparticles. Simultaneously, the degree of silicate condensation increases. Aluminum is present exclusively in four-fold coordination to silicate within the nanoparticles. During heating the formation of zeolite beta proceeds via nucleation within the amorphous nanoparticles, followed by crystal growth from the zeolite nuclei. The resulting zeolite beta crystallites are of the same size as the amorphous tertiary nanoparticles, indicating a successive transformation of the amorphous particles into the crystalline materials. Particle growth as expected from Ostwald ripening is thus observed only for the amorphous silicate nanoparticles but not for the crystalline zeolite.

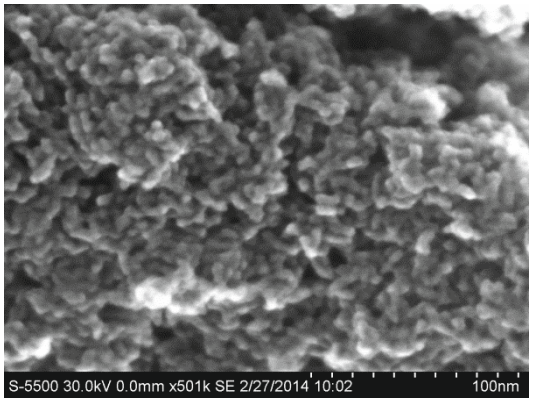


Fig. 2. SEM image of zeolite beta nanorods obtained with amphiphilic structure-directing agent.

Using alternative structure directing agents with long hydrophobic alkane chains, we could show that the basic formation processes are quite similar to those described above. However, due to the amphiphilic nature of these structure directing agents, cylindrical primary and secondary nanoparticles with core-shell structure are formed. Nucleation and crystallization proceed then from these cylindrical silicate nanoparticles whereby the hydrophobic side chains of the structure directing agents prohibit the formation of larger zeolite particles. The resulting materials consequently consist of zeolite beta nanorods (Figure 2) with diameters of about 4 nm and lengths of about 10 nm. The zeolite nanorods are aggregated to form materials with hierarchical micro- and mesopores, the mesopores being the voids between the aggregated rods.

Future directions: The studies on zeolite formation will be extended to other systems to expand the understanding of zeolite formation and modified zeolites will be used as the basis of bi-functional catalysts for the catalytic conversion of poisonous gas compounds.

Publications resulting from this research area: 10, 44, 83, 84

Cooperations: F. Taulelle (Versailles, FR); C. Kirschhock (Leuven, BE), V. Alfredsson (Lund, SE), F. Schüth (Mülheim/Ruhr, DE)

2.3.9 Research Area "Carbon-supported Transition Metal Oxide Catalysts" (W. Schmidt)

Involved: C. Weidenthaler, A. Pommerin, J.C. Tseng, H. Bongard, S. Puthenkalam, D. Gu, G. Wang

Objective: Nanoscopic transition metal oxides have been shown to be efficient catalysts for the conversion of gaseous compounds, such as CO, from gas steams even at room temperature. The investigation of supported transition metal based materials for removal of poisonous compounds from gas streams and chemical conversion is subject of this research area.

Results: A number of transition metal oxides has been deposited within the nanopores of activated carbons [85,88]. The restricted space in the nanopores of the carbons allowed only for formation of nanoscopic oxide particles. As for an example, the materials obtained by deposition of CuO/ZnO or hopcalite-like within activated carbon were efficient in removal of NO_2 and NH_3 from air streams at room temperature [87,89,90]. The efficiency of the active adsorbers were significantly better than those of the pure carbon materials. XRD analyses of the oxide particles within the activated carbons showed that the nanoscopic CuO is generally present as a crystalline phase whereas ZnO is present preferentially as amorphous oxide or hydroxide at lower oxide loading.

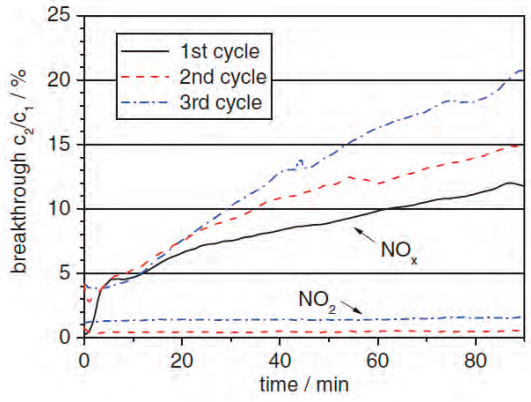


Fig. 1a. Breakthrough of NO_2 and NO_x through activated carbon impregnated with CuO/ZnO. (23 °C, 50% RH, $c_1(NO_2)$ = 4 ppmV, $c_1(NO)$ = 0 ppmV) [90..

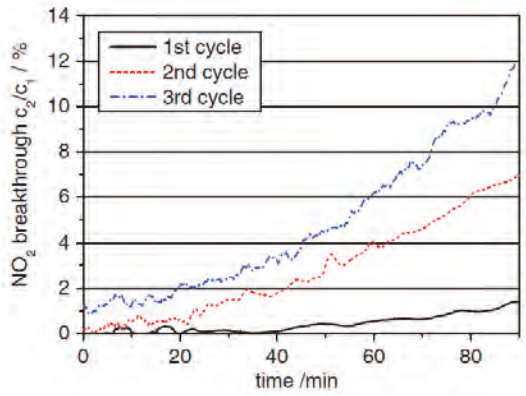


Fig. 1b. Breakthrough of NO_2 through pristine activated carbon. (23 °C, 50% RH, $c_1(NO_2)$ = 4 ppmV, $c_1(NO)$ = 0 ppmV) [90.]

At higher loading a fraction of ZnO is also observed as crystalline phase. Line profile analyses of XRD data show that the average particle sizes of the oxidic phases lie in the range of 2.5 – 3.5 nm [89]. EDX mapping proves that the oxides are dispersed homoge-

nously over the entire activated carbon particles. The activated carbons with different loadings of mixed oxides are active in reducing the concentration of NO_2 if used in thin layer adsorbers as used in car cabin air filters. As shown in Figure 1a, NO_2 breakthrough is greatly reduced in carbons impregnated with CuO/ZnO if compared with the pristine activated carbon (Figure 1b) and long term activity of the adsorber material is significantly enhanced if impregnated with the mixed oxides.

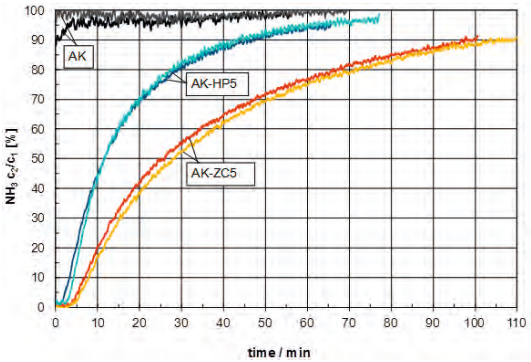


Fig. 2. Breakthrough of NH_3 through activated carbon impregnated with 5 wth% hopcalite or CuO/ZnO. (23°C, 50%RH, c1(NH_3)=4ppmV).

Similarly, even though not as efficiently as for NO_2, NH_3 breakthrough through activated carbon loaded with hopcalite or CuO/ZnO is reduced (Figure 2). NH_3 retardation from can be increased to some extent by increasing the oxides loading but oxide contents of more than 30 wt% do not result in significant further increase of NH_3 removal [90].

The oxidic compounds enhance the interaction of the adsorber material with NO_2, NO_x and NH_3, likely due to interaction of the oxide surfaces with the respective molecules. Furthermore, NO_2 gets reduced to NO by reaction with the carbon. This reaction proceeds much faster if the mixed oxides are deposited within the carbon. Catalytic activity of the oxide seems to exist even at room temperature, e.g., via cooperative interaction of the gas molecules with the oxide surfaces and the carbon.

Future directions: The studies on metal oxide loaded activated carbons or on ordered mesoporous carbons have shown the potential of such materials as catalysts. However, the role of the oxidic compounds, catalytic or not, and its cooperative interaction with the carbon surface remains speculative and further research must focus on the understanding of this interaction.

Publications resulting from this research area: 31, 42, 85, 87-90

External funding: Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF, stipend to J. C. Tseng)

Cooperations: U. Sager, F. Schmidt (Duisburg, DE), F. Schüth (Mülheim/Ruhr, DE)

2.3.10 Research Area "Nanostructured Inorganic and Hybrid Materials for Water Splitting" (H. Tüysüz)

Involved: K. Chen, X. Deng, G. Dodekatos, T. Grewe, S. Öztürk, S. Schünemann, M. Yu

Objective: The motivation behind this research area is the development of new methods and the improvement of existing synthetic approaches for the preparation of novel nanostructured inorganic and hybrid materials for solar energy conversion, with a focus on the different aspects (photocatalytic, electrochemical, and photoelectrochemical) of water splitting. The aim is the evaluation of the key physical and chemical properties of nanostructured materials to allow the development of more effective water splitting catalysts.

Results: *Regarding photocatalytic water splitting*, the role of junctions in tantalate based composite materials—where a more effective charge separation is expected—was investigated. By using a hydrothermal method, a series of novel amorphous and crystalline tantalates with various morphologies was prepared. The junctions between amorphous and crystalline tantalates and also junctions between two crystalline phases, namely perovskite and pyrochlore, were found to improve the efficiency of the photocatalysts significantly [95, 98]. In order to investigate the influence of the junctions in a more well-defined system, a new process based on soft templating was developed. By using this modified approach, a series of amorphous ordered mesoporous tantalates with similar textural parameters and different sodium to tantalum ratios was prepared. The effect of the junctions and improved hydrogen production rate could also be observed for this series of materials, if sodium was incorporated into the composite structure [113]. Besides the modified hydrothermal and templating methods, a new approach was developed for *in-situ* photocatalyst preparation. The process—which is called direct injection— utilizes a metal alkoxide as starting precursor that undergoes hydrolysis, condensation and poly-condensation in a methanol-water mixture under light illumination. This results in nanostructured amorphous materials that show even higher hydrogen production rates than crystalline materials [100].

Regarding electrochemical water splitting, we use ordered mesoporous structures as model system to evaluate the effects of key physical and chemical properties on the performance of materials to gain new insight on the oxygen evolution reaction (OER) and develop more effective non-noble metal based electrocatalysts. By doing so, the effects

of the morphology, symmetry, dimension, doping, and composition of the materials on the activity of the OER catalysts could precisely be demonstrated [86, 92, 96]. Furthermore, it was discovered that there is a strong synergy between cobalt and nickel that results in one of the most active transition metal oxide based electrocatalysts for water splitting. After a simple electrochemical activation, which was attributed to incorporation of iron species from the electrolyte, the performance of nickel cobalt oxide could be significantly enhanced. Furthermore, an effective pentlandite ($Fe_{4.5}Ni_{4.5}S_8$) catalyst for electrochemical hydrogen evolution under acidic conditions was discovered. The developed catalyst is as effective as platinum and has the potential to replace this noble metal for electrochemical hydrogen production [109].

In addition, some novel templates were implemented that allow the preparation of hierarchical nanostructured metal oxides. Spent tea-leaves were used as hard templates to prepare nanostructured Co_3O_4 and also mixed oxides. The outcome of this cheap and scalable templating approach is uniform, high surface area nanocrystals with remarkable activity for OER [104]. A hierarchical Co_3O_4 structure that consists of a solid mesostructured skeleton decorated with small Co_3O_4 was prepared via hard templating, using mesoporous silica spheres as a dual template. The pores and the voids between the mesoporous silica spheres can be simultaneously templated, which yields a multifunctional hierarchical structure. This material shows good performance for photo- and electrochemical water splitting [112].

Regarding photoelectrochemical water splitting, we have been focusing on the synthesis of hybrid organometal halide perovskite (OHP, see right SEM image) and $BiVO_4$ in well-defined inverse opal morphology to construct a tandem cell for hydrogen production. For this purpose, an innovative process, based on a colloidal crystal templating approach, was developed to prepare organometal halide perovskites in an inverse opal morphology [99]. Through solvent engineering and the choice of the polystyrene spheres as hard template, a range of different OHP in inverse opal morphology was fabricated. Furthermore, a systematic post-treatment process was established where the halide ions in the perovskite structure could be exchanged in the gas phase to tune the crystal structure and the band gap of perovskite semiconductors with retention of morphology [111]. In addition, OHP and

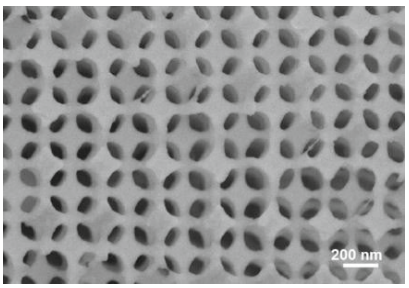


Fig. 1. SEM image of OHP inverse opal

$BiVO_4$ inverse opals were also prepared as thin films on conductive substrates through the same approach by using an assembly of polystyrene spheres as a hard template [108].

Future directions: Future research will include investigations to achieve a better understanding of the activity of amorphous materials for solar water splitting; this includes the design of binary and ternary non-noble metal oxides for electrochemical water splitting and *in-situ* Raman spectroscopy studies on electrocatalysts, in order to monitor surface changes in the materials and determine the possible active species. For the photochemical water splitting, the goal will be to improve the stability of the OHP and the construction of a tandem cell for solar hydrogen production. Moreover, nanostructured carbon based materials will be designed for electrochemical water splitting, and work on the oxidation of glycerol will be developed as a new direction.

Publications resulting from this research area: 24, 86, 92, 95, 96, 98, 99, 100, 101, 104, 108-114

External funding: Fonds der Chemischen Industrie, DFG Cluster of Excellence RESOLV, MAXNET Energy Consortium, IMPRS RECHARGE, BMBF

Cooperations: F. Schüth, C. Weidenthaler, W. Schmidt (Mülheim, DE), C. Chan (Tempe, US). U. Apfel (Bochum, DE), E .Garnett (Amsterdam, NL)

2.3.11 Research Area "Advanced X-ray Diffraction Techniques" (C. Weidenthaler)

Involved: T. Bernert, M. Felderhoff, W. Kersten, J. Knossalla, R. Moury, S. Ortatatli, L. Pagliari, O. Petrova, W. Schmidt, V. Tagliazucca, J. Ternieden, J.C. Tseng, H. Tüysüz, A. Woyk

Objective: Major focus of all research activities is on methods for the analysis of structure-properties relations of nanosized functional materials. These include crystal structure solution from powder diffraction data, microstructure analysis and atomic pair distribution function analysis (PDF). Over the last decade the realization of *in situ* analytics, especially using in-house instrumentation, became more important. The coupling of two or more probes opens new insights into functional materials under reaction conditions. New tailor-made sample environments for different applications have been designed and built in cooperation with the workshop of the institute.

Results: As a continuation of detailed crystallographic investigations of complex hydrides as potential hydrogen storage materials (see report 2011-2013), different sample environment cells were developed for *in situ* diffraction studies of dehydrogenation and rehydrogenation reactions of potential hydrogen storage materials using *in-house* powder diffractometers [57, 61, 63, 64]. Usually, such experiments are performed at synchrotron facilities which provide high fluxes. However, the special design of the sample cells and

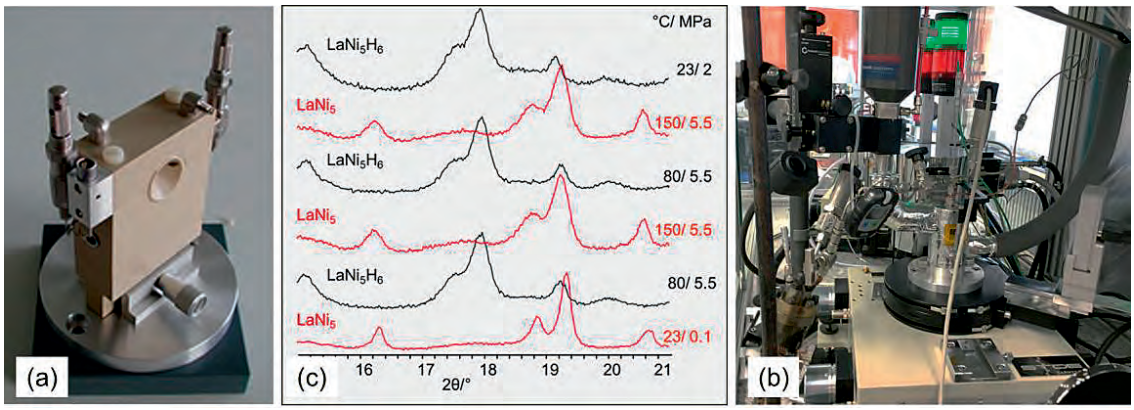


Fig. 1.(a) *in situ* XRD cell made of PEEK, (b) *in situ* diffraction patterns collected during hydrogenation and dehydrogenation of $LiNi_5$ at 5.5 MPa but different temperatures, (c) low temperature-high-pressure cell.

the choice of window materials make the cells suitable for laboratory diffractometers. One type of sample cells shown in Fig.1a covers the temperature range between r.t. and 180 °C and H_2 pressures up to 30 MPa [64]. Phase changes during reversible hydrogenation can be quickly monitored by *in situ* diffraction experiments as illustrated for $LaNi_5$ (Fig.1b) Data quality after 10 min data collection time per scan is sufficient to follow the structure changes qualitatively. Another sample cell which enables diffraction experiments between 173-500 K and H_2 pressures up to 20 MPa (Fig. 1c) is currently under evaluation. This sample environment was designed for the special investigation of unstable aminoalanes as prospective hydrogen carriers in combination with high pressure gas tanks or as catalysts [66, 69].

In situ diffraction can be performed during catalytic reactions even under harsh experimental conditions. Ammonia decomposition is one of the reactions which has not been intensively studied under reaction conditions in the past due to the corrosive properties of ammonia. We have installed a reaction chamber with a computer-controlled gas distribution system which makes studies of catalysts in pure ammonia feasible. Based on the *in situ* studies, we obtained very detailed insights into changes of inorganic catalysts with respect to crystal structures, chemical composition, and microstructure which are not accessible by any *ex situ* experiment [120, 122]. A direct coupling of the reaction chamber on the diffraction instrument with a gas analysis system (GC, MS) for the direct analysis of the reaction gases could also be realized. Unfortunately, parts of the commercial reaction chamber are made of steel which acts as catalyst itself. To overcome this problem, a new catalysis cell was designed which is completely built of inert quartz glass and which can be coupled with gas detection systems (Figure 2). This setup enables the simultaneous collection of diffraction data and catalytic conversion data.

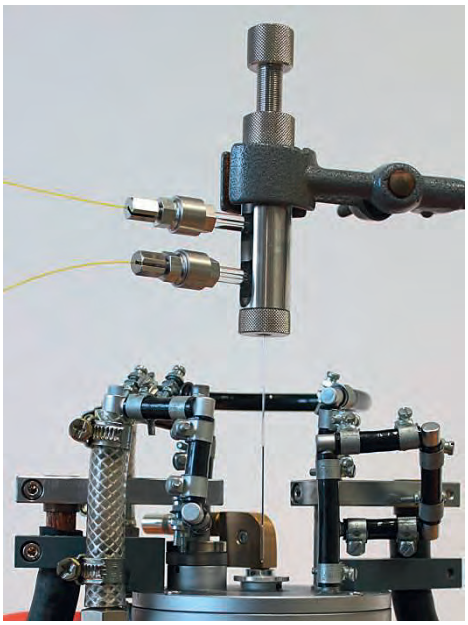


Fig. 2: reaction cell for *in situ* catalysis XRD experiments

Not only crystalline compounds are active catalysts but also disordered or even amorphous materials can be highly active. The local structures of such compounds become accessible if the diffuse scattering contribution to a diffraction pattern is considered by atomic pair distribution function analysis (PDF). Recently, we have performed temperature dependent *in situ* PDF studies of electrocatalysts at

a synchrotron radiation source. From the analysis of the data, the formation of alloys from the precursors can be monitored as well as disordering/ordering phenomena taking place during heating and cooling of the catalysts.

Future directions: In addition to the development of *in situ* diffraction methods we will also establish *in situ* techniques to the surface spectroscopy (XPS) of inorganic catalysts. The *in situ* PDF studies will be extended to study the formation and local structures of highly active amorphous photocatalysts such as sodium tantalum oxides or titanium oxide.

Publications resulting from this research area: 57, 61, 63, 64, 66, 69, 120, 122.

External funding: BMBF

Cooperations: F. Schüth, M. Felderhoff, W. Schmidt (MPI Mülheim, DE), B. Hauback (Kjeller, NO), J. C. Jia (Shandong, VC), Michael Römelt (Bochum, DE), Drew Sheppard (Curtin, AU), M. Fischer (Bremen, DE), J. Ruiz-Fuertes (Valencia, ES), F. Mertens (Freiberg, DE)

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2.4 Department of Organometallic Chemistry

Director:

Alois Fürstner (born 1962)

Further group leader:

Manuel Alcarazo (born 1978)
Group leader from December 2008 - June 2015

Curriculum Vitae: Alois Fürstner

1962	Born in Bruck/Mur, Austria
1980-1987	Studies at the Technical University Graz, Austria; Ph.D. with Prof. H. Weidmann
1990-1991	Postdoctoral Fellow, University of Geneva, Switzerland, with Prof. W. Oppolzer
1987-1992	"Habilitation", Technical University Graz, Austria
1993-1997	Research group leader at the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, Germany
1998-	Director at the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, and affiliated as Professor ("apl. Prof.") with the TU Dortmund University, Germany
2009-2011	Managing Director of the Institute
2016-2017	Managing Director of the Institute

Awards and Honors

1994	Chemical Industries Prize ("Dozentenstipendium"), Chemical Industry Fund
1998	Ruhr Prize for Arts and Sciences, Mülheim/Ruhr
1999	Leibniz Award, German Research Foundation
2000	Thieme-IUPAC Prize for Synthetic Organic Chemistry
2000	Astra-Zeneca Award for Organic Chemistry
2001	Victor Grignard - Georg Wittig Lecture, Société Francaise de Chimie
2002	Arthur C. Cope Scholar Award, American Chemical Society
2002	Member, National Academy of Sciences Leopoldina
2004	Centenary Lecture, Royal Society of Chemistry
2004	Member, North Rhine-Westphalian Academy of Sciences, Humanities and the Arts
2004	Corresponding Member, Austrian Academy of Sciences
2004	Tetrahedron Chair
2005	Junior Award, International Society of Heterocyclic Chemistry
2005	First Mukaiyama Award, Society of Synthetic Organic Chemistry, Japan
2006	Otto Bayer Prize
2006	Heinrich Wieland Prize
2008	Janssen Pharmaceutica Prize for Creativity in Organic Synthesis
2009	Lord Todd-Hans Krebs Lectureship, RSC

2011	Lilly European Distinguished Lectureship Award
2011	Prelog Medal, ETH Zurich, Switzerland
2013	Elhuyar-Goldschmidt Lectureship, Royal Spanish Society of Chemistry
2013	Prix Jaubert, University of Geneva, Switzerland
2013	Karl Ziegler Prize, German Chemical Society
2014	Hans Herloff Inhoffen Medal, Braunschweig
2014	Gay-Lussac/Humboldt Pize, France
2014	Thomson Reuters Highly Cited Researcher
2015	Thomson Reuters Highly Cited Researcher
2015	Adolf-Windaus-Medal, University of Göttingen
2016	H. C. Brown Award for Creative Research in Synthetic Methods, ACS

more than 30 Name Lectureships (in the report period: Siegfried Hünig Lecture (DE, 2014); Heathcock Lecture (US, 2014); Irvine Organic Synthesis Lecture (US, 2015); Adolf Windaus Memory Lecture (DE, 2015); Sandin Lecture (CA, 2015); Adolf Lieben Lecture (AU, 2016)

Special Activities

2001-2006	Member, Board of Editors of "*Organic Syntheses*"
2001-2007	Scientific Editor, "*Chemical Communications*"
2002-2009	Member of the Scientific Advisory Board, Leibniz Institute for Catalysis at the University of Rostock (LIKAT Rostock)
2002-2010	Member and since 2006 Chairman of the Selection Committee of the Alexander-von-Humboldt Foundation (Feodor-Lynen-Program)
2004-2011	Member, Board of Governors, German Chemical Society
2012-	Member of the Scientific Advisory Board, ISIQ Tarragona, Spain
2013-	"*Angewandte Chemie"* Chairman of the Editorial Board
2014	Chairman, BOSS-XIV Symposium, Louvain-la-Neuve, Belgium
2015-	Member of the Selection Committee of the Alexander-von-Humboldt Foundation (Humboldt-Professorship)

International Advisory Boards (active memberships only): "*Topics in Organometallic Chemistry*" (1997-); "*Advanced Synthesis & Catalysis*" (2000-); "*Progress in Heterocyclic Chemistry*" (2005-); "*Science of Synthesis*" (2009-); „*Israel Journal of Chemistry*“ (2010-), "*Angewandte Chemie*" (2010-), "*Comptes Rendus de Chimie*" (2013-); "*Bull. Chem. Soc. Jpn*." (2015-)

Organometallic Chemistry

The research in this Department is focused on the development of organometallic catalysts of preparative relevance, the investigation of their mode of action, and on applications to the synthesis of natural products of biological significance.

Several group leaders started successful careers while affiliated with the Department: Frank Glorius (2001-2004; now Full Professor in Münster), Stefan Hecht (2005-2006; now Full Professor in Berlin), Lisbet Kvaerno (2007-2008, left for a position in industry), and Manuel Alcarazo (2008-2015), who became Professor of Organic Chemistry (W3) at the University of Göttingen. His research encompassed the design of new ligands that impart exceptional π-acidity on the derived metal complexes. Moreover, he developed a promising class of high valent sulfur compounds as stable alternatives to hazardous hypervalent iodine reagents commonly used in the literature.

A new research group leader will be appointed to the Department to fill the vacancy. An offer has been made, the acceptance of which is currently bending.

The major lines of research in Prof. Fürstner's own group comprise investigations in the following fields of catalysis research, which are partly interwoven:

- metathesis
- carbophilic Lewis acid catalysis
- stereochemical unorthodox *trans*-addition chemistry
- organoiron chemistry and catalysis
- natural product total synthesis

Following our early work on alkene metathesis (macrocyclization reactions; ruthenium indenylidene catalysts etc), the related metathesis of alkynes has become a focal point of research since the turn of the millennium. This reaction had no practical relevance at that time; gratifyingly though, a new generation of catalysts developed in our laboratory shows remarkable activity and functional group compatibility and hence upgrades alkyne metathesis to the strategy level. Our catalysts are now commercial available and increasingly used by others. Furthermore, we recently showed that triple bond metathesis might even be relevant for the activation of small molecules since our catalysts cleave the N≡N-bond of aryldiazonium salts with remarkable ease. This transformation serves as prospect for an unconventional way of nitrogen activation.

With alkyne metathesis rapidly maturing, the focus of our attention is gradually shifting to the downstream chemistry which ultimately defines the outreach of this method. Many creative ways of using alkynes can be envisaged, but some seemingly simple transformations remain surprisingly difficult to accomplish. Thus, it is by no means trivial to convert alkynes into *E*-alkenes under conditions that are compatible with sensitive functionality. This challenge was met in 2013 when we described an alkyne *trans*-hydrogenation that tolerates relevant functional groups. This unorthodox outcome seemingly violates the basic rules of hydrogenation reigning since Sabatier's ground-breaking work. The underlying concept has been generalized in that practical methods for *trans*-selective hydroboration, hydrogermylation and hydrostannation of alkynes were developed quickly thereafter. Detailed experimental and computational studies provided insights into the mechanism of these perplexing transformations.

While the use of carbophilic π-acids based on Au, Pt, Rh, Ru etc. has become tremendously popular since the turn of the millennium, the field is in its childhood with regard to firm mechanistic analyses. Of key relevance is a better understanding of the structure and reactivity of the metal carbenes commonly invoked. During the report period, we managed to isolate the first reactive gold carbenes and determined their structure by X-ray diffraction and NMR. Along the same lines, the first reactive rhodium carbenes were isolated and characterized, which had defied experimental inspection for decades.

In the area of iron catalysis, we were able to find several previously unknown reaction modes. This includes an unconventional way of ring opening/cross coupling of a heterocyclic scaffold, as well as an unprecedented merger of cross coupling and cycloaddition chemistry. Moreover, the intricate redox behavior of a prototype iron precatalyst was largely clarified, which had been subject to debate in the past.

All methodologies of interest to our group are scrutinized by applications to the total synthesis of structurally complex natural products of biological significance. Because the target compounds are highly precious and hardly available otherwise, we team up with external cooperation partners to study their biochemical and/or biological properties. Where deemed appropriate, we are prepared to adjust the original syntheses such that they allow for larger material throughput as well as for the preparation of non-natural analogues ("diverted total synthesis").

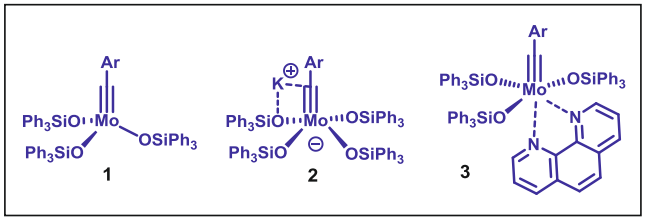
Over the years, close collaborations with Prof. Thiel and coworkers have become an integral part of many of our projects. Moreover, it is emphasized that our work would not be possible without the excellent support by and cooperation with the different analytical groups of the Institute. These mutually beneficial collaborations have led to several joint publications during the report period.

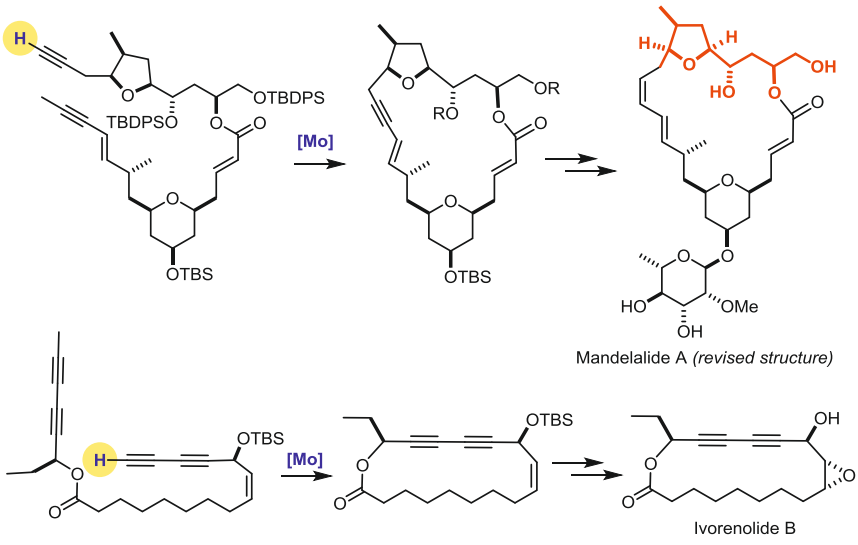
2.4.1 Research Area "Metathesis" (A. Fürstner)

Involved: K. Gebauer, L. Hoffmeister, M. K. Ilg, A. Lackner, R. Llermet, S. Schaubach, J. Willwacher, F. Ungeheuer

Objectives: Teaching olefin metathesis "simple" stereochemistry is arguably the single most important issue of contemporary metathesis research. Whereas other laboratories managed to develop prototype examples of *Z*-selective alkene metathesis catalysts, our group pursues complementary approaches via triple bond metathesis. The alkyne products have the distinct advantage of providing access to many different structural motifs upon adequate downstream functionalization. Finally, it is shown that metathesis provides – at least in principle – even opportunities for the activation of N≡N triple bonds as exemplified by the cleavage of the [N_2]-unit of aryldiazonium salts.

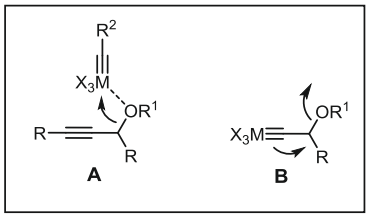
Results: During the preceding report period (2011-2013), our group had developed a new generation of catalysts for alkyne metathesis such as **1**-**3** which outperform all ancestors in terms of activity and functional group compatibility. They capitalize on the synergy between a molybdenum alkylidyne core and a silanolate ligand sphere; moreover, reversible adduct formation with phenanthroline renders them bench-stable and hence easy to use. These catalysts are now commercially available and have been used by a number of groups worldwide in exigent applications.



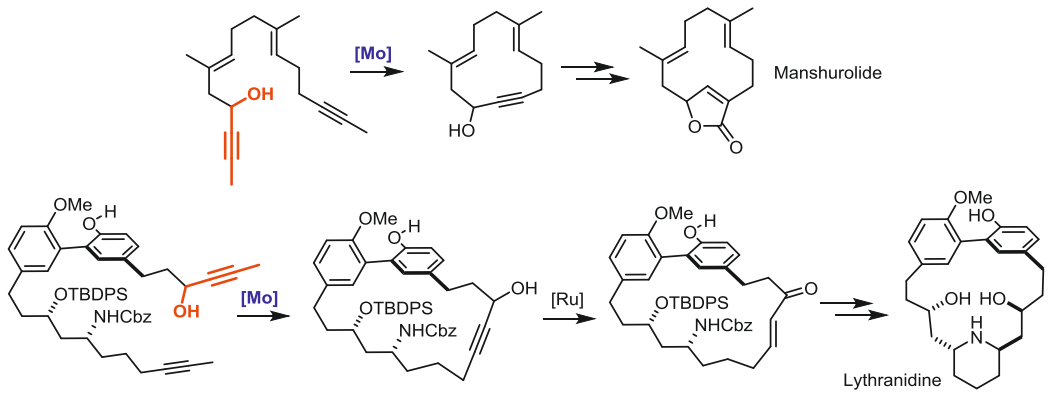


While our work had previously been focused on the understanding of these catalysts, attention has now shifted towards exploitation of their truly enabling application profile.

Terminal acetylenes are an important class of substrates that were traditionally beyond reach of alkyne metathesis because they polymerize on contact with a metal alkylidyne. Gratifyingly though, complex **3** is capable of inducing highly effective alkyne cross metathesis as well as ring closing alkyne metathesis reactions of terminal alkynes that were basically inconceivable before. Likewise, conjugated 1,3-diynes proved well behaved. The robustness of this methodology is apparent from applications to natural products such as ivorenolides A and B as well as mandelalide A. The latter project also led to the revision of the structure originally proposed by the isolation team: since the stereochemistry of the entire northern sector had been mis-assigned, this goal was reached only after a massive synthetic effort.



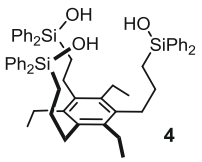
Propargyl alcohol derivatives are another class of challenging substrates for two major reasons: all alkyne metathesis catalysts are Schrock alkylidynes, and as such comprise an early transition metal in its highest oxidation state. Unless appropriately tempered by the ligand set, the inherent Lewis acidity endangers substituents at any activated position; propargylic alcohol derivatives fall into this category (see the generic structure **A**) because of the resonance stabilization of the resulting carbocations. Even if this serious pitfall is overcome and the chosen catalyst engages productively with the triple bond, the ensuing alkylidyne of type **B** might decompose by extrusion of the potential leaving group next to the nucleophilic site. Therefore it was gratifying to learn that our molybdenum alkylidynes allow such substrates to be metathesized with ease.



Because of the rich follow-up chemistry of propargyl alcohol derivatives, this outcome is particularly rewarding. The total syntheses of the strained sesquiterpene lactone manshurolide and the biphenyl alkaloid (–)-lythranidine illustrate just two of the many possibilities. As a spin-off of our studies, we developed a much improved catalyst for

the redox isomerization of propargyl alcohols, which is subject to further investigations in the laboratory.

These examples illustrate yet another important point: because Schrock alkylidynes are nucleophilic at carbon, none of the classical catalysts had shown any meaningful compatibility with protic groups; in contrast, our molybdenum alkylidynes work well even in the presence of alcohols, phenols, amines, amides, sulfonamides etc. It is perhaps not surprising that formal replacement of the Ph_3SiO- ligands in the standard precatalyst **1** by a potentially chelating ligand environment, as materialized in **4**, imparts even higher stability (although the corresponding catalyst is oligomeric rather than a well-defined monomeric entity). In any case, the functional group tolerance of molybdenum alkylidynes endowed with silanolates as ancillary ligands is remarkable. Several total syntheses referred to in the different chapters of this report illustrate this aspect.



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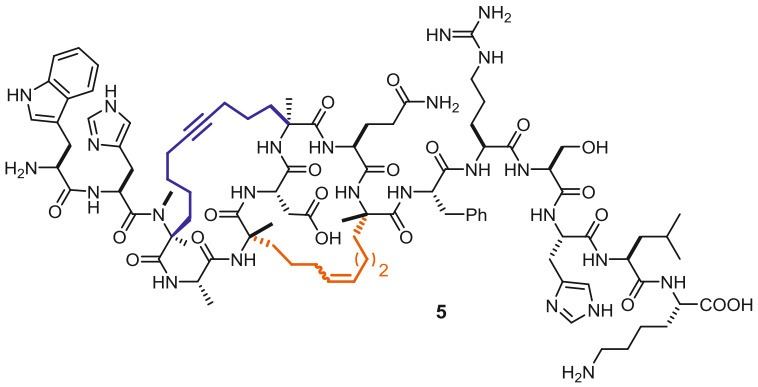
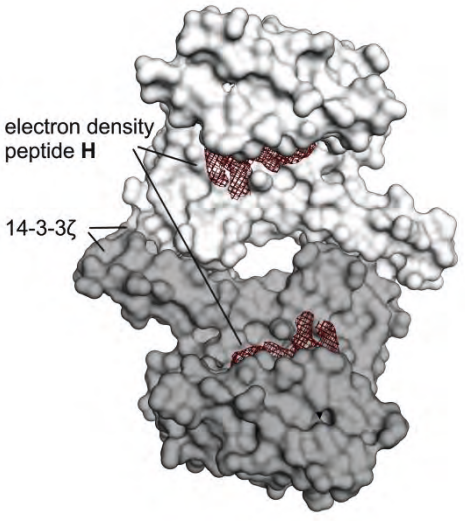
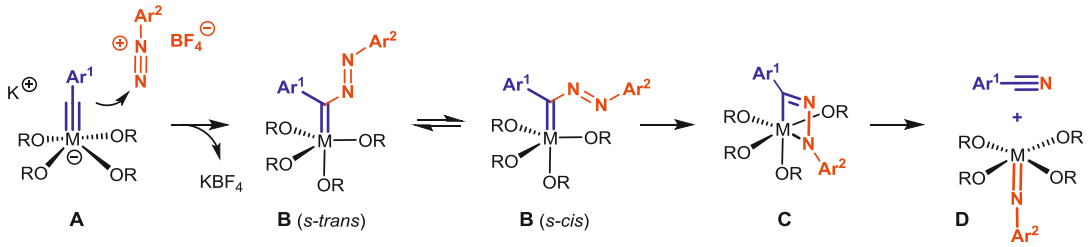

5

Another instructive case pertains to the formation of stapled peptides, which also represents the first application of alkyne metathesis on solid support. The compatibility of the molybdenum catalysts with olefins of all sorts made it even possible to prepare bicyclic peptide architectures such as **5** via consecutive ring closing alkene/alkyne metathesis. Compound **5** shows high affinity to an activated Rab GTPase; this protein superfamily comprises several clinically relevant yet particularly challenging drug targets that are key regulators of intracellular vesicular transport and trafficking.



In parallel work, alkyne metathesis was used to prepare a monocyclic stapled peptide that could be co-crystallized with its protein target; therefore it serves as a valuable tool to study the 14-3-3ξ

binding motif of the exo-enzyme virulence factor S of *Pseudomonas aeruginosa*.



The power of triple bond metathesis is also evident from an entirely different application to aryldiazonium salts. This choice may seem counterintuitive since these compounds loose N_2 with ease, whereas the formal N≡N triple bond itself is very stable. Yet, on treatment with molybdenum or tungsten alkylidyne ate-complexes endowed with triphenylsilanolate ligands, the [N_2] unit is metathesized even at low temperature. The reaction transforms the alkylidyne unit into a nitrile and the aryldiazonium entity into an imido ligand to the metal center, as unambiguously confirmed by X-ray diffraction. Since the bonding situation of an aryldiazonium salt is similar to that of certain metal complexes with end-on bound dinitrogen, this unprecedented transformation might represent a conceptually novel strategy for dinitrogen cleavage that is devoid of any redox steps and hence orthogonal to the established methods.

Future directions: Fill the few remaining gaps with regard to functional group tolerance, find strategic applications were alkyne metathesis is uniquely enabling, and expand the scope of triple bond metathesis beyond ordinary alkynes.

Publications resulting from this research area: 3-10, 17, 19-22, 24, 25, 27, 29, 30, 32-34, 39, 44, 46

External funding: Alexander-von-Humboldt Foundation (fellowship to A. Lackner), Fonds der Chemischen Industrie (fellowships to S. Schaubach and J. Willwacher)

Cooperations: T. N. Grossmann (Amsterdam, NL), W. Thiel (Mülheim/Ruhr, DE), H. Waldmann (MPI Dortmund, DE)

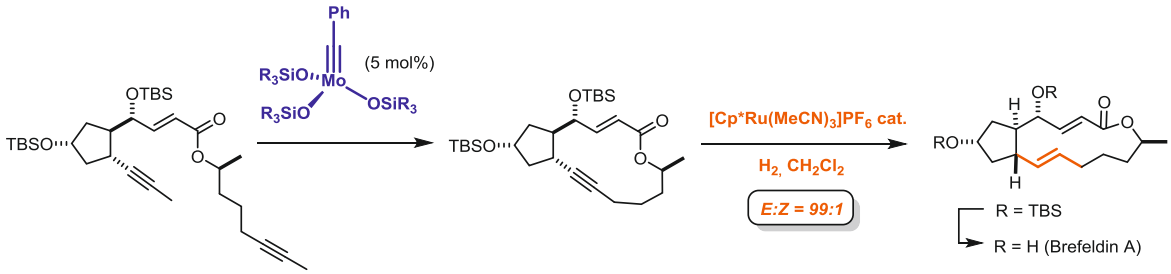
2.4.2 Research Area: "*trans*-Addition Chemistry" (A. Fürstner)

Involved: T. G. Frihed, M. Fuchs, K. Michigami, J. Preindl, K. Radkowski, D.-A. Rosca, S. Rummelt, S. Schaubach, H. Sommer, B. Sundararaju

Objective: We try to find broadly applicable catalytic addition reactions to π-bonds that violate the reigning paradigms of organometallic chemistry.

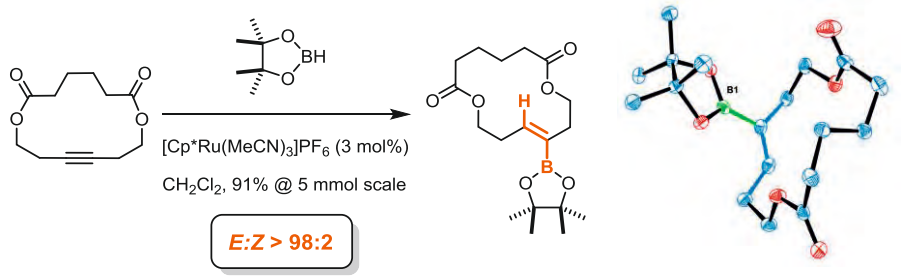
Results: Alkyne metathesis in combination with a Birch-type reduction opens a stereoselective entry into *E*-alkenes; this sequence fills an important gap in methodological coverage, since inherently *E*-selective alkene metathesis catalysts are unknown. With the advent of the powerful and practical alkyne metathesis catalysts described in the previous chapter, however, it became increasingly clear that the weak point of this tactics is the semi-reduction step, which, in its classical format, requires strongly reducing conditions that preclude many functional groups.

At the outset of our project, the best current alternative was the *trans*-hydrosilylation chemistry introduced by Trost and coworkers shortly after the turn of the millennium. When combined with a subsequent proto-desilylation of the resulting alkenylsilanes, *E*-alkenes can be formed in an indirect manner. This remarkable discovery was rapidly embraced by the synthesis community, despite the fact that non-symmetrical substrates almost always lead to the formation of regioisomers.

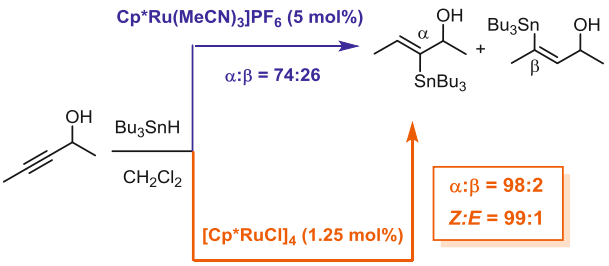


Intrigued by the then unknown reasons for this unorthodox stereochemical outcome and spurred by the potential preparative significance of *trans*-addition chemistry in general, we initiated a long-term research program in this area. A first notable success was reached when we managed to develop a method that allows internal alkynes to be directly hydrogenated with remarkable levels of *trans*-selectivity; this perplexing result had been briefly mentioned in the last progress report. A number of control experiments proved that the net stereochemical outcome is not the result of a canonical *cis*-reduction followed by isomerization; rather, it is an inherent virtue of the ruthenium catalyst

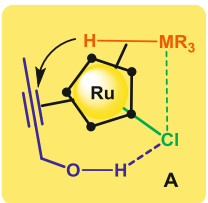
which seemingly violates the fundamental rule of suprafacial *syn*-selective hydrogen delivery that governs hydrogenation since the pioneering work of Sabatier. The novel *trans*-hydrogenation proved compatible with many (reducible) functional groups and already stood the test of natural product total synthesis. Specifically, it served as the cornerstone of a highly productive entry into brefeldin A, which is a widely used probe molecule in the biosciences for its ability to target the Golgi apparatus.



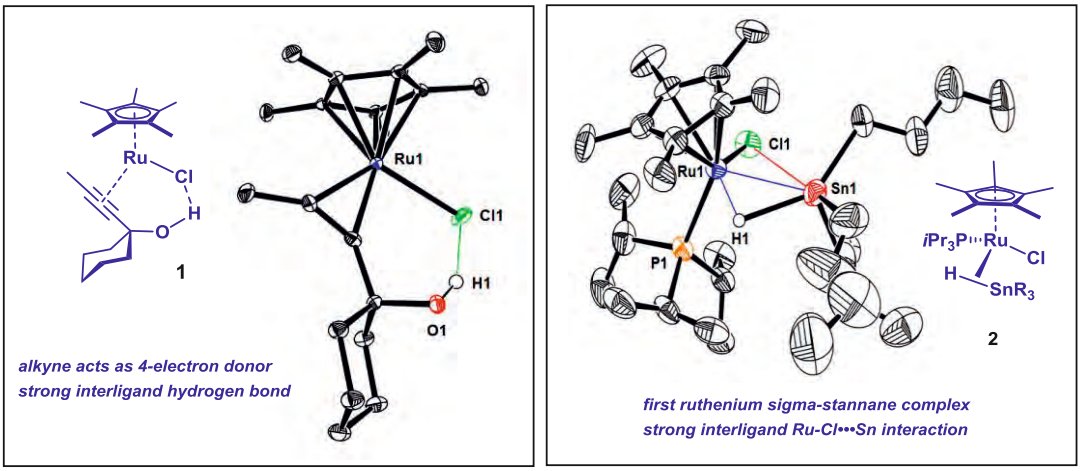
A first mechanistic study provided strong evidence for the intervention of a σ-H_2 complex on the catalytic cycle. Since silanes are also capable of forming σ-complexes, this preliminary information suggested that *trans*-hydrogenation and *trans*-hydrosilylation basically follow the same principles. Under this premise, other reagents able to form ruthenium σ-complexes might also qualify for *trans*-addition chemistry. This notion was quickly proven correct: it allowed us to establish the *trans*-hydroboration, *trans*-hydrogermylation and *trans*-hydrostannation of internal alkynes, which again violate the paradigms of organometallic chemistry and prove highly versatile in synthetic terms.



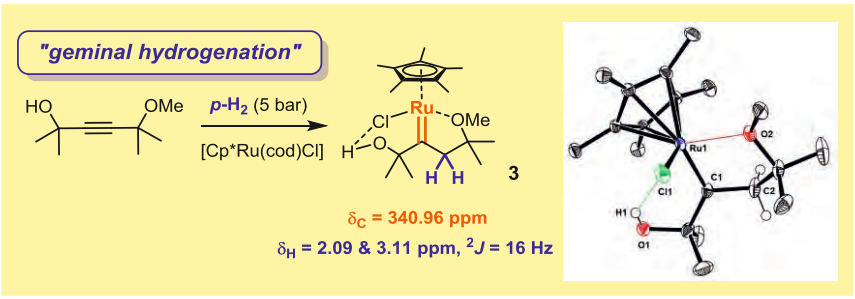
Irrespective of the stereochemical outcome, any hydrometalation of an unsymmetrical π-bond gives mixtures of regioisomers. In the present context, however, this severe handicap is easily circumvented by using neutral precatalysts comprising a [Ru–Cl] bond. Under the proviso that the alkyne substrate carries a protic functional group, the R_3M unit is faithfully delivered to the acetylene-C-atom proximal to the steering substituent. The effect is massive and therefore of considerable preparative significance (see below). It originates from the ability of the polarized [Ru–Cl] bond to engage in hydrogen bonding with the protic group, which helps upload, activate and lock the alkyne substrate in the coordination sphere. An additional interligand contact of the



chloride with the $-MR_3$ center (M = Si, Ge, Sn) positions the incoming reagent in the loaded complex of type **A** in a matching orientation that ultimately translates into high regioselectivity.

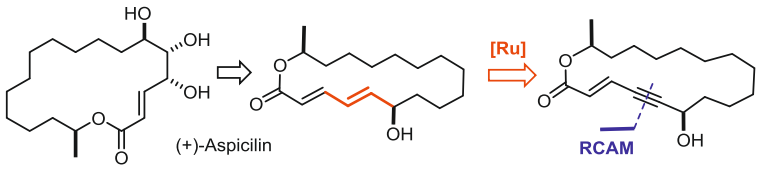


The proposed secondary interactions are manifest in a host of spectral and crystallographic data. Specifically, a number of ruthenium alkyne π-complexes such as **1** were isolated that feature strong interligand hydrogen bonds between an –OH group in the substrate and the Ru–Cl entity of the catalyst. Likewise, the first ruthenium complex with a σ-bound stannane ligand was obtained, which corroborates the notion that σ-coordination is instrumental for alkyne *trans*-addition chemistry. The strong peripheral $Ru–Cl\cdots MR_3$ contacts manifest in complex **2** are in excellent accord with model **A** meant to describe the loaded complex formed en route to product. Importantly, these experimental data are in full agreement with high level DFT calculations of the entire reaction path.

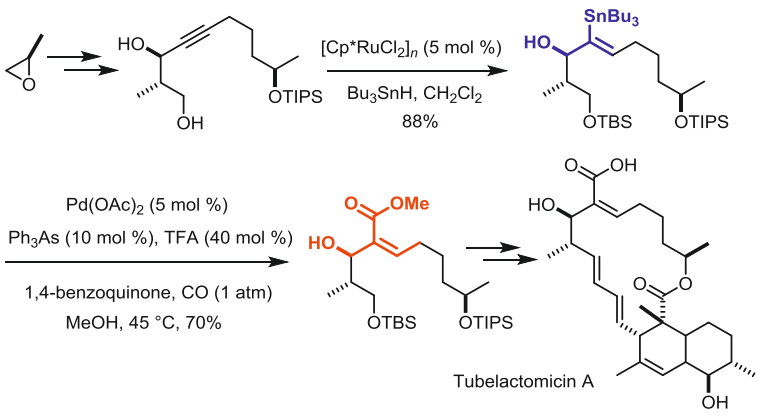


Valuable insights into the origins of the unorthodox *trans*-addition mode were gained by *para*-hydrogen (*p*-H_2) induced polarization (PHIP) transfer NMR spectroscopy. Surprisingly, it turned out that the productive *trans*-reduction concurs with a pathway in which both H-atoms of H_2 are delivered to a single alkyne C-atom of the substrate, whilst the second alkyne C-atom converts into a metal carbene. This intriguing "*geminal*-hydrogenation" is unprecedented in the realm of organic chemistry; it was confirmed by isolation and

structural characterization of the ruthenium carbene complex **3** stabilized by secondary interligand interactions. An in-depth DFT study showed that the *trans*-alkene and the carbene complex originate from a common metallacyclopropene intermediate. Moreover, the computational analysis and the PHIP NMR data concur in that metal carbenes analogous to **3** are a gateway to olefin isomerization and over-reduction, which interferes with regular alkyne *trans*-hydrogenation.

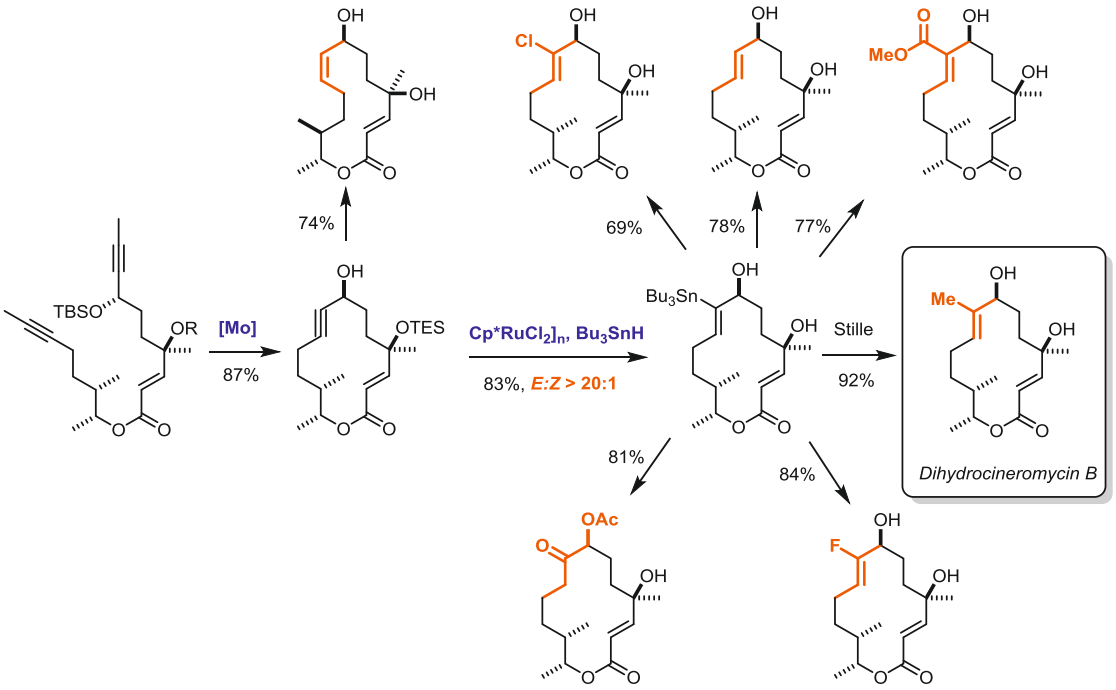


In parallel work, we were striving to showcase the preparative significance of the emerging *trans*-addition chemistry by increasingly complex applications to target oriented synthesis. In addition to the brefeldin case mentioned above, formal total syntheses of the lichen-derived macrolide aspicilin and the antibiotic tubelactomicin A were accomplished. The former project served to illustrate that a strategically-placed hydroxyl group allows substrates to be activated that are not amenable to *trans*-addition otherwise (e. g. 1,3-enynes). The tubelactomicin project, on the other hand, provided an opportunity to develop conditions for the direct methoxycarbonylation of alkenylstannanes. Key to success was the use of 1,4-benzoquinone in combination with trifluoroacetic acid for the regeneration of the palladium catalyst. The acid is essential for lowering the LUMO of the quinone and for marshaling the critical assembly of the reaction partners. Under the optimized conditions, competing proto-destannation is marginal.



Countless natural products of polyketide origin comprise an (*E*)-configured 2-methyl-but-2-en-1-ol substructure. An unconventional entry into this important motif was developed as part of a total synthesis of the antibiotic 5,6-dihydrocineromycin B. Our approach consisted of a sequence of alkyne metathesis followed by a hydroxyl-directed *trans*-hydrostannation and an uncommon methyl-Stille coupling. The excellent yield and remarkable selectivity with which the signature trisubstituted alkene site of 5,6-dihydrocineromycin B was procured is best appreciated when compared with the rather

poor outcome of a classical RCM reaction that had previously been exercised to form this motif.



Finally, we showed how the unorthodox ruthenium-catalyzed *trans*-hydrostannation can be used as a handle for diversity-oriented synthesis. To this end, it proved necessary to develop new conditions that allow the C-Sn bond of alkenylstannanes to be oxidized, fluorinated, methoxycarbonylated or protodestannated under conditions that are sufficiently mild to leave other vulnerable groups untouched. None of these transformations has had a satisfactory solution prior to our work; the generality of the new procedures is currently under investigation.

Future directions: Explore the scope and limitations of the ruthenium catalyzed *trans*-addition reactions and search for alternative and complementary catalyst systems; development of the downstream chemistry of readily available hydrometalated motifs.

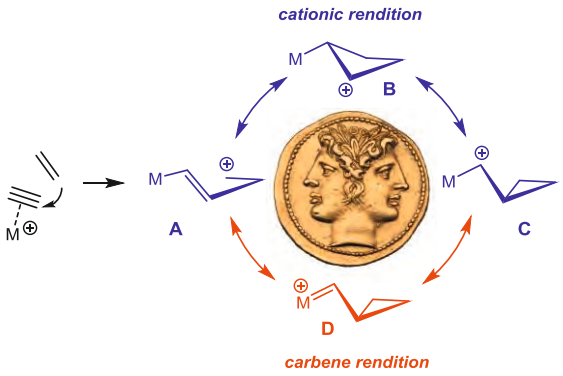
Publications resulting from this research area: 3, 11, 19, 25-28, 36, 45, 46

External funding: Alexander-von-Humboldt Foundation (fellowships to D.-A. Rosca and B. Sundararaju), Fonds der Chemischen Industrie (Kekulé stipend to S. Schaubach), FWF Austria (fellowship to M. Fuchs), Villum Foundation Denmark (fellowship to T. G. Frihed), JSPS (fellowship to K. Michigami).

Collaboration: C. Farès (Mülheim/Ruhr, DE), W. Thiel (Mülheim/Ruhr, DE)

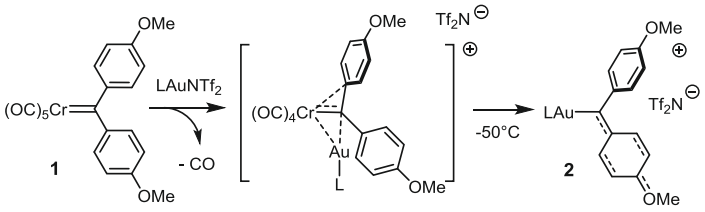
2.4.3 Research Area "Carbene Chemistry and π-Acid Catalysis" (A. Fürstner)

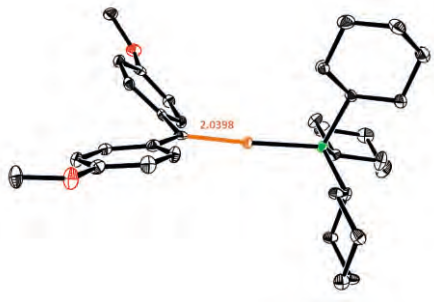
Involved: M. Ilg, L. Mantilli, G. Seidel, C. Werlé



Objective: Guided by our own early mechanistic proposal, we investigate the mode of action of carbophilic catalysts. Other lines of research concern asymmetric gold catalysis and rhodium carbene chemistry.

Results: The intervention of carbene intermediates in platinum or gold catalysis has originally been proposed by our group as early as 1998 and is now largely undisputed. Structure and bonding in these species, however, has been subject to considerable debate because they defied direct inspection. During the report period, we finally managed to isolate and fully characterize the first reactive gold carbene able to cyclopropanate styrene even at –30°C. The structure of complex **2** in the solid state shows that there is only very little back donation of electron density from gold to the carbene center and hence truly modest Au–C double bond character; rather, it is the organic ligand framework that is responsible for stabilizing the species by resonance delocalization of the accumulated positive charge. Following this lead finding, other groups reported related gold carbenes and reached similar conclusions. These data nicely confirm our previous view that such intermediates exhibit significant cationic character. Therefore we strongly recommend not to use the very popular but largely misleading [Au=C] notation whenever referring to distinct intermediates of this type in condensed phase.

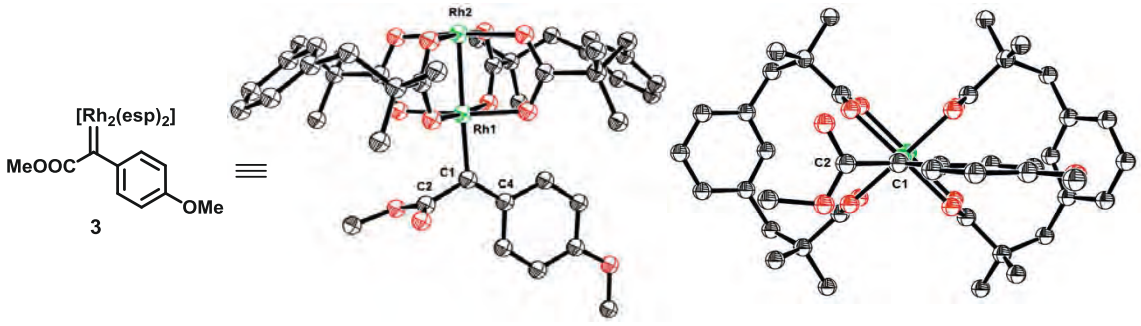




Access to this prototype gold carbene **2** was originally gained by transmetalation of a tailored Fischer chromium

carbene complex **1**. While this approach proved highly effective, it is not overly practical for a more systematic investigation. A much more convenient alternative was found by "transmetalation" of transient dirhodium carbenes with an appropriate $[LAu]^+$ source, which in turn allows readily available diazoalkanes to be used as substrates (that tend to decompose on attempted direct reaction with $[LAu]^+$). This new method furnished a number of additional gold carbenoids differing from **2** in the ancillary ligand and/or the carbene backbone. Several representative examples could be characterized by X-ray diffraction; therefore structural information about this class of reactive intermediates – which was nil prior to our 2014 paper – is now deemed fairly consolidated.

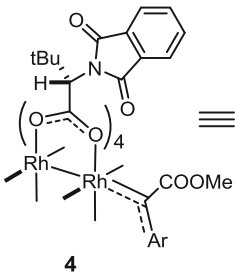
During this study we became aware that structural information about dirhodium carbenes themselves is also largely missing. The only experimental reference point was a singular ^{13}C NMR and EXAFS spectrum reported by Davies, Berry and coworkers in 2013. This situation is more than inappropriate in view of the tremendous importance that rhodium carbenes in general have gained during the last decades, not least in the areas of asymmetric catalysis and C–H activation.



In an attempt to fill this gap, we made massive efforts to isolate representative members of this class of "superelectrophilic" intermediates in pure form. Because of their exceptional sensitivity, the project proved unusually challenging. Major difficulties arose from the fact that even the pure crystalline material decomposes in less than 12 h at –20°C; solute CH_2Cl_2 and toluene are necessary to ensure meta-stability but tend to be highly disordered within the unit cell. Considerable experimentation was necessary to find conditions that allowed crystals of sufficient quality to be grown. These serious issues notwithstanding, we were able to determine the structures of a dozen reactive dirhodium(II) tetracarboxylate and mononuclear half-sandwich Rh(III) carbenes in the solid state.

Our experimental data correct and/or refine previous computational studies and allow the stereochemical course of rhodium catalyzed reactions to be rationalized. They reveal the importance of stereoelectronic rather than steric arguments as the major selectivity-determining factors. The carbene ligand occupies an axial coordination site on the dirhodium cage and the Rh2-Rh1–C1 axis is almost linear. The Rh1–C1 bond distance is substantially longer than that previously computed for various model compounds. This fact suggests that back-donation of electron density from the metal into the carbene center is minute. To compensate, C1 strongly engages with the flanking arene, whereas the electron withdrawing ester group of the donor/acceptor carbene is positioned orthogonal to the carbene lobe to disrupt any destabilizing electronic communication. In all cases investigated, the carbene entity adopts a staggered conformation relative to the O–Rh–O unit, whereas previous computations had predicted an eclipsing orientation.

An extension of this study to dirhodium carbenes endowed with chiral ligand sets proved unexpectedly difficult. It was only after considerable experimentation that two representative chiral complexes were obtained in crystalline form. They carry the widely used *N*-phthalimide protected amino acid derivatives (PTTL) as auxiliary ligands originally introduced by Hashimoto and coworkers. The chiral binding pocket is primarily defined by the conformational preferences of the *N*-phthaloyl protected amino acid ligands and reinforced by a network of interligand interactions. NMR data confirm that the structure determined by X-ray diffraction persists in solution and provide additional information about the dynamics of this species. Our experimental results resolve the controversial issue as to which conformation of the chiral binding site is responsible for asymmetric induction. For the very first time, we could interpret the stereochemical course of an asymmetric cyclopropanation solely on the basis of experimental data without need to make any assumptions about the chiral ligand environment.



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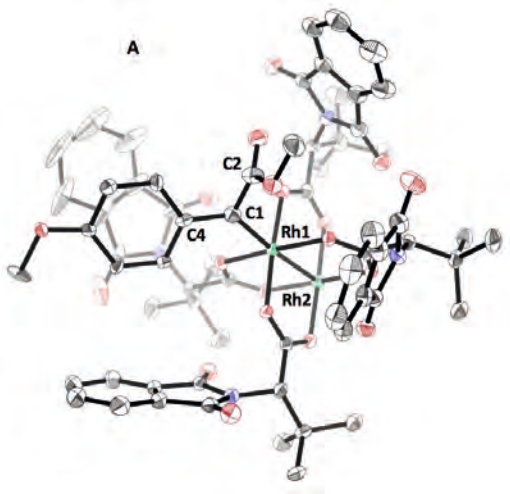
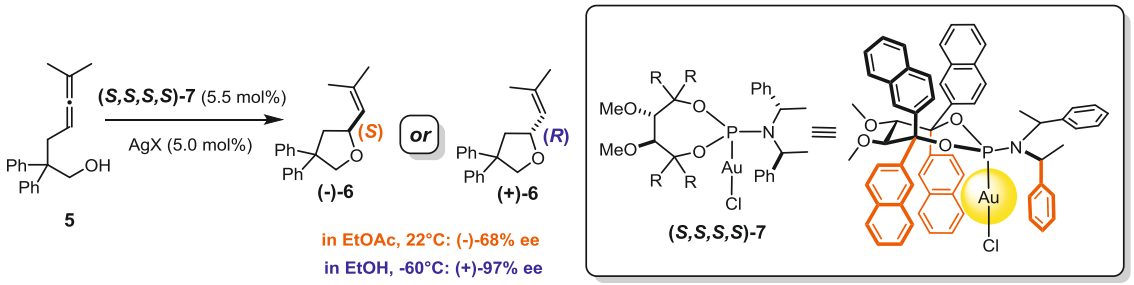


The last project to be mentioned in this chapter refers to the perplexing observation that the cyclization of the hydroxy-allene **5** to the tetrahydrofuran **6** catalyzed by the chiral gold complex **7**, after ionization with an appropriate silver salt AgX, is one of the most striking cases of enantioinversion known to date. The sense of induction can be switched from (*S*) to (*R*) solely by changing either the solvent or the temperature or the nature of the counterion X.



The governing TADDOL-related phosphoramidites featuring an acyclic (rather than acetal) backbone had been introduced as powerful ligand set for asymmetric gold catalysis by our group a few years ago. A combined experimental/computational study showed that the major reason for the stereoinversion phenomenon is likely found in the bias of the organogold intermediates to undergo assisted proto-deauration. Such assistance can be provided either by a protic solvent, by a reasonably coordinating counterion, or even by a second substrate molecule itself; in this way, the reaction free energy profile gains a strong entropic component that ultimately dictates the stereochemical course. At the meta-level, our analysis shows that particular attention must be paid to the entropic changes along a reaction coordinate that are often disregarded in discussions of asymmetric catalysis in general.

Future directions: Refine our mechanistic understanding of π-acid catalysis, calibrate mechanistic studies by the isolation of pertinent reactive intermediates, expand the scope of asymmetric gold catalysis, and scrutinize the methodology by selected applications

Publications resulting from this research area: 1, 3, 5, 8, 12, 13, 22, 23, 30, 31, 33, 38, 41, 42

External funding: Swiss National Science Foundation (fellowship to L. Mantilli), Fonds der Chemischen Industrie

Cooperations: C. Farès (Mülheim, DE), R. Goddard (Mülheim, DE), W. Thiel (Mülheim, DE)

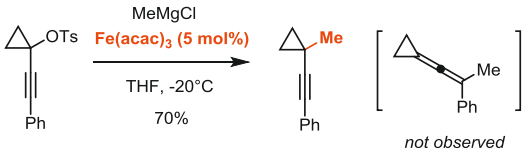
2.4.4 Research Area "Iron Catalysis" (A. Fürstner)

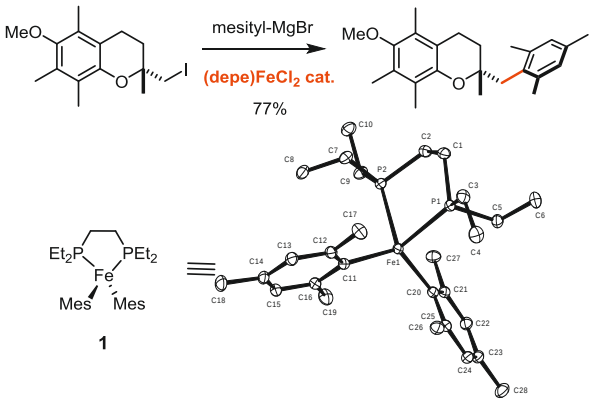
Involved: A. Casitas, P.-G. Echeverria, H. Krause, K. Lehr, S. Schulthoff, C.-L. Sun, D. J. Tindall, Y. Ueda, C.-X. Zhuo

Objectives: Centered in the middle of the d-block and able to support formal oxidation states ranging from –II to +VI, iron hold the promise of being able to encompass organic synthesis at large. Catalysts based on this metal are expected to serve reductive as well as oxidative regimes, can emulate "noble tasks", but are also able to adopt "early" transition metal character. Our group strives to discover useful transformations and to investigate their mechanistic background, most notably in the areas of cross coupling, cycloaddition and cycloisomerization chemistry.

Results: Homogeneous iron catalysis has been a topic of considerable interest for the group since we reported the first successful examples to alkyl-aryl cross coupling shortly after the turn of the millennium. These studies were predicated on the conception that iron is potentially capable of serving as a cheap, benign and readily available substitute for noble metal catalysts. In parallel, we try to harness the peculiarities of this element, which is located in the center of the d-block and hence endowed with "early" as well as "late" transition metal character.

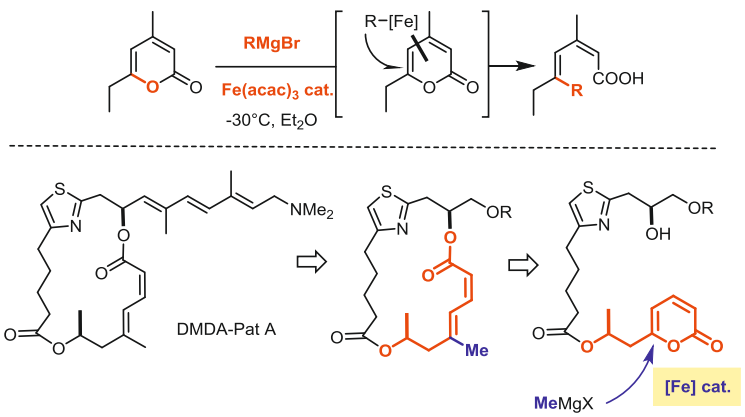
Notable progress in the cross coupling arena relates to the successful coupling of 1-alkynylcyclopropyl tosylates with alkyl-magnesium halides in the presence of catalytic [Fe(acac)$_3$] under net propargylic substitution; allene formation, which is the prevalent reactivity mode of propargylic substrates otherwise, is insignificant. (1-Alkylcyclopropyl)ethynyl groups, as readily accessible by this new method, are present in a number of drug candidates and crop protection agents. To the best of our knowledge, this transformation represents the first successful iron catalyzed cross coupling of a *tert*-alkyl electrophile.



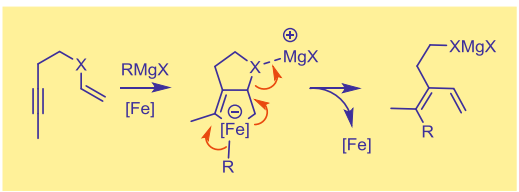


Another largely unmet chemical need concerns the coupling of sterically hindered Grignard reagents which often fail and/or lead to competing homo-dimerization. We found that

commercially available bis(diethyl-phosphino)ethane (depe) is an adequate ancillary ligand for such purposes. This chelating bis-phosphine is slim enough not to interfere with the loading of the iron center even by *ortho,ortho*-disubstituted arylmagnesium halides, yet capable of preventing premature reductive coupling of the resulting organoiron complex [(depe)Fe(mesityl)$_2$] (**1**); this species was isolated and characterized by X-ray diffraction; it proved competent in a number of stoichiometric as well as catalytic control experiments. The method is compatible with various polar functional groups as well as substrates containing β-heteroatom substituents; it allows even encumbered neopentylic electrophiles to be arylated with donors as bulky as mesitylmagnesium bromide, which had not been possible before.

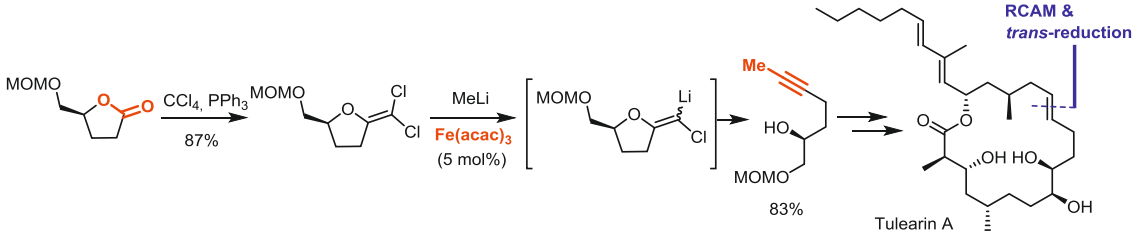


In late 2013 we described a formal ring opening/cross coupling process that epitomizes a largely underrepresented reaction mode. 2-Pyrones react with Grignard reagents in the presence of Fe(acac)$_3$ to give diene carboxylic acids after work up. In all cases investigated, the reaction was stereospecific in that the incoming nucleophile replaces the lactone leaving group with retention of configuration. Therefore this unorthodox transformation formally represents a “cross coupling” process, although it likely proceeds via 1,6-addition followed by electrocyclic ring opening. It served as the key step of a concise synthesis of desmethyl-desamino-pateamine A (DMDA-Pat A), a highly potent translation inhibitor endowed with remarkable *in vivo* activity against two different melanoma mouse models. Our novel entry is significantly more productive than the literature route; it capitalizes on the masking of the signature *Z,E*-configured dienoate subunit as a 2-pyrone ring, which was crafted by a gold catalyzed cyclization also developed in our laboratory (see the following chapter of this report). While the robustness of the heterocycle greatly facilitated the entire assembly stage, the highly isomerization-prone seco-*Z,E*-dienoic acid could be unlocked in due time for macrolactonization by iron catalyzed ring opening/cross coupling.

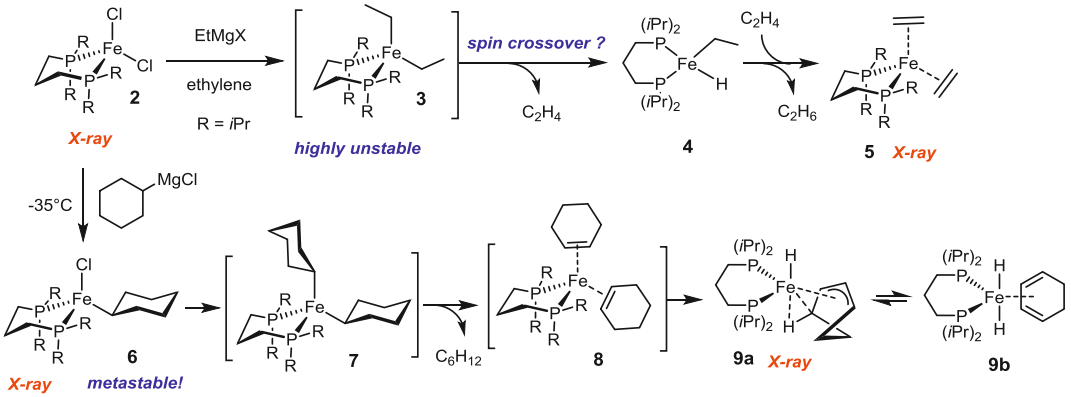


Treatment of readily available enynes with alkyl-Grignard reagents in the presence of

catalytic amounts of $Fe(acac)_3$ engenders a reaction cascade that results in the net formation of two new C–C bonds while a C–X entity in the substrate backbone is broken. Not only does this manifold lend itself to the extrusion of heteroelements (X = O, NR), but it can even be used for the cleavage of activated C–C bonds. The reaction likely proceeds via metallacyclic intermediates, the iron center of which gains ate-character before reductive elimination does occur. The overall transformation represents a previously unknown merger of cycloisomerization and cross coupling chemistry and provides ready access to functionalized 1,3-dienes comprising a stereodefined tetrasubstituted alkene unit, which are difficult to make by conventional means.

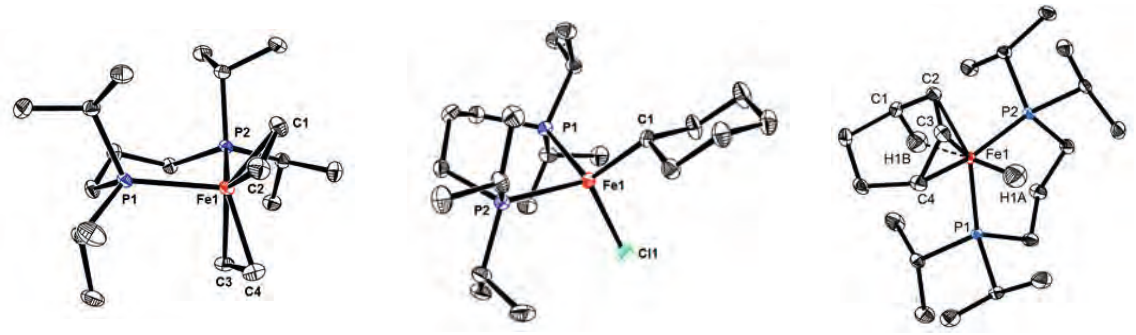


As briefly mentioned in the previous report, a high-yielding route to non-terminal alkynes starting from lactones was developed. Formation of the corresponding *gem*-dichloroalkenes followed by treatment with RLi generates lithium carbenoids that are sufficiently electrophilic to intercept an additional equivalent of RLi prior to collapse and release of the product. Although the reaction proceeds uncatalyzed in Et_2O or THF, it is best performed in the presence of either catalytic $Fe(acac)_3$ or $Cu(acac)_2$. Under these conditions, the method is broadly applicable and preserves chiral centers at the α-position; it has already powered our total syntheses of tulearin A and C, brefeldin A, muscenone, kendomycin and 5,6-dihydrocineromycin B.



Finally, the report period has seen extensive mechanistic investigations into organoiron catalysis. In a first foray, we studied the alkylation of the iron complex **2** (and related species) with Grignard reagents containing β-hydrogen atoms. Although seemingly trivial, this process is of considerable relevance for the understanding of C–H activation

as well as C–C bond formation mediated by low-valent iron species. Specifically, reaction of **2** with EtMgBr under an ethylene atmosphere affords the Fe(0)-complex **5** almost quantitatively, which is an active precatalyst for prototype [2+2+2] cycloaddition reactions and a valuable probe for mechanistic studies.



On the other hand, alkylation of **2** with 1 equivalent of cyclohexylmagnesium bromide furnished the unique iron alkyl species **6** with a 14-electron count that contains no less than four β-H atoms but is meta-stable against β-hydride elimination. In contrast, exhaustive alkylation of **2** with cyclohexylmagnesium bromide in the presence of cyclohexene triggers two consecutive C–H activation reactions mediated by a single iron center. The resulting complex has a diene-dihydride character in solution (**9b**), whereas its structure in the solid state is more consistent with an η^3-allyl iron hydride rendition featuring an additional agostic interaction (**9a**). These well-defined species are the starting point for ongoing investigations into low-valent iron complexes of relevance for cross coupling, CH-activation and cycloaddition chemistry.

Future directions: Search for unconventional and useful transformations catalyzed by iron complexes, and investigations into their mechanistic background.

Publications resulting from this research area: 3, 5, 15, 18, 25, 35, 37, 40, 43, 47

External funding: Alexander-von-Humboldt Foundation (fellowships to C.-L. Sun and C.-X. Zhuo), Fundación Ramón Areces (fellowship to A. Casitas), Kyoto University Education Program (scholarship to Y. Ueda)

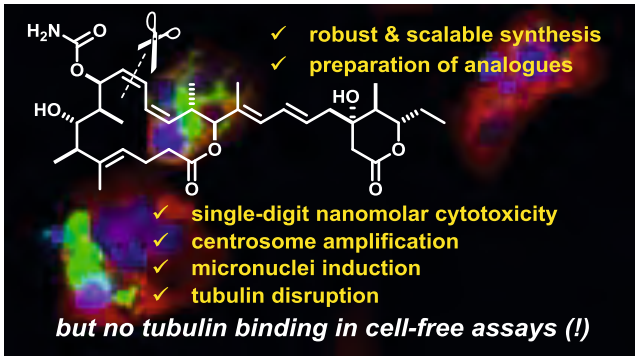
Cooperations: E. Bill (MPI for Chemical Energy Conversion, Mülheim, DE)

2.4.5 Research Area "Catalysis Based Syntheses and Evaluation of Bioactive Natural Products" (A. Fürstner)

Involved: A. Ahlers, T. Fukuda, T. de Haro, L. Hoffmeister, K. Jouvin, D. Mailhol, P. Persich, G. Pototschnig, J. Preindl, S. Schulthoff, J. Willwacher, G. Valot

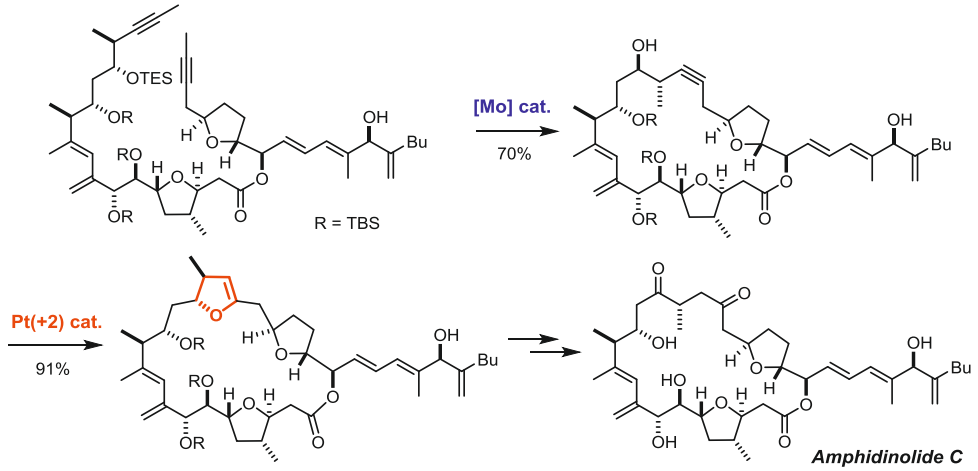
Objectives: We pursue the synthesis of complex natural products by catalysis-based routes, evaluate their biochemical and biological properties in cooperation with external partners, and investigate structure/activity relationships by molecular editing.

Results: In addition to the total syntheses mentioned in the previous sections, further projects were pursued that were meant to scrutinize the methodology developed in the group in complex settings; in most cases, questions concerning the biochemical and biological properties of the target compounds are of equal importance. This aspect is apparent in a rather comprehensive project aiming at the synthesis, molecular editing and biological assessment of the marine cytotoxin leiodermatolide. In the first foray, we managed to elucidate the previously unknown stereostructure of this demanding target by preparation of two possible diastereoisomers which the isolation team had proposed but was unable to distinguish. This synthesis illustrates that ring closing alkyne metathesis (RCAM) is particularly well-suited for applications to polyunsaturated targets where olefin metathesis (RCM) often finds its limits; a *Z*,*Z*-diene unit, as present in leiodermatolide, is certainly beyond reach of contemporary RCM catalysts.



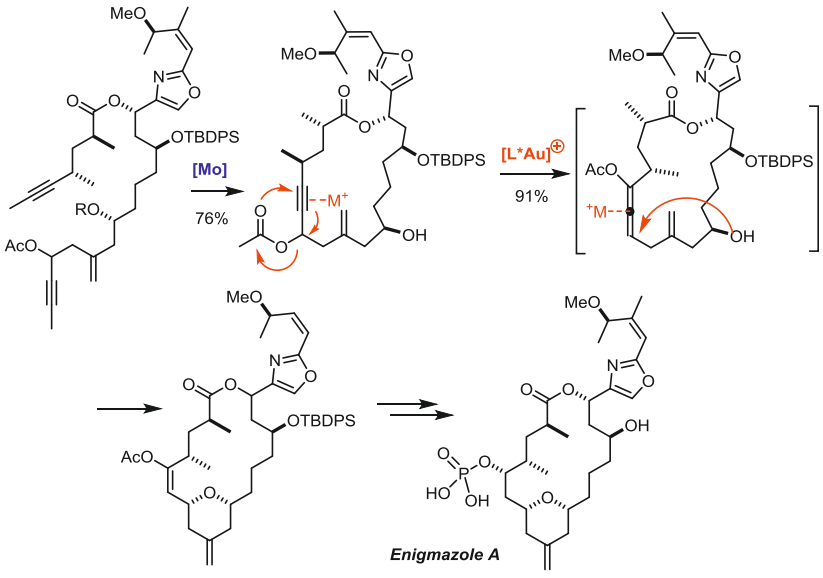
With the target unambiguously defined, our mission changed to secure a meaningful supply of this exceedingly rare natural product derived from a deep-sea sponge. To this end, a scalable route was developed in the second phase of the project that nicely showcased the scalability of alkyne metathesis; moreover, a Binol-catalyzed allylation of a highly enolizable β-keto-lactone allowed the conspicuous axial carbon branch on the δ-lactone ring to be set in a practical manner. Deliberate digression from this robust blueprint brought a series of non-natural analogues into reach for the study of the lead qualities of this compound. Leiodermatolide was shown to be a highly potent cytotoxin in human tumor cell proliferation assays, distinguished by GI_{50} values in the ≤ 3 nM range even

for cell lines expressing the Pgp efflux transporter. It causes mitotic arrest, micronucleus induction, centrosome amplification and tubulin disruption, even though it does not bind tubulin itself in cell-free assays. This paradoxical profile has little – if any – precedent: indirect evidence points at centrosome declustering as a possible mode of action, which holds promise of being inherently selective for malignant over healthy human tissue.

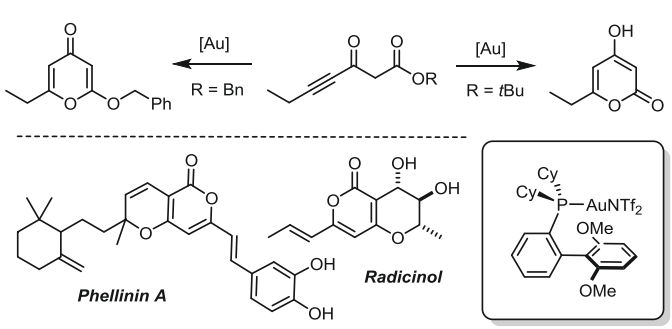


As part of our long-term commitment to the amphidinolides, a family of exceptionally potent secondary metabolites derived from marine dinoflagellates, we were able to finish the total synthesis of amphidinolide C as one of the most cytotoxic and – at the same time – structurally most complex members of this series. Our approach hinged upon alkyne metathesis with the in-house molybdenum alkylidynes followed by platinum catalyzed transannular hydroalkoxylation; notably, this simple carbophilic catalyst nicely selected for the triple bond over no less than five alkenes. This delicate strategic maneuver at a very late stage of the synthesis is deemed one of the most challenging applications of π-acid catalysis known to date.

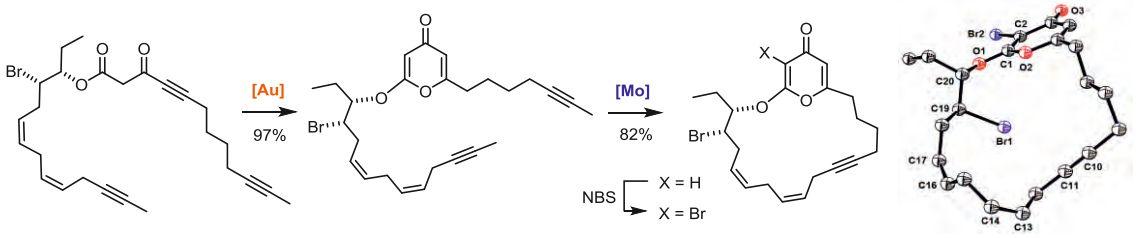
Of arguably similar complexity is the key reaction cascade en route to the phosphorylated macrolide enigmazole A. It commenced with a gold catalyzed [3,3]-sigmatropic rearrangement that walks a propargyl

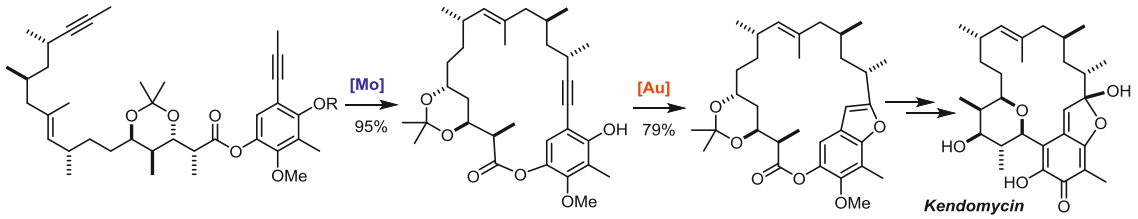


acetate along the periphery of the macrocyclic scaffold forged by RCAM; the resulting transient allenyl acetate immediately succumbs to a regio- and stereoselective transannular hydroalkoxylation. This transformation mandated the use of a chiral gold catalyst to override the inherent substrate bias. Another noteworthy step of this synthesis is the preparation of the oxazole building block by palladium catalyzed CH-activation.

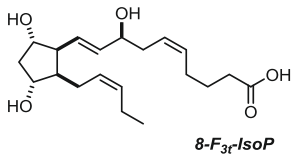


We developed a new entry into pyrones derivatives based on the cyclization of 3-oxo-5-alkynoic acid esters upon treatment with a carbophilic catalyst. Depending on the choice of the ester group, 2-pyrones or 4-pyrones can be selectively prepared. The reliability of the method was first proven by applications to various members of the radicinol and phellinin families. Subsequently, it stood a truly challenging test during the total synthesis of an unnamed 4-pyrone of algal origin, which also allowed us to determine the previously unknown stereostructure of this remarkable natural product: it comprises a rare brominated 4-pyrone nucleus linked via a ketene-acetal to a polyunsaturated macrocyclic scaffold comprising a homoallylic bromide entity. Our synthesis was based on the elaboration and selective functionalization of an exceptionally fragile cyclization precursor endowed with no less than six (skipped) sites of unsaturation, including the enolized oxo-alkanoate function. Yet, the formation of the 2-alkoxy-4-pyrone ring by a novel gold catalyzed transformation worked nicely, engaging only the acetylenic β-ketoester substructure while leaving all other π-bonds untouched. The synthesis was completed by RCAM to forge the signature cycloalkyne motif, followed by selective bromination of the ketene-acetal site without touching the skipped diene-yne substructure resident within the macrocyclic tether.





A total synthesis of kendomycin provides yet another illustration of the power of alkyne metathesis in concord with π-acid catalysis. The intriguing *ansa*-architecture of this target had provided inspiration for many groups in the past; our synthesis is conceptually different from the literature precedent in that it disconnects the macrocyclic frame of kendomycin at the rather sensitive heterocyclic *para*-quinonemethide/lactol substructure. In the forward sense, this motif was formed by RCAM followed by a gold-catalyzed benzofuran synthesis/oxidation sequence of the type previously developed in our laboratory. This foray proved rewarding in that it opened the arguably most productive entry into this strongly cytotoxic agent.



Finally, studies on isoprostanoids such as 8-F_{3t}-IsoP need to be briefly mentioned. These scarce compounds are non-enzymatic metabolites of polyunsaturated fatty acids and, as such, stress markers of high medicinal interest. In order to enable detailed preclinical and clinical investigations, authentic samples were prepared by a flexible strategy that allows for considerable structural variation.

Future directions: Identify, synthesize and evaluate (hopefully) relevant targets; prepare functional analogues by diverted total synthesis; sustain the network of collaborations with academic and industrial partners to ensure professional testing

Publications resulting from this research area: 1, 3, 5-8, 10, 17, 19-22, 25, 27, 29, 30, 32-34, 36, 38, 39, 43-46

External funding: Fonds der Chemischen Industrie (fellowship to J. Willwacher), FWF Austria (fellowship to G. Potoschnig), JSPS (fellowship to T. Fukuda), Swiss National Science Foundation (fellowship to T. de Haro)

Cooperations: Pfizer Oncology and Medicinal Chemistry (Groton, US); J.-M. Galano (Montpellier, FR)

2.4.6 Research Area "α-Cationic Phosphines" (M. Alcarazo)

Involved: H. Tinnermann, E. González, J. Dube, S. Holle, E. Haldón, L. Gu, P. Linowski, A. Zannardi, L. Nicholls

Objective: Synthesis of structurally differentiated α-cationic phosphines/arsines and evaluation of their potential as ancillary ligands in catalysis.

Introduction: The world of ligands is dominated by anionic and neutral species. This is not surprising considering that they have been designed to coordinate metals, which usually behave as Lewis acids. Cationic ligands are exceptions and when they are used, the positive charged group is mostly located at a remote position from the donating atom. However, beneficial effects can be expected from the incorporation of positive charges in close proximity to the donor position. The strong –I inductive effect of positive charges reduces the σ-donor abilities of α-cationic phosphines. Simultaneously, the new very low lying σ*(P-C^+) orbitals increase their π-acceptor character and, as a consequence, the global electron donation of these ligands to the metal is quite low.

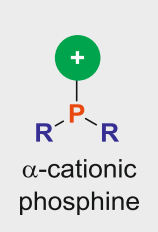
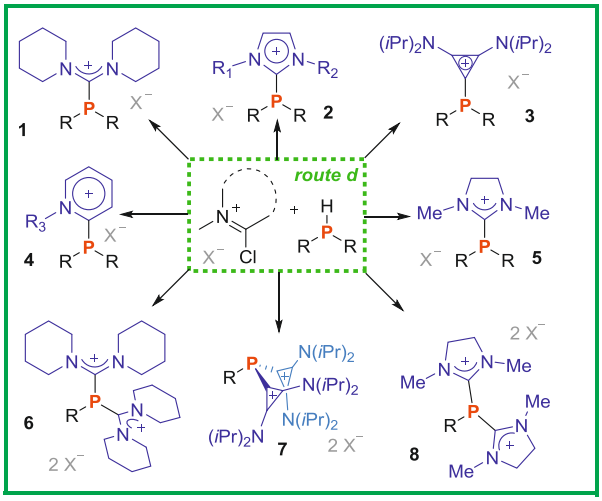


Fig. 1

This may have interesting consequences in catalysis: if the rate-determining step of a catalytic cycle is facilitated by an increase of the Lewis acidity at the metal center, an acceleration of the process is expected by the use of such ancillary ligands. Interestingly, this situation is found more frequently than one might think: many common elementary steps involved in catalytic cycles, such as reductive eliminations, coordination of substrates to metals, or the attack of nucleophiles to coordinated substrates, belong to this category and are often fostered by electron poor metal centers.

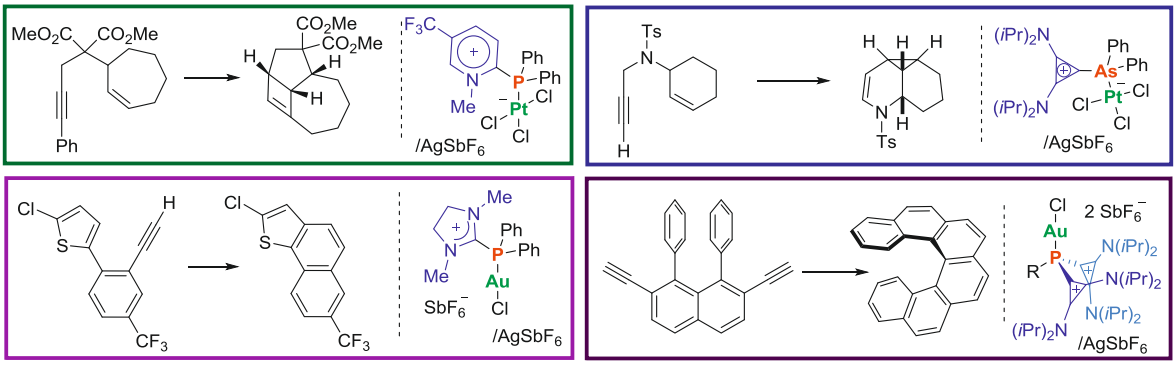
Results: We have implemented a general synthetic method for the synthesis of α-cationic phosphines based on the reaction of secondary phosphines and Vilsmeier-type salts. The availability of both starting materials and the high yields of the condensation reactions make this route very reliable even on multigram scale.
Since then, the repertoire of α-cationic phosphines incorporated to the ligand tool box has been truly expanded, and it now includes cyclopropenio-, imidazolinio-, pyridinio-, and formamidiniophosphines, **1**-**8** respectively (Scheme 1). Moreover, α-dicationic phosphines and α-cationic arsines can be prepared after only small variations of this synthetic methodology.



Scheme 1. Synthetic route for the preparation of mono- and dicationic phosphines.

The structural analysis of compounds **1-5** reveals two parameters that are crucial in understanding their coordination properties. The central phosphorus atom of **1-5** displays a pyramidal environment (sum of angles around P1: 300-318°, depending on the steric demand of the substituents), while all P-C(+) bonds lengths are, within experimental error, very similar to those of the other two P-C(Ph) bonds. These observations suggest that the non-shared electron pair is retained at phosphorus. For this reason the coordination chemistry of cations **1-5** seems to be as rich as that of traditional phosphines; up to now the formation of complexes with Au, Ag, Cu, Pt, Pd, Ni, Ir and Rh have been described. On the other hand, dicationic phosphines are less prone to coordinate metals. Up to now, we have only been successful on the preparation of Pt(II), and Au(I) derivatives of **7**.

Illustrative examples of the use of the newly prepared cationic phosphines in π-acid catalysis are depicted in Scheme 2. In these cyclisation processes the rate determining step is usually the attack of the nucleophile to the activated alkyne; therefore, the employment of cationic ligands that augment the Lewis acidity at the metal center proves beneficial. The reaction rates observed with cationic ancillary phosphines are between 20 and 500 times faster than those measured when Ph_3P-derived catalysts are used under otherwise identical conditions.



Scheme 2. Selected examples of the use of α-cationic phosphines in π-acid catalysis.

Future directions: We anticipate that the intensive acceleration effects observed in π-acid catalysis by the use of α-cationic phosphines might have tremendous implications in the area of asymmetric catalysis, where catalysts able to work at lower temperatures are usually required to obtain good enantiomeric excess. The development of chiral versions of the ligands prepared is one of our current research topics.

Publications resulting from this research area: 49, 51, 53-55, 57, 59, 60

External funding: Deutsche Forschungsgemeinschaft (projects AL1348 4-2 and AL1348 5-1); NSERC Canada (stipend to J. Dube); China Scholarship Council (stipend to L. Gu).

Cooperations: W. Thiel (Mülheim/Ruhr, DE)

2.4.7 Research Area "Development of New Electrophilic Transfer Reagents" (M. Alcarazo)

Involved: G. Talavera, J. Pena, B. Waldecker, A. Barrado, Y. Zhang, A. Zielinski

Introduction: The unique ability of hypervalent iodine compounds to act as electrophilic group-transfer reagents has been extensively exploited during the last several years in a variety of synthetically useful transformations. These include trifluoromethylation, alkynylation, arylation, amination, halogenation and cyanation of a wide variety of electron-rich substrates under mild conditions. Considering this tremendous synthetic utility, it is surprising that other structurally related scaffolds, yet not based in iodine, have not been evaluated for similar purposes. We recently envisaged that imidazolium sulfuranes **A,** that are isolobal to I(III) species **B** and exhibit the key three-center four-electron bond motif, might be considered alternative platforms for the development of new electrophilic group-transfer reagents (Figure 1).

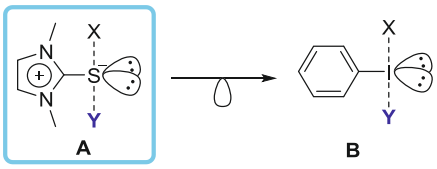
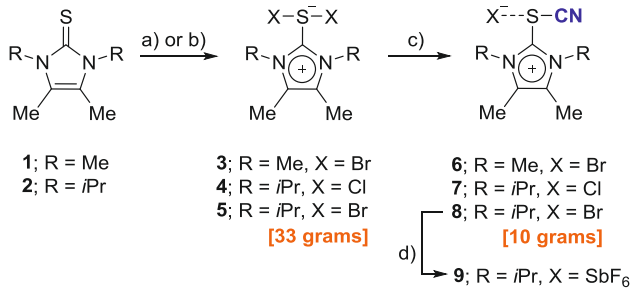


Fig. 1. Isolobal relationship between I(III) species and sulfuranes.

Objective: The implementation of this working hypothesis to the specific design of new sulfur-based electrophilic transfer reagents. Specifically, we have already developed cyanation, alkynylation and thioalkynylation reagents.

Results: We submitted thioureas **1** and **2** to previously described halogenation conditions, and obtained the corresponding hypervalent sulfur compounds **3-5** as bright yellow to orange solids in high yields and analytic purity (Scheme 1). Subsequent addition of one equivalent of Me_3SiCN caused the immediate disappearance of the color and formation of the desired imidazolium thiocyanates **6-8**. Compounds **6-8** were isolated as air stable pale yellow solids in excellent yields, and can be stored at room temperature for months without evident decomposition. Interestingly, compounds **6-9** depicted excellent ability to transfer



Scheme 1. Synthesis of 2-thiocyanoimidazolium salts.

the CN group to organic nucleophiles such as amines, sulfides, enolates, enamines, activated methylenes and electron rich aromatic compounds (Figure 2).

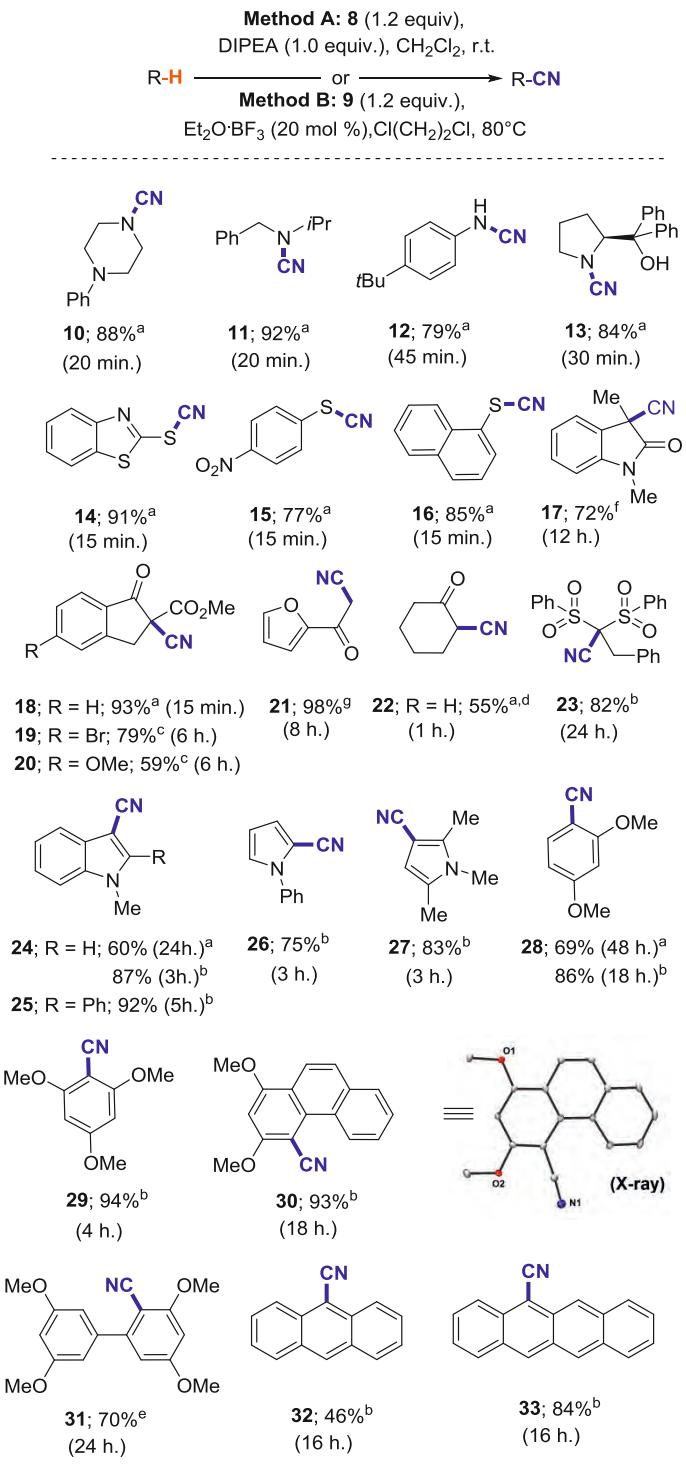
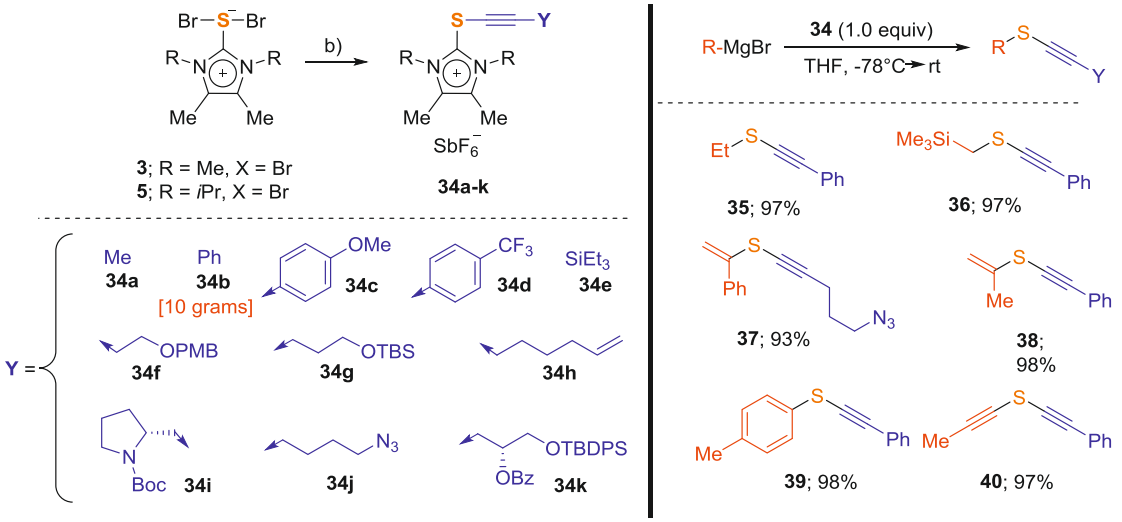


Fig. 2. Substrate scope of the electrophilic cyanation using 2-thiocyanoimidazolium salts **6-9**.

Encouraged by this discovery we set up to explore whether alkynylthioimidazolium salts **34a-k** could also participate in this transformation. Thus, a series of these compounds bearing different functionalizations on the alkyne rests was prepared by reaction of **5** with the desired alkynylzinc bromide. However, already during preliminary investigations, we came across an unexpected finding: simple commercially available Grignards regioselectively attack these salts *at the sulfur atom* affording the corresponding alkynylthioethers in excellent yields (Scheme 2). This unique behavior makes alkynylthioimidazolium salts convenient synthetic equivalents of a formal $[R-C\equiv C-S]^+$ cation.

Alkyl-, aryl-, alkenyl- and even alkynyl-Grignard reagents were found to smoothly react under optimized conditions with salts **34a-k**, providing a library of alkynylsulfides **35-40** in good to excellent yields. Specifically, the robustness and applicability of this transformation is highlighted by the successful preparation of

fairly hindered thioethers, vinylthioacetylenes, and a series of asymmetric bis(alkynyl)thioacetylenes that are non-obvious to obtain through other routes. Note however, that the preparative significance of this method is limited at this stage by the use of Grignard reagents.



Scheme 2. Synthesis and reactivity of 2-alkynylthioimidazolium salts.

Future directions: The potential of imidazolium sulfuranes to become platforms for the development of new reagents able to promote the umpolung of synthetically useful organic groups has been demonstrated. Ongoing studies in our laboratory intend to demonstrate the generality of the concept, and to further evaluate the synthetic utility of the new reagents.

Publications resulting from this research area: 58

External funding: Deutsche Forschungsgemeinschaft (project AL1348 7-1); Regional Government of the Basque Country, Spain (stipend to G. Talavera).

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Alcarazo group

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Publications by Other Members of the Department

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(62) **Weber**, D.; Gagné, M. R. In *Homogeneous Gold Catalysis*; Slaughter, L. M., Ed.; *Top. Current Chem.*; Springer International Publishing, 2015; Vol. 357; pp 167-211.

2.5 Department of Theory

Director:

Walter Thiel (born 1949)

Further group leaders:

Mario Barbatti (born 1971)
Left the Institute in 2015

Elsa Sánchez-García (born 1976)

Matthias Heyden (born 1981)

Michael Roemelt (born 1982)
Joined the Institute in 2015

Curriculum Vitae: Walter Thiel

1949	Born in Treysa, Germany
1966-1971	Chemistry studies at Universität Marburg
1971-1973	Doctoral studies at Universität Marburg, with A. Schweig
1973-1975	Postdoctoral fellow at the University of Texas at Austin, with M. J. S. Dewar
1975-1982	Research scientist at Universität Marburg
1981	Habilitation for Theoretical Chemistry
1983-1992	Associate Professor of Theoretical Chemistry at Universität Wuppertal
1987	Guest Professor at the University of California at Berkeley
1992-1999	Full Professor of Chemistry at Universität Zürich
1999	Director at the Max-Planck-Institut für Kohlenforschung in Mülheim/Ruhr
2001	Honorary Professor at Universität Düsseldorf

Awards and Honors

1969-1974	Studienstiftung des deutschen Volkes
1975-1977	Liebig Fellowship, Verband der Chemischen Industrie
1982	Heisenberg Fellowship, Deutsche Forschungsgemeinschaft
1988	Förderpreis, Alfried-Krupp Stiftung
1991	Member, European Academy of Sciences and Arts
2002	Schrödinger Medal, World Association of Theoretical Chemists
2007	Member, Deutsche Akademie der Naturforscher Leopoldina
2007	Member, International Academy of Quantum Molecular Sciences
2008	Member, Nordrhein-Westfälische Akademie der Wissenschaften
2009	Festschrift, Journal of Physical Chemistry A 2009, 113 (43), 11455-12044
2012	Liebig Medal, German Chemical Society
2014	ERC Advanced Grant, European Research Council
2014	Robert Bunsen Lecture, Deutsche Bunsengesellschaft

Special Activities

1986-1992	Member of the Board, Institut für Angewandte Informatik, Wuppertal
1990-1992	Speaker, DFG-Forschergruppe: Reaktive Moleküle
1997-2014	Advisory Editor, Theoretical Chemistry Accounts
1998-	Advisory Editor, Journal of Computational Chemistry
2000-2008	Reviewer (Fachkollegiat), Deutsche Forschungsgemeinschaft

2000-2006	Member of the Board (Lenkungsausschuss), Bavarian Supercomputer Center (Höchstleistungsrechenzentrum Bayern)
2001-2005	Chairman, Arbeitsgemeinschaft Theoretische Chemie
2002-2008	Section Editor, Encyclopedia of Computational Chemistry
2004-2007	Member, Ständiger Ausschuss der Bunsengesellschaft
2004-2017	Member of the Scientific Advisory Board, Lise Meitner Minerva Center for Quantum Chemistry, Jerusalem/Haifa, Israel
2006-2008	Managing Director, Max-Planck-Institut für Kohlenforschung
2006-2012	Chairman, BAR Committee of the Max Planck Society
2006-2013	Member of the Kuratorium, Angewandte Chemie
2008-	Associate Editor, WIRES: Computational Molecular Sciences
2009-	Member of the International Advisory Board, State Key Laboratory of Physical Chemistry (PCOSS), Xiamen, China
2010	Chairman, Gordon Conference on Computational Chemistry
2011-2014	Member of the International Advisory Board, Institute of Organic Chemistry and Biochemistry, Prague, Czech Republic
2011-2017	President, World Association of Theoretical and Computational Chemists
2012-2013	Editorial Advisory Board, ACS Catalysis
2012-2014	Editorial Advisory Board, Accounts of Chemical Research
2012-2015	Member of the Board of Governors, German Chemical Society
2013-	Member of the Scientific Advisory Board, Institute of Chemical Research of Catalonia, Tarragona, Spain
2015	Managing Director, Max-Planck-Institut für Kohlenforschung

Research in the Department of Theory

In the reporting period, the Department of Theory comprised the research group of Prof. Walter Thiel and up to four junior groups headed by PD Dr. Mario Barbatti, Dr. Elsa Sánchez-García, Dr. Matthias Heyden, and Dr. Michael Roemelt.

The central research objectives in the Department are theoretical developments to extend the scope of computational methodology, and applications to study problems of current chemical interest by computation. Such applications are mostly conducted in close cooperation with experimental partners.

In the group of Prof. Thiel, the main field of research is quantum chemistry. Methodological developments and chemical applications are considered to be of equal importance. The research interests range from accurate and almost quantitative calculations on small molecules to the approximate modeling of very large molecules. The activities of the group cover ab initio methods (e.g., coupled cluster approaches), density functional theory (DFT), semiempirical methods (orthogonalization models, OMx), and combined quantum mechanical/molecular mechanical methods (QM/MM). Applications in these four areas mainly focus on the vibration-rotation and electronic spectroscopy of small molecules, catalytic reactions of transition metal compounds, electronically excited states in large molecules, and reaction mechanisms in enzymes.

The group of Dr. Barbatti uses ab initio and density functional methods to study photoinduced processes in organic molecules. One major aim is to improve excited-state simulation methods by implementing new algorithms in the Newton-X code. Applications include nonadiabatic dynamics simulations of ultrafast excited-state relaxation processes in biologically relevant molecules and in photovoltaics.

The research in the group of Dr. Sánchez-García focuses on molecular interactions in organic and biological systems, on their relevance in the realm of chemical and biochemical reactivity, and on the development and application of multi-scale modeling approaches. Current research topics include protein-ligand and protein-protein interactions, computational mutagenesis, and solvent effects on reactivity.

The group of Dr. Heyden uses classical molecular dynamics methods to investigate biomolecular solvation phenomena. The group develops novel simulation and analysis procedures to study microscopic contributions to the solvation free energy, with a

partitioning into local enthalpy and entropy terms. Another aim is to improve implicit solvent simulations of concentrated biomolecular solutions on the meso-scale.

The group of Dr. Roemelt aims at the development of highly accurate ab initio quantum-chemical methods for complex molecular systems, with focus on the density matrix renormalization group (DMRG) approach. Targeted are extensions to the DMRG ansatz that improve its accuracy and allow the calculation of magnetic properties. DMRG applications address the properties of transition metal compounds.

Several cooperations between the Department of Theory and the experimental groups in the Institute have been established over the past years. There have been major collaborative projects on transition-metal catalysis (Fürstner, Alcarazo, Maulide, Klussmann), organocatalysis (List), and cellulose depolymerization (Schüth). Several groups of the Department (Thiel, Sánchez-García, Heyden) enjoy close cooperations with experimental partners in the RESOLV Cluster of Excellence on solvation science.

More detailed information on the research areas of the Department is available in the following eight individual reports and in the scientific papers published in 2014-2016. For the sake of brevity, some of these papers have not been discussed in the individual reports and should therefore be consulted directly, if necessary.

The tenure of the Director of the Department, Prof. Thiel, will end in March 2017. As an Emeritus, he will continue to do research in the framework of an ERC Advanced Grant (2014-2018), which targets the development of improved semiempirical methods with orthogonalization and dispersion corrections, as well as the application of these methods, for example, in excited-state dynamics simulations. Among the group leaders, Dr. Barbatti has left the Institute in 2015 to take up a professorship at the Université Aix-Marseille. Dr. Sánchez-García has been offered a professorship (W2) in computational biology at the University Duisburg-Essen (UDE) and is expected to move to UDE in early 2017. Dr. Heyden has been selected as junior group leader in a thematically open RESOLV competition and is hosted by our Institute during the term of his appointment (currently 2014-2017). In recognition of his outstanding Ph.D. thesis, Dr. Roemelt has been awarded the leadership of an Otto Hahn group by the Max Planck Society for the period 2015-2017.

The Institute has selected Prof. Frank Neese as next Director of the Department of Theory. Assuming a smooth appointment process, he can start in April 2017.

2.5.1 Research Area "Ab Initio Methods" (W. Thiel)

Involved: A. Altun, J. Breidung, G. Cui, A. Nikiforov, A. Owens

Objective: Vibration-rotation and electronic spectra of small molecules are computed with high accuracy using high-level ab initio calculations with large basis sets. The vibration-rotation studies make use of a general variational treatment of nuclear motion previously developed in our group that allows the accurate prediction of rovibrational energies and intensities. Correlated ab initio methods are also applied for validation and benchmark purposes, especially in studies on electronically excited states.

Results: The theoretical prediction of vibration-rotation spectra requires the generation of accurate potential energy and dipole moment surfaces, followed by the variational calculation of rovibrational energies and intensities. For the former task, we employ ab initio electronic structure methods, typically coupled cluster theory with complete basis set extrapolation and corrections for core-valence correlation and relativistic effects. For the latter, we have developed and coded a variational treatment of nuclear motion that is based on the Hougen-Bunker-Johns approach with an Eckart-frame kinetic energy operator and thus also handles large amplitude motion. This has led to a general and robust variational code (TROVE) that was published in 2007 and has since been refined in several stages.

Over the past three years, the focus has been on the computation of comprehensive line lists for molecules of astrophysical interest, for example with regard to studies of the atmosphere of exoplanets (in collaboration with the Tennyson group at UCL). In this context, highly accurate ab initio potential energy surfaces were computed for methane [79], chloromethane [43], and silane [46], and ab initio dipole moment surfaces were generated for the latter two molecules [46, 78]. This enabled the simulation of accurate rovibrational spectra and the computation of extensive line lists. In the case of methane, sub-wavenumber accuracy was achieved for the majority of experimentally known vibrational energy levels, and the four fundamentals of $^{12}CH_4$ were reproduced with a root-mean-square error of 0.70 cm^{-1} [79]. In the case of chloromethane, the computed line lists for $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ cover vibrational band origins up to 4400 cm^{-1} and states up to J=85 [78]. As an illustrative example, Figure 1 documents the excellent agreement between the computed and observed spectrum for the ν_5 band of chloromethane. The line positions are again predicted with sub-wavenumber accuracy, and the computed absolute line intensities are accurate to a few percent [78].

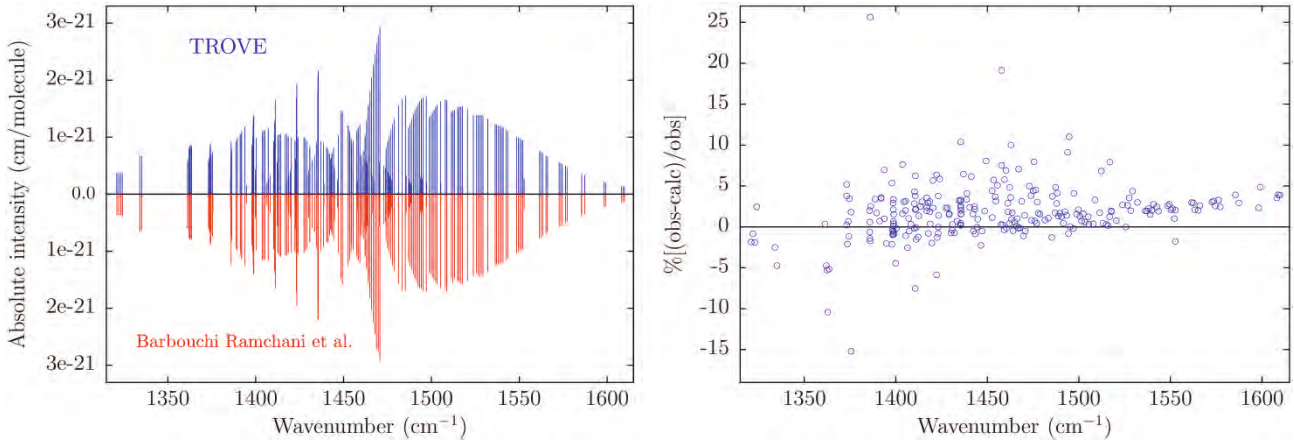

Fig. 1. Absolute line intensities of the ν_5 band of chloromethane for transitions up to $J = 15$ (left) and the corresponding residuals (right) when compared with measurements from Ramchani et al. Transitions for both $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ are shown and the intensities have not been scaled to natural abundance. For illustrative purposes TROVE line positions have been shifted by −0.40 cm^{-1} (from Ref. 78).

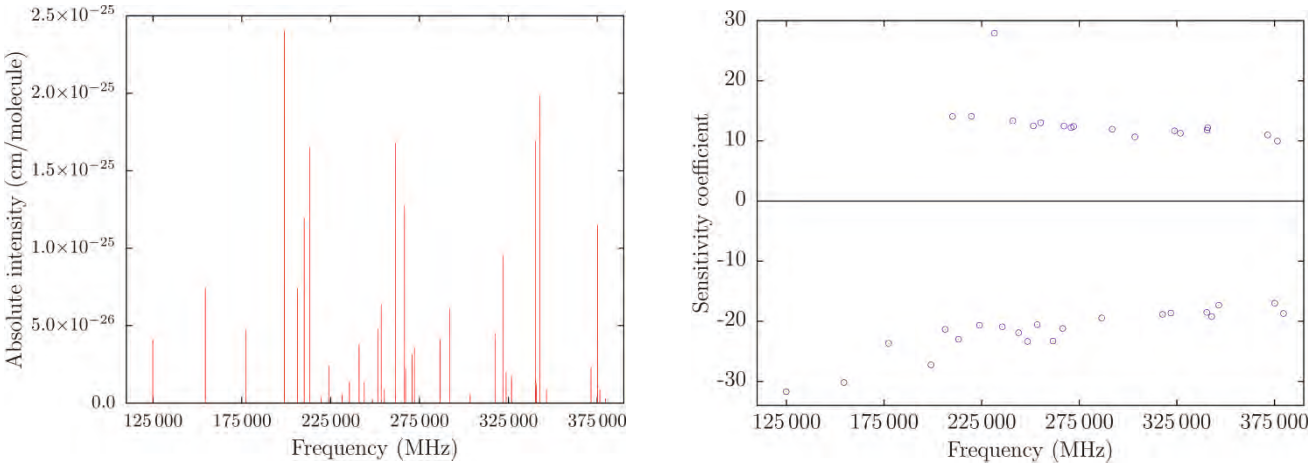

Fig. 2. Observed frequencies and simulated intensities at temperature T = 296 K (left panel) with the corresponding sensitivity coefficients (right panel) for transitions involving the $2\nu_2$ and ν_4 vibrational states of ammonia (from Ref. 77).

Experimentally, high-resolution rovibrational spectroscopy is accurate enough to allow for tests on fundamental theories of physics. In the search for a theoretical framework beyond the established Standard Model of Physics, there has been speculation that the natural constants may indeed not have remained constant over the entire age of the universe and that there may have been changes, for example, in the proton-to-electron mass ratio μ. This would lead to temporal shifts in rovibrational transition energies, which could be detected by high-precision laboratory experiments over a short time scale (say one year) or by astronomical observation of spectral lines at high red-shifts. Such measurements have already put rather tight constraints on the size of possible changes in μ. Theoretically, the effect of changes in μ can be determined through

TROVE calculations that employ suitably scaled mass values. Hence, it is possible to identify transitions that are particularly sensitive to changes in μ and thus especially promising for experimental study. We have performed such calculations for NH_3, H_3O^+, and D_3O^+ to determine the relevant sensitivity coefficients [44, 45, 77], and have indeed found a number of transitions with sensitivity coefficients that are significantly higher than those in the currently available best measurements on methanol. Our calculations indicate that the constraints on possible changes in μ may be tightened by about an order of magnitude by measuring these transitions in ammonia [77]. Figure 2 shows the frequencies and predicted selectivity coefficients of some of the most promising transitions in ammonia [77].

Further ab initio activities included a joint experimental and theoretical study on the high-resolution rovibrational spectrum of PF_3 [27] and a continuation of our ab initio benchmarks on electronically excited states using the SOPPA approach [47]. In comparative evaluations of the performance of computational methods, high-level ab initio calculations were carried out to generate reference data, for instance in studies of conical intersections [15] and of the reaction between FeO^+ and H_2, the prototypical example of two-state reactivity [1]. Finally, in our investigations of electronically excited states and electronic spectroscopy, correlated ab initio calculations (e.g. at the MS-CASPT2 level) were performed for comparison or validation on a regular basis in projects that mainly utilize lower-level methods (see the next chapters).

Publications resulting from this research area: 1, 4, 15, 27, 30, 43, 44-47, 77, 78, 79

External funding: None

Cooperations: W.-H. Fang (Beijing, CN); F. Neese (Mülheim/Ruhr, DE); S. P. A. Sauer (Copenhagen, DK); V. Spirko (Prague, CZ); J. Tennyson (London, UK); S. N. Yurchenko (London, UK)

2.5.2 Research Area "Density Functional Methods" (W. Thiel)

Involved: G.-J. Cheng, D. Escudero, D. Fazzi, G. Gopakumar, P. Gupta, J. P. Götze, B. Heggen, B. Karasulu, C. Loerbroks, M. Patil, K. Sen, L. M. Wolf, Y. Zheng

Objective: Density functional methods are applied in studies of transition metal and other compounds in order to understand and predict their properties. Much of the work on homogeneous transition metal catalysis and organocatalysis involves a close collaboration with experimental groups at our Institute and aims at a detailed mechanistic understanding of the reactions studied experimentally. Time-dependent density functional theory is used in combination with other computational methods to interpret electronic spectra and to understand excited-state properties and processes.

Results: In many of our applications in this area, we employ state-of-the-art density functional theory (DFT) to explore the ground-state potential energy surface and to characterize all relevant intermediates, transition states, and reaction pathways. Geometry optimizations are normally done using standard functionals (RI-BP86, B3LYP) with dispersion corrections (D2, D3) and medium-size basis sets, followed by higher-level single-point energy evaluations that utilize either correlated ab initio methods (e.g., local CCSD(T) treatments with large basis sets) or modern density functionals (e.g., from the M06 series) with large basis sets and dispersion corrections (if appropriate). Effective core potentials are normally used to represent the core electrons of heavy elements. Thermal and entropic corrections are computed at the level applied for geometry optimization.

Joint projects with the Fürstner group: In continuation of a long-standing cooperation, we performed DFT calculations on the mechanism of catalytic reactions investigated experimentally in the Fürstner group [17, 34, 37, 52, 66]. An illustrative example is the Ru-catalyzed hydrogenation of internal alkynes that leads to the formation of ruthenium carbenes and of trans-alkenes, with minor amounts of side products (isomerized alkenes and alkanes) [37]. The DFT-based modeling of this reaction (precatalyst Cp*Rh(cod)Cl, substrate 2-butyne) provides a mechanistic scenario (Figures 3-5) that is consistent with all the experimental evidence (NMR, X-ray, product analysis) [37]. Oxidative addition of H_2 to the catalyst-substrate complex (**A1**) yields a dihydride (**A2**) that rearranges in a rate-limiting step to a η^1-vinyl complex (**A3**). Ring closure of **A3** involves twisting of the vinylic C=C double bond, which can occur in opposite directions and thus lead to two different ruthenacyclopropenes (**E1**, **Z1**) that are precursors to the trans-butene (**E2**)

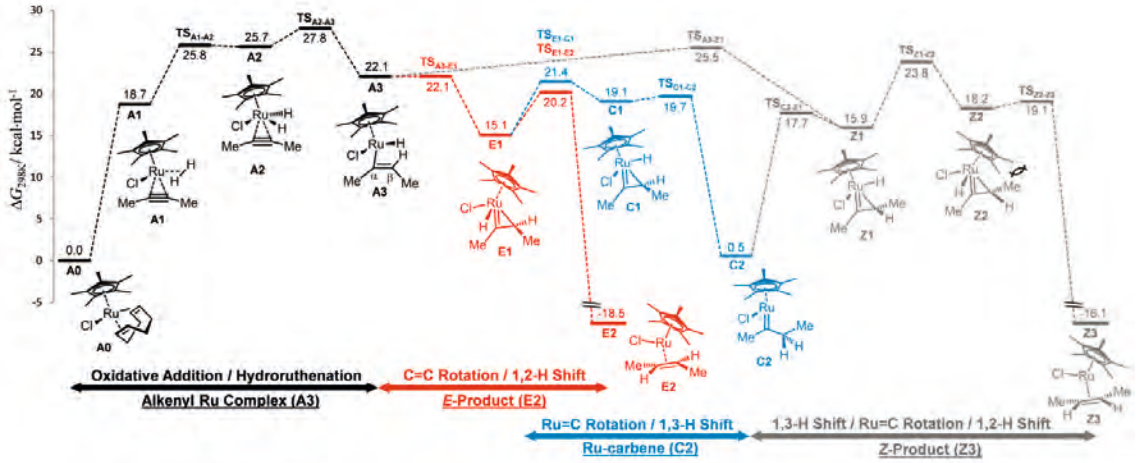

Fig. 3. Free energy profile for the hydrogenation of 2-butyne with complex **A0** at 298 K; computed structures of pertinent intermediates (from Ref. 37).

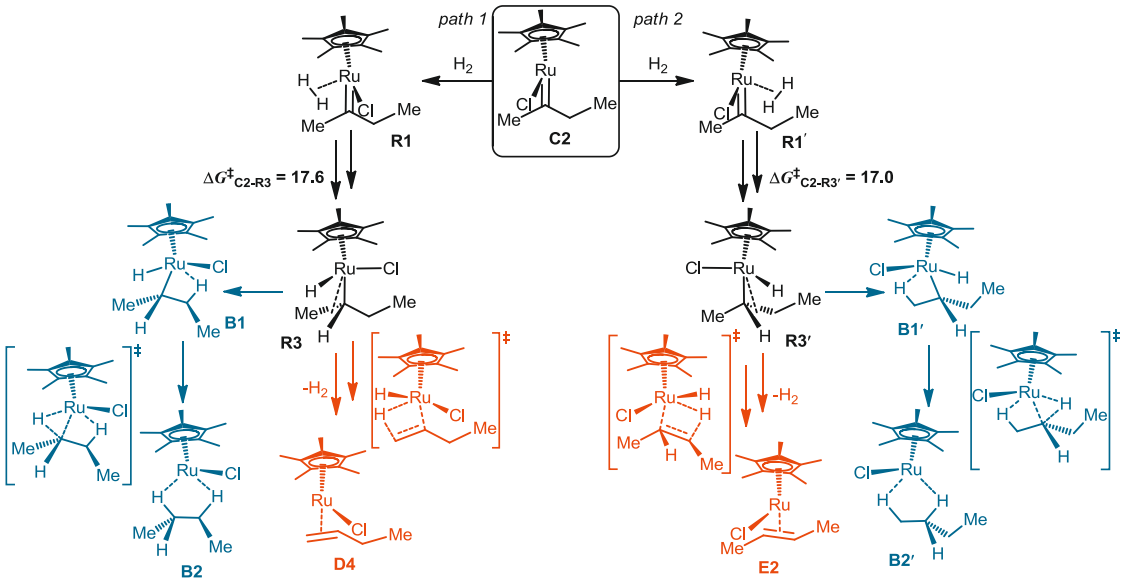

Fig. 4. Computed fate of the carbene formed by *geminal* hydrogenation upon addition of a second H_2 molecule (from Ref. 37).

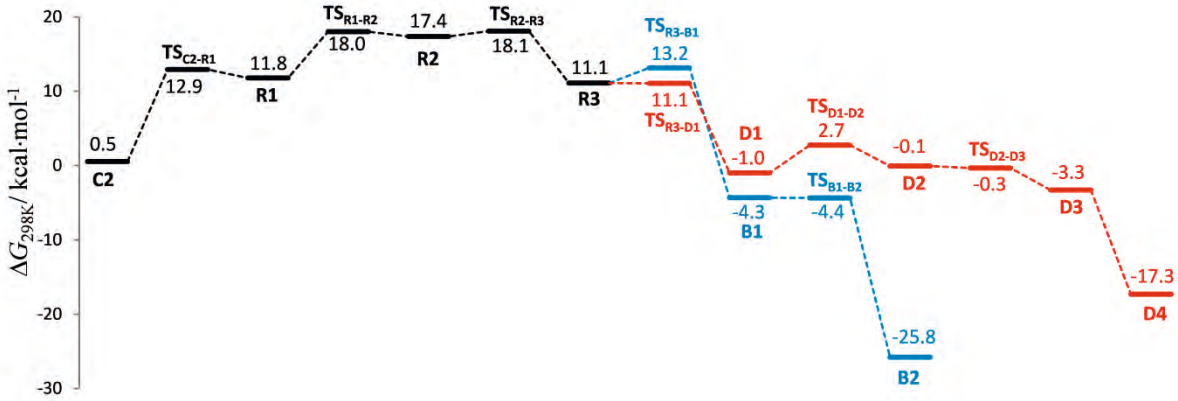

Fig. 5. Free energy profile for path 1 from the left side of Figure 4 at 298 K (from Ref. 37).

and cis-butene (**Z2**) product complexes. According to the computed free energy profile (Figure 3) the *trans/cis*-selectivity is determined by the relative ease of ring closure: $\mathbf{TS_{A3\text{-}E1}}$ is favored over $\mathbf{TS_{A3\text{-}Z1}}$ by more than 3 kcal/mol, consistent with the observed *trans*-hydrogenation. The ruthenium carbene (**C2**) is accessible from **E1** through an alternative rearrangement (involving Ru-C rotation) that requires only slightly more activation (ca. 1 kcal/mol) than the pathway to **E2**, in agreement with the observed formation of such carbenes. Various intramolecular transformations of carbene **C2** can be conceived, but none of the computed barriers is lower than that for the back-reaction to **E1**. However, **C2** can react with another molecule of H_2 (Figure 4), which provides a rather facile route to the observed side products, butane **B2** and 1-butene **D4** (Figure 5). Single-point coupled cluster calculations at the DLPNO-CCSD(T)/TZVP level confirm the validity of the DFT energy profiles (M06/TZVP, Figures 3-5), with minor changes in the computed energies of up to 2 kcal/mol (unpublished results by L. M. Wolf). To summarize, our combined experimental and computational approach has succeeded in rationalizing the preference for *trans*-hydrogenation and the unprecedented formation of ruthenium carbenes in our target system [37].

Having discussed the preceding DFT reactivity study at some length to convey a feeling of this type of collaborative work, we will be brief in the remainder of this section. A second major joint project concerned enantioinversion in gold catalysis [34]. In the cyclization of a hydroxy-allene to the corresponding tetrahydrofuran catalyzed by a TADDOL-related gold-phosphoramidite complex, it was found experimentally that the sense of induction can be switched from (*S*) to (*R*) solely by changing either the solvent or the temperature or the nature of the counterion; our DFT calculations provide a mechanistic scenario that allows us to rationalize these observations: key is the bias of the organogold intermediates to undergo assisted proto-deauration – a process strongly influenced by entropic effects that can ultimately dictate the stereochemical outcome [34]. Further computational DFT work on topics studied in the Fürstner group addressed the electronic structure and chemical bonding in hetero-bimetallic complexes obtained in attempts to prepare germane gold carbenoids devoid of stabilizing substituents via transmetalation [17], the NMR spectra and conformational preferences of mandelalide A and related compounds [52], and the mechanism of iron-catalyzed cross coupling reactions via ferrate intermediates [66]. Completed but still unpublished are mechanistic DFT studies on *trans*-hydrostannation (by L. M. Wolf) and on regio- and stereoselective Ru-catalyzed alkyne-alkene coupling (by G.-J. Cheng).

Joint projects with the Alcarazo group: The research in the Alcarazo group is directed towards the design and synthesis of unusual ligands and coordination compounds and their application in novel catalytic transformations. In our collaborative work, we perform DFT calculations to characterize the electronic structure of key species and to unravel the detailed mechanism of the catalytic reactions. In the reporting period, we addressed bis- and tris(pyrazolyl)borate/methane-stabilized P(III)-centered cations [9], the reactivity of tetrakis(trifluoromethyl)cyclopentadienone towards carbon-based Lewis acids [33], and the electronic properties of α-cationic arsines [60]. In the latter case, the DFT calculations also helped elucidate the mechanism of cycloisomerization of enynes to cyclopropanes, catalyzed by novel Pt(II) complexes containing α-cationic arsines as ligands [60]. Furthermore, DFT results are available from another joint project that addresses α-dicationic phosphines and their role as ligands in the Rh-catalyzed hydroarylation of dienes with electron-rich aromatic molecules (work by L. M. Wolf, manuscript submitted).

Joint projects with the List group: The collaboration with the List group in the field of organocatalysis has intensified during the reporting period, as shown by a growing number of publications [38, 57, 65, 72, 75, 90]. Following the development of a highly enantioselective carbonyl-ene cyclization using a confined imidodiphosphate catalyst, ESI-MS, NMR, and DFT studies were combined to unravel the mechanism of this reaction, which proceeds stepwise and involves a novel covalent intermediate [38]. In a similar vein, DFT calculations provided insight into the mechanism of the asymmetric oxa-Pictet-Spengler reaction catalyzed by nitrated confined imidophosphates [57]. DFT modeling was also used to elucidate the origin of the unusually high *trans*-diastereoselectivity of the chiral imidodiphosphoric acid-catalyzed Prins cyclization reaction [90]. After establishing heterodimerizing self-assembly between a phosphoric acid catalyst and a carboxylic acid as a new activation mode in Brønsted acid catalysis, the underlying mechanism was investigated both experimentally and theoretically; the DFT calculations served to characterize the nature of the supramolecular heterodimer and to rationalize the observed catalyst structure-selectivity relationships [75]. Further DFT investigations addressed the nature of the transition state in the catalytic 6π electrocyclization of unsaturated hydrazones [65] and the CD spectra of enantiopure 2*H*- and 3*H*-pyrroles synthesized by a novel organocatalytic approach [72].

Joint project with the Maulide group: The collaboration with the Maulide group has been phased out in view of their move to the University of Vienna. Our final joint paper concerns the dynamic behavior of internally coordinated monohaptoallylpalladium

complexes [54]. DFT modeling was used to characterize the investigated cyclobut-2-enyl η^1-allyl palladium complexes and to elucidate the detailed mechanism of the metallotropic shift in these systems (stepwise π-σ-π interconversion) [54].

Joint project with the Klussmann group: Our first collaborative project with the Klussmann group addressed the question whether hydrogen atom transfer (HAT) or electron transfer (ET) is the key step in the activation of *N*-aryl tetrahydroisoquinolines in oxidative coupling reactions using CuBr as catalyst and *tert*-butyl hydroperoxide [55]. The combined experimental and computational evidence clearly favors the HAT mechanism. The DFT calculations contributed a computational Hammett plot analysis, predictions of kinetic isotope effects, and free energy profiles for competitive HAT reactions involving the *t*BuO· and *t*BuOO· radicals [55].

Joint projects with the Rinaldi and Schüth groups: These projects on biomass conversion had started in the previous reporting period and have meanwhile been finished. The focus was on the computational modeling of the depolymerization of cellulose to glucose. The initial DFT results for cellobiose (glucose dimer) had shown that cellulose is protected against hydrolysis not only by its supramolecular structure (as commonly accepted), but also by its electronic structure (especially the anomeric effect). Subsequent DFT/MM calculations on the depolymerization of larger cellulose models (up to 40 linked glucose units) in water confirmed the basic mechanistic features deduced from the initial DFT study, while providing detailed information on the influence of nearby solvent molecules [40]. Classical molecular dynamics and metadynamics simulations of these larger models in water and in a ionic liquid indicate that the latter eases hydrolysis through stronger solvent-cellulose interactions and that hydrolysis should start from the ends of cellulose chains [39]. In a related project, the isomerization of glucose to fructose in water was studied at the DFT level to clarify the detailed reaction mechanism and to rationalize the observed differences in the catalytic efficiency of different metal cations [12].

Other ground-state DFT projects: Some ground-state DFT studies have been carried out without involvement of experimental groups from the Institute [11, 24, 48, 67, 80]. These include detailed investigations on the origin of the stereochemical preferences (inversion versus retention) in the oxidative addition step of Pd-catalyzed allylic alkylation [24], on the influence of halogen bonding on the spin state of diphenylcarbene [67], and on the mechanism of ylide transfer to carbonyl compounds using two different sulfur reagents [80].

Electronically excited states: Our research on electronically excited states makes use of the full arsenal of quantum-chemical methods. In the realm of DFT, we mostly rely on time-dependent density functional theory (TD-DFT) and on DFT-based multireference configuration interaction (DFT/MRCI). In the following, we summarize studies on excited states that were mainly carried out at the DFT level (possibly in combination with some ab initio calculations), while we do not cover DFT-based calculations that were done for comparison or validation purposes in our semiempirical excited-state dynamics work (see the next chapter).

Excited-state DFT projects: The performance of DFT/MRCI and several TD-DFT schemes (pure, hybrid, and long-range corrected functionals) was assessed for a set of 3*d* and 4*d* transition metal complexes, by comparing against high-level ab initio reference data for transition energies and oscillator strengths; DFT/MRCI performed best [5]. DFT/MRCI also gave satisfactory results for the spectroscopic and second-order nonlinear optical properties of selected Ru(II) complexes [30]. Different Franck-Condon methods for computing vibrationally broadened UV-Vis absorption spectra were implemented and assessed for flavin derivatives in order to set up a protocol with recommended options [10]. The photoinduced intramolecular charge transfer (ICT) was investigated at the TD-DFT (CAM-B3LYP) and DFT/MRCI levels for roseoflavin, a push-pull flavin derivative, in different environments; the perpendicular-twisted ICT mechanism was found to be favored [35]. A DFT-based computational screening of flavin derivatives absorbing in the blue-green region revealed that certain thioflavins are potentially suitable candidates as cofactors in biomimetic photoswitches [14]. An analysis of the excited-state energy levels of two carotenoids (violaxanthine, zeaxanthine) from TD-DFT (CAM-B3LYP) and DFT/MRCI suggested that carotenoids may act as a shortcut for chlorophyll Soret-to-Q band energy flow in the light-harvesting complex LHCII [8]. The exploration of the relevant triplet excited-state potential energy surfaces of a cyclometalated Pt(II) complex at the TD-DFT level (with inclusion of spin-orbit coupling) indicated non-Kasha behaviour (Figure 6), i.e. emission from a higher-lying triplet state [6]. The mechanism for catalytic photooxidation of benzene to phenol with 2,3-dichloro.5,6-dicyano-*p*-benzoquinone (DDQ) was found to involve nonadiabatic orientation-dependent proton-coupled electron transfer processes [28]. Finally, the mechanism of the [2+2] photocyclization of atropisomeric maleimides was elucidated in detail through DFT calculations, which rationalize the observed regioselectivity as well as the substituent effects on enantioselectivity and diastereoselectivity [56].

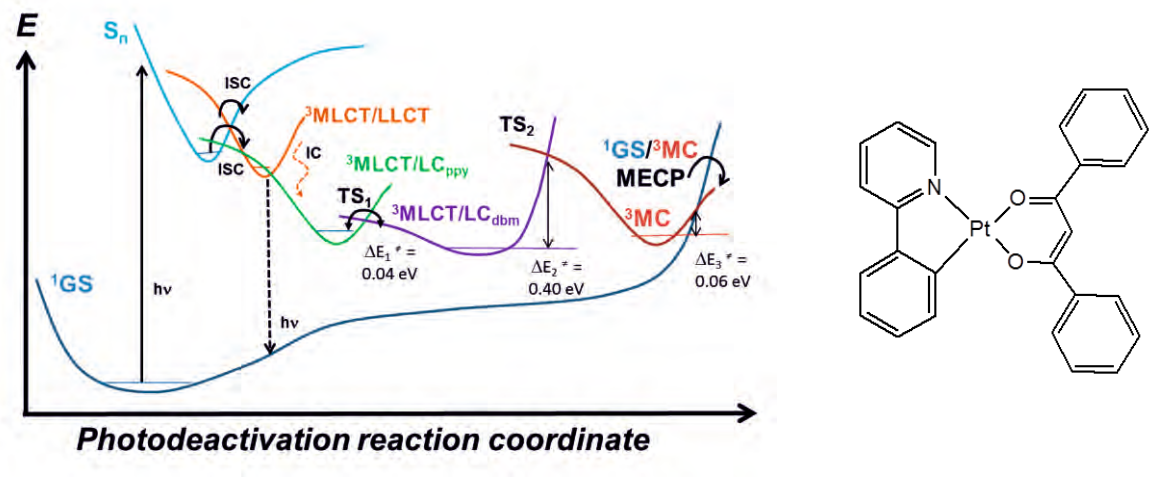

Fig. 6. Schematic Jablonski diagram for the Pt complex shown on the right, including the lowest-energy states involved in the proposed radiative and non-radiative deactivation pathways (from Ref. 6).

Photovoltaics: Our recent DFT-based research on photovoltaics (in collaboration with M. Barbatti) has led to three computational papers [19, 31, 62] and four collaborative publications with external experimental partners [13, 69, 74, 86]. The first study addressed the electronic structure and electronic spectra of three squaraine dyes and their donor-acceptor complexes with fullerene C_{60}. For these complexes, the measured open-circuit voltage is correlated to the charge-transfer energy, and anticorrelated to the energy of the first excited state, which can be rationalized by a simple non-Marcus model [19]. The other two computational studies involved excited-state dynamics simulations of oligothiophenes (300 fs) using trajectory surface hopping (TSH) at the TD-DFT level. The intramolecular dynamics in a tetrathiophene chain leads to exciton localization over three repeat units after ca. 140 fs, consistent with experimental observations in polymers [31]. Photoexcitation into the high-energy (HE) band of a dithiophene dimer generates hot charge transfer states within ca. 50 fs, but the subsequent ultrafast decay to the low-energy (LE) states causes localization of the excitation at one monomer followed by internal conversion to the ground state with C-S bond cleavage [62]. This suggests that the lifetime of the hot excitons (favoring charge transfer and ultimately charge separation) might be increased by designing functionalized aggregates with a higher HE-LE energy gap (disfavoring exciton transfer to the LE regime) [62]. In the collaborative projects with experimentalists, the DFT calculations provided insight into the structure-function relationships of high-electron mobility naphthalene diimide copolymers [13], into the polaronic properties of narrow band gap polymers [69] and n-doped ladder-type conducting polymers [86], and into the electronic structure of carbazole-containing copolymers used in solar cells [74].

Reviews: Surveys of DFT studies are given in reviews on computational catalysis [23] and on excited-state methods [68].

Publications resulting from this research area: 5, 6, 8-15, 17, 19, 23, 24, 28, 30, 31, 33-35, 37, 38, 48, 52, 54-57, 60, 62, 65-69, 72, 74, 75, 80, 86, 90

External funding: Cluster of Excellence RESOLV (DFG), SusChemSys (NRW)

Cooperations: M. Alcarazo (Mülheim/Ruhr, DE); M. Barbatti (Mülheim/Ruhr, DE); A. G. M. Barrett (London, UK); C. J. Brabec (Erlangen, DE); B. Champagne (Namur, BE); S. Fabiano (Linköping, SE); W.-H. Fang (Beijing, CN); A. Fürstner (Mülheim/Ruhr, DE), M. Klussmann (Mülheim/Ruhr, DE); M. A. Loi (Groningen, NL); B. List (Mülheim/Ruhr, DE); C. M. Marian (Düsseldorf, DE); N. Maulide (Mülheim/Ruhr, DE); T. C. Ramalho (Lavras, BR); E. Sánchez-García (Mülheim/Ruhr, DE); W. Sander (Bochum, DE); F. Schüth (Mülheim/Ruhr, DE); M. Sommer (Freiburg, DE)

2.5.3 Research Area "Semiempirical Methods" (W. Thiel)

Involved: G. Cui, P. Dral, J. A. Gámez, B. Heggen, A. Koslowski, Z. Lan, J. Liu, Y. Lu, A. Nikiforov, A. Rodriguez, N. Sahu, L. Spörkel, D. Tuna, X. Wu

Objective: This long-term project aims at the development of improved semiempirical quantum-chemical methods that can be employed to study ever larger molecules with useful accuracy. This includes the development of more efficient algorithms and computer programs. Our current focus in this area is on the development of improved orthogonalization-corrected methods and on non-adiabatic dynamics simulations of electronically excited states.

Results: Over the past years, we have developed semiempirical methods that go beyond the standard MNDO model by including orthogonalization corrections at the NDDO level. This has led to three new approaches labelled OM1, OM2 and OM3 (orthogonalization models 1-3) that offer significant improvements over established MNDO-type methods in several areas, including conformational properties, hydrogen bonds, reaction barriers, and electronically excited states.

In the reporting period, the underlying theoretical formalism, the implementation, and the parametrization of the OMx methods were described in full detail [58]. This paper also addressed the efficiency of the OMx code on different hardware platforms and the use of *a posteriori* dispersion corrections for a much improved treatment of noncovalent interactions (OMx-Dn approach) [58]. In a companion publication, the performance of the OMx and OMx-Dn methods was evaluated for a variety of ground-state properties using a large and diverse collection of benchmark sets from the literature, with a total of 13035 reference data [59]. Extensive comparisons with established semiempirical methods show that the OMx and OMx-Dn methods outperform the other methods for most of the benchmark sets by a significant margin [59]. Similar comprehensive evaluations of the OMx/MRCI methods were carried out for electronically excited states, covering vertical and adiabatic excitation energies, excited-state equilibrium geometries, minimum-energy conical intersections, and excited-state zero-point vibrational energies, for a total of 520 molecular structures and 412 excited states [82]. Comparisons with high-level ab initio and TD-DFT reference data indicate that the OMx/MRCI methods perform reasonably well for many of the excited-state properties [82]. This paper also summarizes recent improvements of our semiempirical MRCI code, which include the implementation of a shape-driven version of the GUGA-CI

algorithm (GUGA, graphical unitary group approach) and of a direct variant of the code (with the CI coupling coefficients being recomputed as needed) [82].

Ongoing work addresses the further development and refinement of the OMx methods. This includes the theoretical analysis of the existing formalism, the design and test of new integral approximations, the improvement of parametrization techniques, the assembly of suitable reference data, and the actual parameterization of the refined OMx methods for as many elements as possible. Progress has been made on all these fronts. It is clear that the next generation of OMx methods will have fully integrated dispersion corrections (rather than an *a posteriori* treatment). New integrals approximations are being developed, e.g., for the resonance integrals. Our arsenal of parametrization methods has been supplemented with machine learning techniques [29]. Extensive high-level reference data for ground-state and excited-state properties are available from our recent benchmark studies [58, 59, 82]. In view of the excellent performance of the OMx methods for first-row elements, their parametrization is being extended to second-row elements (even though the use of an *sp* basis will not allow meaningful calculations for hypervalent compounds); the OM2 parametrization for sulfur is finished and yields superior results for normalvalent compounds (manuscript in preparation). Furthermore, parametrizations of next-generation OMx methods with fully integrated dispersion corrections have been performed for first-row elements, and the currently available results already present significant improvements in overall accuracy. Finally, a large number of test parametrizations are being run to assess the merits and shortcomings of new integral approximations. Much of this is rather tedious work, which is however necessary to develop general-purpose next-generation semiempirical methods with improved overall performance.

Over the past three years, our semiempirical applications have focused on excited-state dynamics. We had previously implemented the trajectory surface hopping (TSH) method with the fewest switches algorithm (Tully) in our software, making use of our semiempirical in-core version of the GUGACI method that handles general CI expansions (up to full CI) efficiently for small active spaces and provides an analytic GUGACI gradient as well as analytic nonadiabatic coupling matrix elements. Technical problems may arise in such TSH simulations with a predefined active space whenever active and inactive orbitals strongly mix and switch in some particular regions. We have largely overcome these problems by employing adaptive time steps when such regions are encountered in TSH simulations [81]. The corresponding computational protocol is easy to implement and increases the computational effort only in the critical regions;

tests on a GFP chromophore model and a light-driven rotary molecular motor show that the number of successful trajectories without technical failures rises significantly by the use of adaptive time steps, from 53 % to 95 % and from 25 % to 96 %, respectively [81]; this is now the default option in TSH simulations. Another methodological advance is a generalization of the TSH method by including spin-orbit coupling, thus allowing the simulation of both internal conversion and intersystem crossing on an equal footing; our implementation considers hops between adiabatic eigenstates of the non-relativistic electronic Hamiltonian (pure spin states), which is appropriate for sufficiently small spin-orbit coupling [4].

Most of our excited-state dynamics studies were carried out at the OM2/MRCI level for medium-size organic molecules in the gas phase. These TSH simulations provided insight into the origin of the enhanced $E \rightarrow Z$ photoisomerization in 2-aminoazobenzene [7], the nonequilibrium H/D isotope effects in excited-state intramolecular proton transfer (ESIPT) processes [21], the photochromism and photoswitching potential of a prototypical Schiff base, salicylidene methylamine [50], the dynamics of an unusual excited-state proton transfer to a carbon atom [53], the enhancement of the fluorescence emission of a locked GFP chromophore by ESIPT-induced trapping of a keto tautomer [73], the computational design of a family of light-driven rotary molecular motors with improved quantum efficiency [76], and the stereospecific unidirectional excited-state relaxation during the photoisomerization of arylazopyrazole photoswitches [87]. The results of these OM2/MRCI studies are generally consistent with the available experimental data and high-level static calculations, but the dynamics simulations often detect pathways and preferences between pathways that are not obvious from the static calculations. These successful applications corroborate the previously available evidence that the OM2/MRCI approach is a suitable tool for investigating the excited states and the photochemistry of large molecules.

For the sake of brevity, it is not possible to discuss all these dynamics studies in detail. Instead we comment on one illustrative example, the photodynamics of GFP model chromophores (Figures 7-8), in order to convey a feeling of the types of results that can be obtained. The native GFP chromophore (p-HBDI in Figure 8) has a *para*-hydroxyl group at the phenyl ring. The *ortho*-isomer (o-HBDI in Figure 8) and the locked *ortho*-isomer (o-LHBDI in Figure 8) have been synthesized and characterized experimentally. Photoexcitation of p-HBDI triggers photoisomerization around the central C=C bond with fast deactivation to the ground state. Excited-state dynamics simulations show that this photoisomerization cannot compete with the ultrafast ESIPT process in o-HDBI and

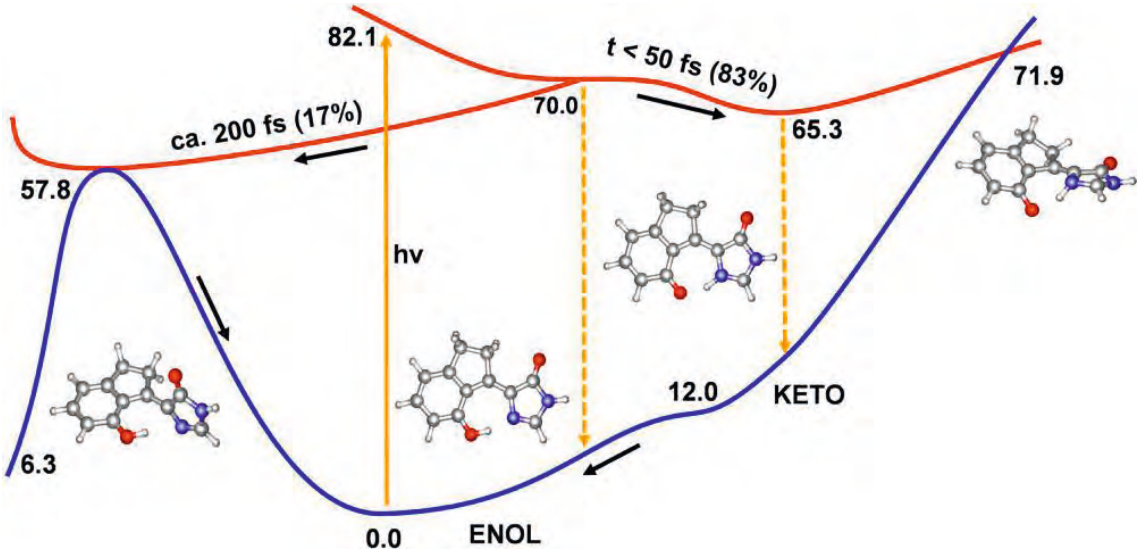

Fig. 7. Photochemical mechanism derived from static electronic structure calculations and nonadiabatic dynamics simulations of o-LHDBI (from Ref. 73).

Note: According to the TSH simulations, photoexcitation of the stable ground-state enol tautomer of o-LHDBI to the S_1 state triggers an ultrafast ESIPT process that populates the keto tautomer within 50 fs (83 %), with a minor fraction of the trajectories (17 %) reaching the enol-type conical intersection with the ground state within ca. 200 fs. The route from the S_1 keto form to the keto-type conical intersection with the ground state is uphill, and hence the S_1 keto form is trapped long enough to fluoresce.

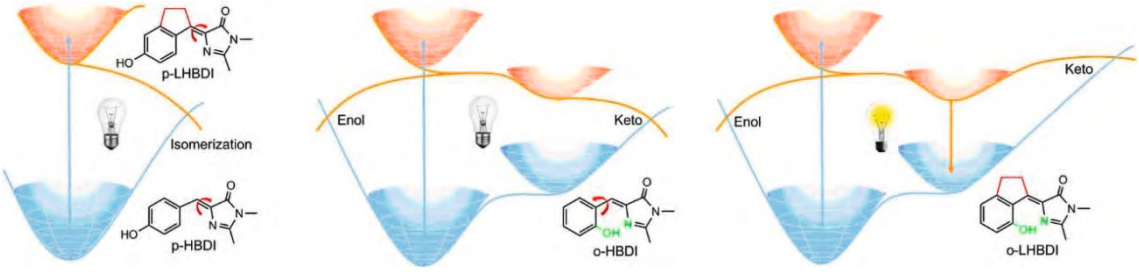

Fig. 8. Comparison of photophysical and photochemical mechanisms of three types of GFP core chromophores. p-HBDI and p-LHBDI are non-emissive in vacuo and solution due to excited-state deactivation induced by cis-trans isomerization. o-HBDI is non-emissive because of ESIPT-induced excited-state deactivation. In o-LHBDI, ESIPT leads to an excited-state trapping that enhances the ability of the S_1 keto species to fluoresce (from Ref. 73).

o-LHDBI, which yields the excited-state keto tautomer (enol/keto tautomerization). They also indicate that the conical intersection with the ground state can thereafter be reached easily in o-HDBI, but not in o-LHDBI because of the chemical locking by the extra five-membered ring, which impedes the required out-pf-plane distortions. The TSH simulations thus rationalize the different photophysical behavior of the three GFP model chromophores considered [73].

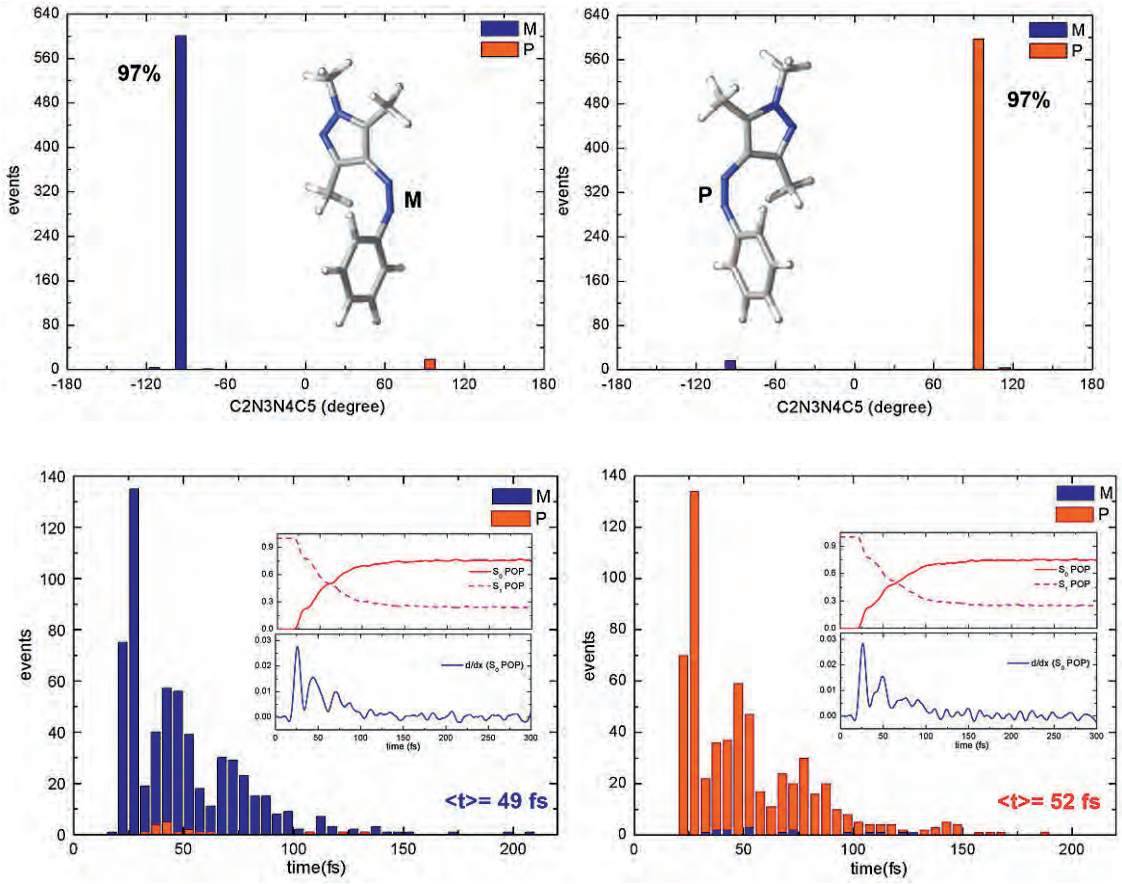

Fig. 9. Distribution of (top) the C2N3N4C5 dihedral angles and (bottom) the hopping times at all $S_1 \rightarrow S_0$ hopping points, with time-dependent state populations and their time derivatives (insets). Left panels, trajectories starting from the M enantiomer (S_0); right panels, trajectories starting from the P enantiomer (S_0). Hops through the M conical intersection (S_1S_0) in blue, hops through the M conical intersection (S_1S_0) in red (from Ref. 87).

A second illustrative example is provided an azo compound (denoted as Z11), in which the central N=N double has one phenyl and one trimethylpyrazolyl substituent (see Figure 9). Like azobenzene itself, the *cis*-isomer of arylazopyrazole Z11 exists in two helical forms (M and P). The *cis/trans*-photoisomerization of Z11 can in principle occur in two different ways, with opposite sense of rotation. The TSH simulations show unidirectional dynamical behavior, with an overwhelming majority of the trajectories retaining the helicity in the preferred mode of rotation (97 %). To our knowledge, this is the first case of an essentially stereospecific excited-state relaxation [87].

Reviews and benchmarks: Recently we published reviews on semiempirical methods in general [22], on the computational modeling of photoexcitation in DNA single and double strands [41], and on the use of graphical processing units for fast semiempirical calculations [88]. A benchmark study confirmed the satisfactory performance of the OM2/MRCI method for conical intersections in organic molecules, through comparisons with ab initio MRCI and DFT-based methods [15].

Future directions: Research in the framework of the ERC Advanced Grant will focus on the further development and application of OMx methods. This includes the reparameterization of the existing OMx methods with inclusion of dispersion corrections aiming at a balanced treatment of ground-state and excited-state properties, the reformulation of the OMx methods with the use of different types of integral approximations to facilitate the extension to heavier main-group elements and transition metals with an *spd* basis, and generic as well as specific parameterizations for transition metals. Semiempirical applications will concentrate on excited states of large complex systems (spectroscopy, photochemistry, solar cells) using both static calculations and dynamics simulations.

Publications resulting from this research area: 4, 7, 15, 21, 22, 26, 29, 41, 50, 53, 58, 59, 64, 73, 76, 81, 82, 87, 88

External funding: ERC Advanced Grant (European Research Council)

Cooperations: M. Elstner (Karlsruhe, DE); W.-H. Fang (Beijing, CN); M. Filatov (Bonn, DE); A. Lübcke (Berlin, DE); O. A. von Lilienfeld (Basel, CH)

2.5.4 Research Area "Combined Quantum Mechanical / Molecular Mechanical Methods and Classical Dynamics" (W. Thiel)

Involved: E. Boulanger, G. Cui, A. Escorcia Cabrera, A. Ganguly, J. P. Götze, S. Hare, B. Heggen, B. Karasulu, G. König, C. Loerbroks, M. Patil, T. Saito, K. Sen, P. Sokkar, J. van Rijn, T. Vasilevskaya, Y. Zheng

Objective: This research focuses on hybrid approaches for large systems where the active center is treated by an appropriate quantum mechanical method and the environment by a classical force field. It involves considerable method and code development. This approach allows a specific modeling of complex systems such that most of the computational effort is spent on the chemically important part. Current applications primarily target biocatalysis and aim at a better understanding of enzymatic reactions including the role of the protein environment, but also address solvation and excited-state processes.

Results: Combined quantum mechanical/molecular mechanical (QM/MM) methods are a popular tool for studying reactions in complex systems such as enzymes. In the preceding reporting periods, we had implemented polarizable force fields in this framework (QM/MMpol) and extended the two-layer QM/MM approach to a three-layer model by introducing boundary potentials that represent the outer part of the MM region and the bulk solvent. We have further refined the QM/MMpol scheme (by improving the treatment of the Drude oscillators and of the QM/MMpol boundary) and assessed its performance for small model systems and for the enzymatic reactions in chorismate mutase (CM) and p-hydroxybenzoate hydroxylase (PHBH), where inclusion of MM polarization affects the computed barriers by about 10 % [2]. As an alternative three-layer scheme, we have developed (in collaboration with E. Sánchez-García) a triple-resolution QM/MM/CG approach for biomolecular systems, in which the outermost layer is represented by the coarse-grained (CG) Martini force field [49]. Tests on the enzymatic reactions in CM and PHBH show that it is important to use an atomistic representation of the water molecules inside the enzyme and in the surface layer (up to at least 5 Å). Hence, the CG force field should only be applied for the bulk solvent, which limits the gains in computational efficiency [49]. The merits of various two-layer and three-layer approaches have been assessed more recently in systematic free energy calculations on CM and PHBH (unpublished work by A. Ganguly).

Most of the published QM/MM work on enzymes makes use of a finite droplet model, with the enzyme being embedded in a sufficiently large water sphere. An alternative is the QM/MM-Ewald approach with periodic boundary conditions (PBC) that evaluates

long-range electrostatic interactions properly by Ewald summation techniques. We have implemented the original semiempirical QM/MM-Ewald scheme proposed by Nam, York, and Gao (*J. Chem. Theory Comput.* 2005, *1*, 2). In addition, we introduced a generalized method (Gen-Ew) for periodic QM/MM calculations that can be used with any QM method in a QM/MM framework [85]. The Gen-Ew approach approximates the QM/MM-Ewald method by representing the PBC potential by virtual charges on a sphere and the QM density by electrostatic potential charges. The deviations between Gen-Ew and QM/MM-Ewald results are generally small enough to justify Gen-Ew applications. The results from periodic QM/MM energy and free energy calculations (QM/MM-Ewald, Gen-Ew) were compared to their nonperiodic counterparts (droplet model) for five test reactions in water and for the Claisen rearrangement in CM; excellent agreement was found in all cases, indicating that long-range electrostatic interactions are well captured by nonperiodic QM/MM calculations in a water droplet of reasonable size (radius of 15-20 Å) [85].

We now turn to recent QM/MM applications. In QM/MM studies on enzymatic reaction mechanisms, we normally use geometry optimization techniques to follow conceivable pathways on DFT/CHARMM potential energy surfaces in order to determine the most favorable one. Optimizations are normally done with efficient DFT approaches (e.g., RI-BP86 with moderate basis sets), while relative energies are determined using more refined functionals (e.g., B3LYP-D3 or M06 with larger basis sets) or even correlated ab initio methods (CCSD(T) or multi-reference treatments). If necessary, QM/MM free energy calculations are performed to include entropic contributions. In the following, we first describe one such mechanistic QM/MM study in some detail and then briefly summarize several others.

As illustrative example, we address amine oxidation mediated by *N*-methyltryptophan oxidase (MTOX) [36]. Amine oxidation is the rate-determining step in the three-step demethylation of *N*-methyltryptophan (NMT) catalyzed by MTOX, which employs a covalently bound flavin adenine dinucleotide (FAD) as cofactor. For the required transfer of a hydride ion equivalent, three pathways (direct/concerted, radical, and adduct-forming/polar nucleophilic) have been proposed (Figure 10), without a consensus on which one is commonly used by amine oxidases. We have combined theoretical pK_a analysis, classical MD simulations, pure QM calculations on active-site models, and QM/MM calculations on the full solvated enzyme (Figure 11) to provide molecular-level insights into the catalytic mechanism of NMT oxidation and to analyze the role of MTOX active-site residues and covalent FAD incorporation for NMT binding and oxidation. The QM(B3LYP-D2/6-31G(d))/CHARMM results clearly favor a direct concerted hydride transfer mechanism involving anionic NMT as the reactive

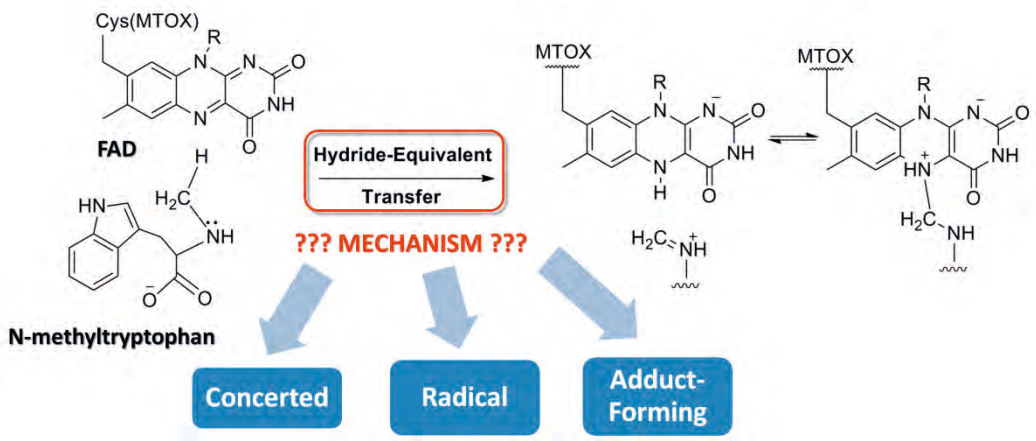

Fig. 10. Mechanistic alternatives for amine oxidation in MTOX (from Ref. 36).

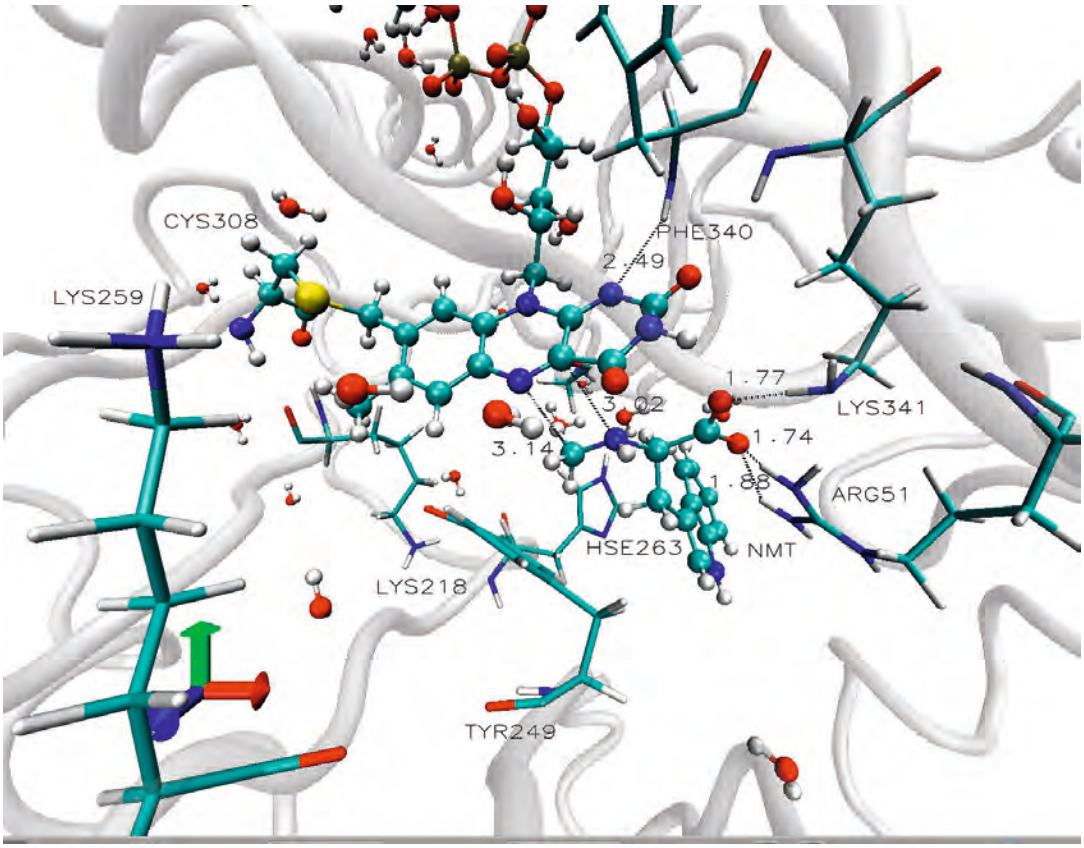

Fig. 11. Typical starting structure for QM/MM modeling of amine oxidation in MTOX, taken from an MD snapshot of the NVT ensemble for anionic *N*-methyltryptophan (K259: protonated, K341: deprotonated). Depicted are FAD and NMT (ball-and-stick), important MTOX residues (stick), and the MTOX structure (cartoon) (from Ref. 36).

species. On the basis of classical canonical MD simulations and QM/MM calculations of wild-type MTOX and two mutants (K341Q and H263N), we propose that the K341

residue acts as an active-site base and electrostatically, whereas H263 and Tyr249 only support substrate alignment. Covalent FAD binding leads to a more bent isoalloxazine moiety, which facilitates the binding of anionic NMT but increases the catalytic activity of FAD only slightly. Our computational results thus provide a detailed and consistent mechanistic scenario for amine oxidation in MTOX [36].

In the following, we briefly summarize the results from several other QM/MM studies on ground-state enzymatic reactions that were carried out during the reporting period.

The reversible oxygen binding in *hemocyanin*, a copper-containing enzyme, was studied at the QM/MM level using a broken-symmetry DFT treatment with spin projection corrections for the QM region [16]. The X-ray structures of the deoxygenated and oxygenated hemocyanin are well reproduced by QM/MM geometry optimizations. The oxygen binding proceeds stepwise with two sequential electron transfer (ET) processes in the triplet state followed by an intersystem crossing to the singlet product. The first ET step leads to a nonbridged superoxo $Cu_B^{II}–O_2•^-$ intermediate via a low-barrier transition state. The second ET step is even more facile and yields a side-on complex with the characteristic Cu_2O_2 butterfly core, accompanied by triplet-singlet intersystem crossing. The computed barriers are very small so that the two ET processes are expected to very rapid and nearly simultaneous [16].

For the *cytochrome P450EryF* enzyme, we investigated the role of two alternate water networks in the formation of the reactive Compound I (Cpd I) species [18]. MD simulations suggest the existence of two water networks around the active site, the one found in the crystal structure involving E360 and another one involving E244. According to the QM/MM calculations, the first proton transfer that converts the peroxo to the hydroperoxo intermediate (Compound 0, Cpd 0) proceeds via the E244 water network with direct involvement of the 5-OH group of the substrate. For the second proton transfer from Cpd 0 to Cpd I, the computed barriers for the rate-limiting homolytic O−O cleavage are similar for the E360 and E244 pathways, and hence both glutamate residues may serve as proton source in this step [18].

For the zinc-containing *matrix metalloproteinase-2* (MMP-2) enzyme, we explored the mechanism of peptide hydrolysis using the oligopeptide Ace-Gln-Gly~Ile-Ala-Gly-NMe as substrate [51]. The four-step mechanism involves an initial nucleophilic attack followed by hydrogen bond arrangement, proton transfer, and C-N bond cleavage. The computed QM/MM barriers for these chemical steps are quite low, and it thus seems likely that product release is rate-limiting in MMP-2 catalysis; this notion is supported by QM/MM reaction path calculations and steered MD simulations for the release

process [51]. In follow-up studies, we addressed the dependence of the QM/MM results on the chosen computational protocol (keywords: initial sampling, thickness of the solvent shell, energy versus free energy calculations) and the origin of the lower catalytic activity of the Glu116Asp mutant [83, 84].

In the area of ground-state enzyme reactivity, we have also published reviews on QM/MM studies of cytochrome P450 enzymes [20] and on computational biocatalysis in general [23]. In ongoing mechanistic QM/MM work (with A. Escorcia Cabrera and J. van Rijn) we investigate the origin of the enantioselectivity of the *Candida antarctica* lipase B (CalB) catalyzed *O*-acetylation of (*R*,*S*)-propranolol [61] and the mechanism of carbocation rearrangements in terpene synthases (manuscripts in preparation).

Turning to QM/MM projects on electronically excited states, we have studied the electronic absorption spectra and the photoinduced processes and reactions in a number of biomolecular systems. In comprehensive QM/MM work on channelrhodopsin-2 wild-type (ChR-WT) and the C128T mutant, the OM2/MRCI method was used with success to simulate the absorption spectra of Chr-WT and C128T as well as several related systems (retinal isomers, bacteriorhodopsin) [64]. In a QM/MM study of the light-harvesting peridinin-chlorophyll a-protein, DFT-based methods were used to compute the relevant excited-state structures, energies, and transition dipole moments, which allowed us to propose an energy transfer model that invokes vibrational relaxation in the lowest two singlet excited states as driving force for wavelength conversion [32]. DFT/MM simulations of phenylbenzothiazole compounds bound to a tyrosine kinase show that excited-state proton transfer can tune the emission properties of these molecules through differences in hydrogen bonding, which suggests the possibility of creating two-color fluorescent markers for protein binding sites [42]. According to QM(CASPT2//CASSCF)/MM calculations on the S65T/H148D double mutant of wild-type green fluorescent protein, the Asp148 residue drives the ultrafast formation (< 175 fs, barrierless ESIPT process) of the anionic fluorescent state (S_1 keto tautomer) that is then quickly deactivated through a concerted asynchronous hula-twist photoisomerization; this explains the low fluorescence quantum yield observed experimentally [25]. Finally, classical MD as well as ab initio QM/MM nonadiabatic dynamics simulations were used to model the photoinduced folding and unfolding processes in the azobenzene cross-linked FK-11 peptide; the interactions between the peptide and the azobenzene cross-linker were found to be crucial for controlling the evolution of the secondary structure of the peptide and responsible for accelerating the folding and unfolding events [89].

QM/MM techniques have also been used to address solvation effects (partly in collaboration with E. Sánchez-García and other RESOLV partners). A combined experimental and theoretical study of diphenylcarbene showed that the spin state of such reactive carbenes can be controlled by halogen bonding (in this case with CF_3I and CF_3Br); on the theoretical side, DFT and ab initio calculations were performed to obtain gas-phase singlet and triplet potential energy surfaces for the corresponding complexes, while DFT/MM simulations were carried out at low temperatures (3 to 75 K) to check for the interconversion of these complexes in an argon matrix under these conditions [67]. A second joint study combined femtosecond transient absorption spectroscopy and QM/MM simulations to investigate two competing pathways for the reaction between singlet diphenylcarbene and methanol (O-H insertion) in methanol/acetonitrile solvent mixtures; the choice between the two pathways was found to be governed by the hydrogen bonding dynamics, with the key role being played not be the nearest solvent molecule but by its neighbor, which is the decision-maker rather than a spectator [70]. Solvent effects also turned out to be important in an ab initio QM/MM investigation of 4-thiothymidine in aqueous solution, which identified the intersystem crossings and the photophysical pathways that enable this molecule to act as a photosensitizer in photodynamic therapy [3]. Finally, the hydrophobicity of different solvents can be assessed experimentally and theoretically by determining the distribution coefficients of compounds between two solvent phases. In the context of the SAMPL5 challenge, we computed these quantities for the SAMPL5 target molecules using MM and QM/MM free energy simulations of water-cyclohexane transfer; both the BLYP/MM and the OM2/MM results turned out to be superior to the pure MM results [71].

Classical MD simulations are an integral part of all our QM/MM studies because they are indispensible for the setup of the system and for generating starting points for QM/MM calculations. In many cases, they also provide chemically relevant information, and they may even be sufficient to solve a given problem. We close this section by briefly mentioning two such examples (collaborative work with B. R. Crane). Classical and replica-exchange MD simulations show that changes in active-site histidine hydrogen bonding trigger the activation of cryptochrome, the principal light sensor of the insect circadian clock; more specifically, the photosensory mechanism of the cryptochrome from *Drosophila melanogaster* involves flavin photoreduction coupled to protonation of His378, whose altered hydrogen-bonding pattern leads to a conformational change in a key regulatory element of the protein (the C-terminal tail helix and its surroundings) [63]. In analogous MD simulations of the blue-sensing LOV (light-oxygen-voltage) protein Vivid, a Gln182 amide flip was found to occur in response to either adduct formation or reduction of the isoalloxazine ring to the neutral

semiquinone; this flip elicits long-distance allosteric responses in the protein that are crucial for signal transduction (manuscript submitted).

The ChemShell software that has been used in our QM/MM applications is available under a license agreement (see www.chemshell.org).

Publications resulting from this research area: 2, 3, 16, 18, 20, 23, 25, 32, 36, 39, 40, 42, 49, 61, 63, 64, 67, 70, 71, 83-85, 89

External funding: Cluster of Excellence RESOLV (DFG), SusChemSys (NRW)

Cooperations: M. Barbatti (Mülheim/Ruhr, DE); B. R. Brooks (NIH Rockville, USA); B. R. Crane (Cornell, USA); M. Elstner (Karlsruhe, DE); W.-H. Fang (Beijing, CN); A. V. Nemukhin (Moscow, RU); P. Nuernberger (Bochum, DE); E. Sánchez-García (Mülheim/Ruhr, DE); W. Sander (Bochum, DE); S. Shaik (Jerusalem, IL)

2.5.5 Research Area "Photoinduced Processes in Organic Molecules" (M. Barbatti)

Involved: L. Stojanović, G. Pereira Rodrigues, D. Mancini, R. Crespo-Otero, W. Arbelo-González

Objective: After UV photoexcitation, organic molecules relax through a manifold of excited states, dissipating the absorbed energy either by photoemission or by vibrational excitation. The objectives of this research area are 1) to characterize these relaxation mechanisms through excited-state computational simulations; and 2) to implement new methods and algorithms to improve these simulations.

Results:

a) Fundamental processes

Photoexcitation may induce electron and proton transfers within the molecule or between neighbor molecules. We have investigated several cases to understand how this transfer process occurs, how it is triggered, and on which time scale it proceeds [93, 95, 96, 103].

In collaboration with E. Sánchez-García and W. Sander, we investigated the formation of weakly bound dimers of N-methylformamide (NMF) and their photochemistry after UV irradiation [95]. The aim was to understand the effect of UV radiation on peptide bonds. Starting from trans(donor)-trans(acceptor) dimers, the experiments carried out in the Sander group showed that the main products formed upon irradiation are the trans(donor)-cis(acceptor) dimers. Moreover, in contrast to the photochemistry of the NMF monomers, no dissociative products were observed upon 248 nm irradiation of the NMF dimers. On the basis of nonadiabatic dynamics simulations, we could explain the absence of dissociative products. The simulations showed that the NMF dimers are protected by a proton-transfer mechanism in the excited state that is faster than the photodissociation.

In another case study, I showed that an electron transfer from solvent molecules to the photoexcited chromophore can also induce internal conversion with little geometric distortion [93]. Using dynamics simulations, I found out that when a specific tautomer of adenine (7H-adenine) in water absorbs UV radiation, it dissipates the photo-energy as heat after receiving an electron from a nearby water molecule. This result revealed an

unknown internal conversion pathway, with implications for the assignment of photoreactions in biological environments and for the design of organic photodevices.

In a recent case study, we addressed the double proton transfer in 7-azaindole (7AI) dimers [103]. Two decades ago, A. Zewail and his team, using time-resolved spectroscopy, proposed that photoinduced double proton transfer in 7AI dimer is a stepwise process. Since then, this conclusion has motivated an uncommonly fierce debate on the nature of this transfer – whether it is really stepwise or alternatively concerted. Using high-level computational simulations of static and dynamic properties, R. Crespo-Otero, N. Kungwan, and I found out that much of these earlier discussions were induced by inappropriate theoretical modeling, which led to a biased interpretation of the experimental results. We showed that earlier models provided either a wrong or incomplete topographic description of the excited-state potential energy surface of the 7AI dimer. They delivered an inadequate balance between the energies of the local-excitation and charge-transfer regions, and completely missed the possibility of internal conversion to the ground state (Figure 12). We concluded that stepwise transfer is thermodynamically and kinetically disfavored and only concerted transfer takes place.

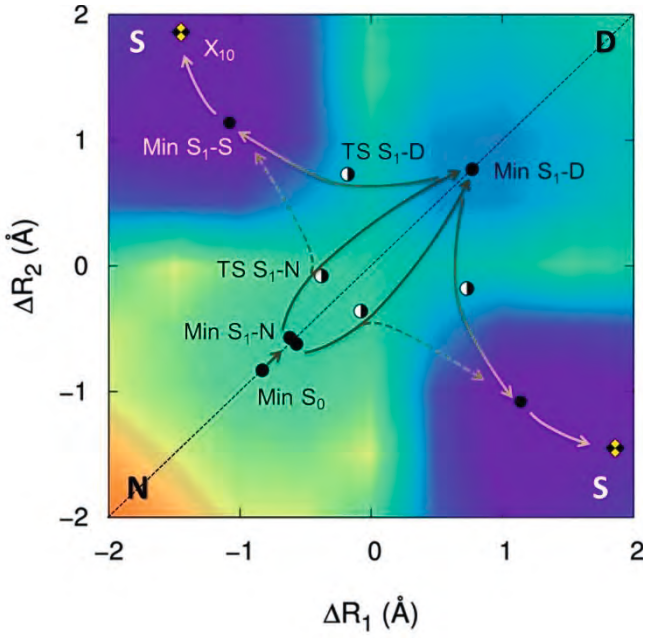

Fig. 12. Potential energy surface of the first excited state of the 7AI dimer. The presence of a conical intersection (X_{10}) blocks the occurrence of stepwise double proton transfer.

b) Applied photophysics

Photophysical and photochemical processes are core phenomena in diverse aspects of life on Earth. In the 2014-2016 period, we continued a long-term research program addressing such processes from a computational standpoint [13, 19, 31, 42, 62, 91, 94, 97, 100-102, 104, 107].

In collaboration with W. Thiel and T. C. Ramalho, we showed that excited-state proton transfer may give rise to new diagnostic tools to follow the clinical evolution of cancer patients [42]. It is well-known that a number of phenylbenzothiazole (PBT) compounds exhibit antitumor activity. Certain PBTs are also well-known for their very large Stokes shifts caused by excited-state intramolecular proton transfer (ESIPT). Aiming at connecting tumor selectivity and proton-transfer properties, we have theoretically designed and studied a new PBT compound, named HABT. Our hypothesis, confirmed by the simulations, is that the proportion and intensity of violet and green emissions from HABT depend on the protein active-site conformation, which modulates the rates of proton transfer, and of radiative and nonradiative decays. Thus, changes in the fluorescence spectrum of HABT bound to tyrosine kinases could be the basis for a new method to detect mutations in cancer cells, usually associated to development of drug resistance.

Still in the health field, I have completed a comprehensive map of processes that produce or cleave pyrimidine dimers (Figure 13) [94]. Cyclobutane pyrimidine dimers (CPD) are closely related to mutagenesis and carcinogenesis; they are formed when UV radiation induces dimerization of adjacent pyrimidine nucleobases. To understand how the dimerization and the repair process happen, I built a benchmark of computational results based on different methods. For these simulations, I used a thymidine-dimer model in the gas phase and explored the ground- and excited-state potential energy surfaces of neutral (singlet and triplet), cationic, and anionic species. The analysis of these surfaces allowed me to describe several reaction pathways for dimerization and repair, some of them completely unknown so far.

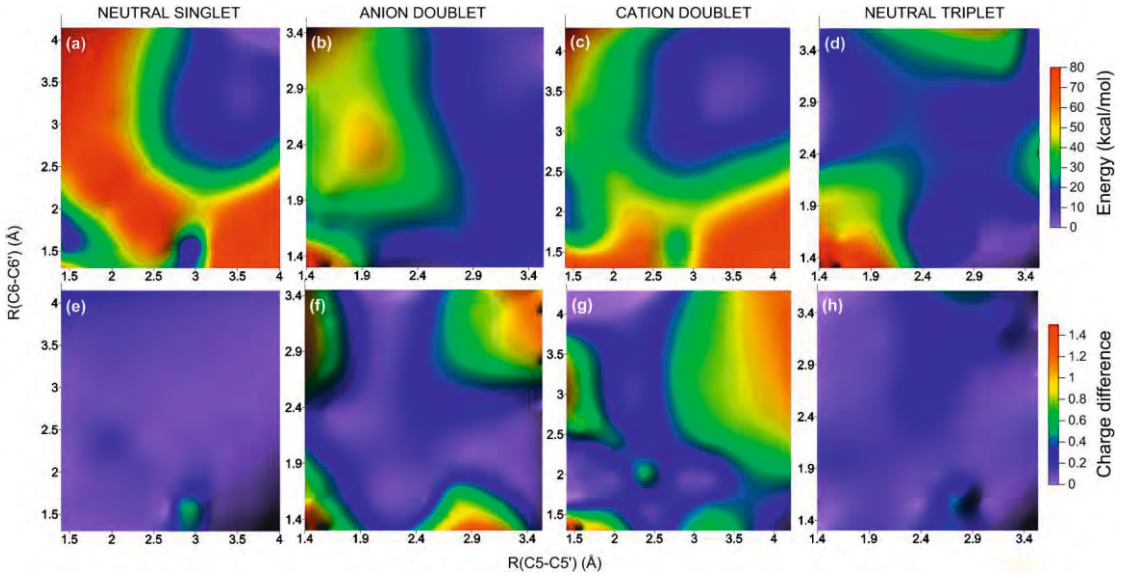

Fig. 13. Potential energy surface and charge distribution in the ground state of neutral and charged thymine dimers.

In collaboration with S. do Monte and R. Hilal, I have investigated the photochemistry of a series of halogen compounds, whose photoproducts may impact atmospheric chemistry [97, 104, 107]. One example is HCFC-132b (CF_2ClCH_2Cl), which is the major compound used for replacing CFC-113 ($CF_2ClCFCl_2$) in different industrial applications [107]. These simulations revealed how the radiation from different UV-wavelength regions interacts with these compounds and leads to formation of diverse products.

In recent years, the research on organic photovoltaics has become central in the field of photochemistry due to its high technological potential. Between 2014 and 2016, we investigated the fundamental properties of diverse organic compounds of interest for photoenergy conversion [13, 19, 31, 62, 102], including oligothiophenes (collaboration with W. Thiel) [31, 62], squaraine-fullerene complexes (also with W. Thiel) [19], and poly-(p-phenylene vinylene) (PPV) oligomers (with H. Lischka) [102]. In all these studies, our focus was the development of analytical tools to characterize charge and energy transport processes. In the case of oligothiophenes, for instance, we developed a new computational approach, in which the energy, relative ordering, and population of productive and unproductive electronic states of a molecular aggregate are monitored during the dynamic relaxation following photoexcitation. Applying this approach to a particular system – the photoexcited bi-thiophene dimer – we showed that few femtoseconds after light absorption, the dimer has two electronic energy bands separated by a sizable energy gap [62]. The high-energy band has a productive state lying on its bottom, while the low-energy band is composed of unproductive states only.

As the dimer relaxes, it populates the productive state on the bottom of the high-energy band. If the gap separating the bands remained constant, this productive state would survive for a long time, contributing to current generation. However, induced by molecular vibrations, the energy gap fluctuates and, when it gets to a minimum, the population is transferred to the low-energy unproductive band. As a result, the productive state survives for not more than 100 fs, rendering poor power conversion performance.

c) Method and program development

Since 2005, we have been designing and developing the Newton-X platform [92]. Newton-X is a collection of programs to perform all steps of excited-state nonadiabatic dynamics simulations, from the generation of initial conditions to the statistical analysis. The project involves collaborations with H. Lischka, J. Pittner, and others. Newton-X is an open-source platform distributed free of charge. Between 2014 and 2016, we finished the development of new interfaces for nonadiabatic dynamics using different wavefunctions and codes: MCSCF / GAMESS (collaboration with T. Windus) [99]; CC2 and ADC(2) / Turbomole; and (U)TDDFT, (U)TDA, and (U)CIS / Gaussian 09 [98, 106].

We have additionally implemented a new method for simulating steady and time-resolved photoelectron spectra based on nuclear ensembles (Figure 14) [105].

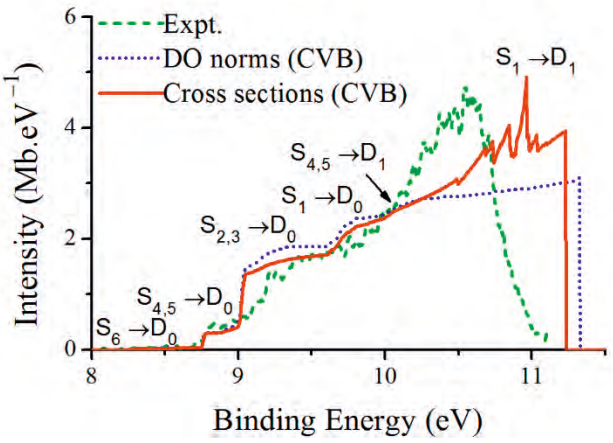

Fig. 14. Simulated time-resolved (0-25 fs) photoelectron spectrum of imidazole compared to experimental results.

Future directions: I was appointed professor of the chair of excellence A*MIDEX at the University Aix-Marseille, where I am since September 2015. A productive

collaboration with W. Thiel's group is still in place. We have been working on the characterization of exciton formation in an ensemble of organic heterojunctions for organic photovoltaics (collaboration with D. Fazzi) and on the development of a new program for computing spin-orbit couplings based on DFT methods (collaboration with X. Gao).

Outreach: Access to the Newton-X platform is gained via the Newton-X webpage (www.newtonx.org), where a full documentation and tutorials are available.

Publications resulting from this research area: 13, 19, 31, 42, 62, 91-107

External funding: DAAD DE/BR; KAU (SA); DAAD DE/HR; A*MIDEX (FR)

Cooperations: I. Antol (Zagreb, HR); A. C. Borin (Sao Paulo, BR): R. Crespo-Otero (London, UK); H. Hilal (Jeddah, SA); N. Kungwan (Chiang Mai, TH); H. Lischka (Lubbock, USA); T. C. Ramalho (Lavras, BR); E. Sánchez-García (Mülheim, DE); W. Sander (Bochum, DE); W. Thiel (Mülheim, DE); S. Ullrich (Athens, US); O. Weingart (Düsseldorf, DE); T. Windus (Ames, US)

2.5.6 Research Area "Molecular Interactions in Organic and Biological Systems. Applications and Methodological Implementations" (E. Sánchez-García)

Involved: K. Bravo-Rodriguez, S. Mittal, P. Sokkar, N. Tötsch, J. Iglesias, M. Fernandez-Oliva, S. Carmignani, G. Gerogiokas, V. Muñoz Robles, J. Mieres, L.Wollny

Objectives: In the Sánchez-García group, molecular interactions are used as a tool to tune the properties of chemical and biological systems. In this context three very much interconnected, general lines are developed (Figure 15). One key topic is the study of ***molecular interactions in biological systems,*** namely protein–ligand interactions, protein–protein interactions, enzymatic activity, and computational mutagenesis, as well as the effect of solvent on these processes. Another research line is the study of ***molecular interactions in chemical reactivity***, where we focus on reactive intermediates and unusual molecules and the effect of molecular interactions on their stability, spectroscopic properties, and reactivity. At the core of these applications lies the use and methodological implementation of ***multi-scale computational approaches***.

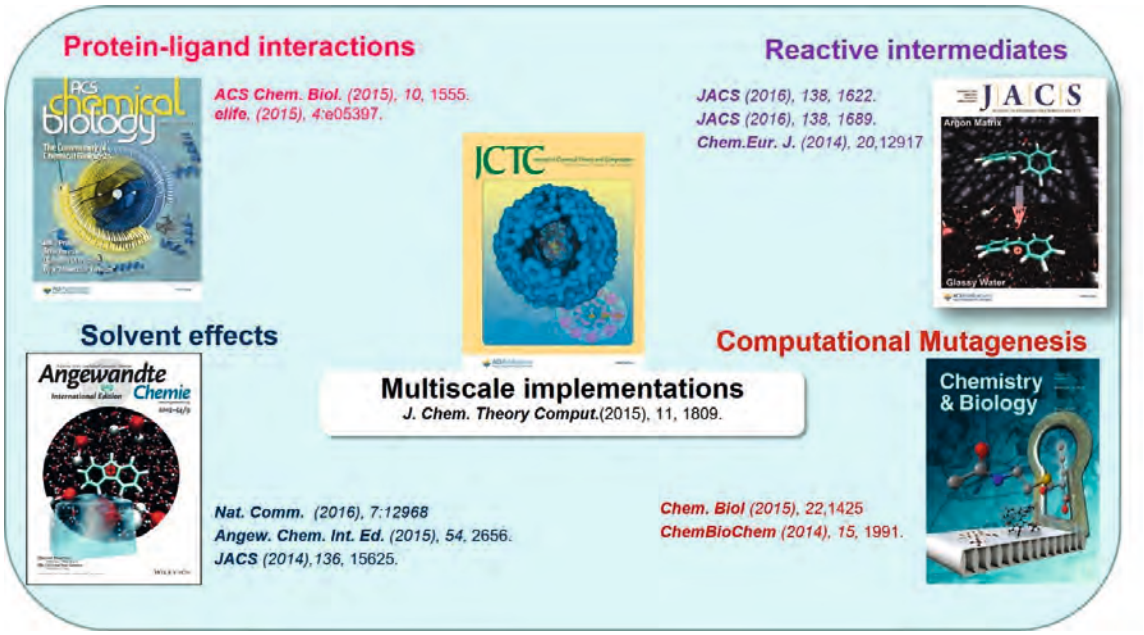

Fig. 15. Main research lines and selected representative publications of the Sánchez-García group in 2014-2016.

Results:

Molecular interactions in biological systems

a) Protein-ligand interactions

Interactions with small molecules can significantly influence the functionality of systems of diverse structural complexity – from amyloidogenic peptides to large proteins and enzymes. In our group we develop computational models of protein-ligand complexes to study their association and how such molecules can modulate protein–protein interactions. The combination of molecular dynamics simulations with free energy calculations and QM/MM methods allows us to predict ligand binding sites in a protein and to identify interactions patterns for an *in silico* design of improved ligands able to reach specific protein regions of biological relevance.

Specifically, we investigate the effect of selective ligands such as molecular tweezers (MT) that bind specifically to lysine and arginine residues, and molecules with a guanidiniocarbonylpyrrole (GCP) moiety targeting negatively charged amino acids. We are also interested in less specific compounds like aromatic heterocyclic derivatives and peptide ligands.

CLR01 is a lysine- and arginine-specific hydrogen phosphate tweezer able to inhibit the self-assembly and toxicity of several amyloid proteins *in vitro* and *in vivo*. In this context, we studied the interactions of the islet amyloid polypeptide (IAPP) with CLR01. Here, the selective binding to critical lysine residues is the molecular basis for the effect of the tweezer that causes IAPP to adopt an off-pathway conformation not found in the absence of CLR01 [117].

$PAP_{248\text{-}286}$ is the prototype amyloidogenic peptide in semen, closely related to the transmission of HIV-1. We found that CLR01 is able to bind all positively charged residues of $PAP_{248\text{-}286}$ in a conserved manner. Conversely, a control molecule consisting of the charged core of CLR01 only features labile interaction patterns with $PAP_{248\text{-}286}$. Thus, we were able to explain the lack of experimental effect of the spacer vs. the inhibition of toxicity by the tweezer [118]. Notably, the experimental studies indicated that CLR01 has a dual activity, namely destroying diverse enveloped viruses (including HIV) and remodeling amyloid fibrils in semen. To clarify how CLR01 can exhibit these two distinct activities, we also studied the molecular tweezer CLR05 that acts as potent anti-viral activity agent with no anti-amyloid activity. Unlike CLR01, the substituents in CLR05 are methylene carboxylate groups. Our previous studies with single amino acids and small peptides indicated that the hydrogen phosphate tweezer CLR01 threads lysine

or arginine side chains very efficiently through its tweezer cavity, while the carboxylate derivative CLR05 is only able to weakly bind the free amino acid outside its cavity by simple ion pairing. Hence, by investigating the CLR05 interaction with $PAP_{248-286}$ we could show that CLR05 is less able to form inclusion complexes with lysine or arginine compared to CLR01. The global minima on the peptide-tweezer free energy surfaces obtained from adaptive biasing force calculations indicated that binding of CLR05 to residues at the N- and C-terminal regions of $PAP_{248-286}$ is not favored. In addition, free energy perturbation calculations predicted that, in $PAP_{248-286}$, CLR01 forms better inclusion complexes than CLR05 for almost all Lys/Arg residues. Thus, we proposed that CLR05 may lack the anti-amyloid activity displayed by CLR01, in agreement with the experimental results (manuscript submitted).

We also studied the interactions of CLR01 with the Huntingtin protein exon-1. This protein is a key target in therapeutic strategies against Huntington's disease (HD), a neurodegenerative disorder without cure. We showed that the lysine residues found at low concentration in the N-terminal fragment of the exon-1 sequence (N17) are crucial for htt aggregation since binding of CLR01 induces structural rearrangements within the htt exon-1 monomer. In a joint experimental and computational study, we also demonstrated that CLR01 potently inhibits htt exon-1 aggregation, underpinning the key role of N17 in modulating htt exon-1 toxicity (manuscript submitted).

We previously reported studies on the selectivity of CLR01 towards Lys residues in a 14-3-3 protein. Now, we wanted to investigate also Arg complexation by molecular tweezers on proteins. In a combined experimental (P. Bayer, Essen) and computational study, we revealed the affinity profile of the tweezers to preferred lysine and arginine residues on the surface of the N-terminus region of the p97 protein (p97-N). Our QM/MM calculations confirmed the preferred complexation sites but also allowed us to discriminate between ambiguous host residues derived from NMR data. The binding of the tweezer to p97-N resulted in the inhibition of the protein-protein interaction between p97 and its cofactor UBXD1 [123].

In another multidisciplinary study using protein crystallography, biophysical affinity determination, and biomolecular simulations, we revealed the structural details of how the molecular tweezer CLR01 influences the 14-3-3/Cdc25CpS216 protein-protein interaction (PPI). CLR01 acts as a supramolecular "Janus" ligand that can bind simultaneously to a flexible peptidic PPI recognition motif and to a well-structured adapter protein (Figure 16). This binding "freezes" one of the conformational states of

the intrinsically disordered Cdc25C protein partner and enhances the apparent affinity of the interaction (manuscript submitted).

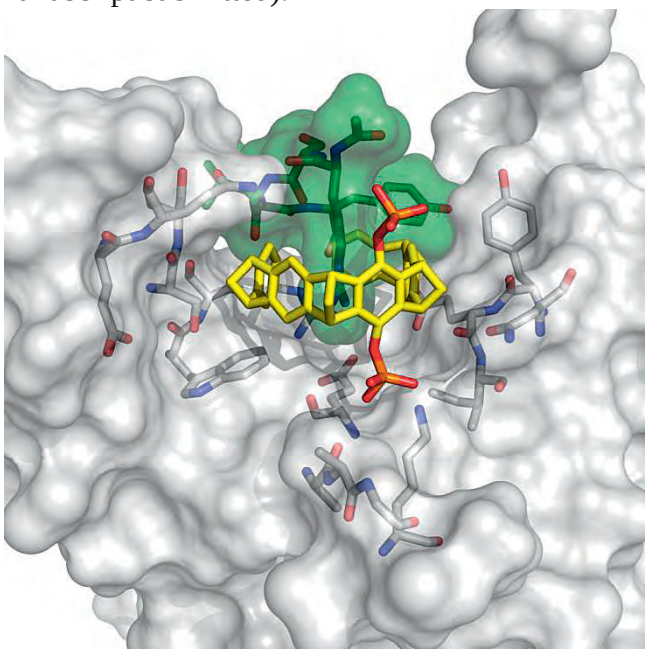

Fig. 16. CLR01 traps Arg 208 of Cdc25C (green surface) inside its cavity and simultaneously establishes contacts with 14-3-3ζ (white surface) via its hydrophobic sidewalls (yellow).

In another study on the 14-3-3ζ protein, we presented the first example of a small molecule binding to the 14-3-3ζ dimerization interface. This compound, featuring a GCP motif, was designed by rational *in silico* optimization of a peptidic ligand identified from a biochemical screening of a peptidic library. The binding was characterized by UV/Vis, MST, multiscale simulations, and X-ray crystallography. QM/MM MD simulations allowed us to investigate the binding of the ligand in solution and confirmed the dimer interface as preferred binding site (manuscript submitted).

The ribosome is a highly relevant but also complex system for ligand design. Macrolides, which are commonly used as antibiotics, are ligands targeting the ribosome. They can selectively bind at the prokaryote ribosome, inhibiting its function. Due to the increased antibiotic resistance of pathogenic strains, there is high interest in designing new synthetic macrolide molecules with enhanced binding to the ribosome. We used molecular dynamics simulations, free energy calculations, and QM/MM methods to study the binding of antibiotic derivatives to the ribosome in explicit solvent. This allowed us to establish which modifications of the macrolide core result in binders with better affinity and to clarify the role of the hydration free energy and conformational entropy on the binding events (unpublished work).

b) Protein-protein interactions and computational mutagenesis

Polyketides are natural products frequently used for the treatment of various diseases, but their structural complexity hinders efficient derivatization. In this context, we introduced enzyme-directed mutasynthesis to incorporate non-native extender units into the biosynthesis of erythromycin. More recently, we extended the molecular rationalization of enzyme-substrate interactions through modeling, to investigate the incorporation of substrates with different degrees of saturation of the malonic acid side chain. This allowed the biosynthesis of new erythromycin derivatives and the introduction of additional mutations into the AT domain for a further shift of the enzyme's substrate scope [113].

We are also interested in the study of disease-causing mutations in complex systems like *high temperature requirement A* (HTRA) serine proteases. Our free energy perturbation calculations predicted which of such mutations strongly destabilize the HTRA1 trimer. Molecular dynamics simulations of the wild type HTRA1 and the mutated systems allowed us to identify key interactions for the integrity of the enzyme. Our data suggested the presence of an intricate network of interactions composed of a hydrophobic cluster and two salt bridges that mediate trimer formation in this enzyme (unpublished work).

In addition to the human HTRA1, we also studied the bacterial serine protease DegP, this time as protein guest in a DNA origami host. Two models were considered for the binding of the 24-mer of DegP ($DegP_{24}$) inside the origami cage. In one model, $DegP_{24}$ interacts with opposite sides of the hexagonal cage while in the second model $DegP_{24}$ interacts with consecutive sides of the hexagonal cage. For each setup two binding motifs were considered. Our atomistic geometric models along with MD simulations suggested that the presence of three ligands per origami face should provide the maximal probability for binding to occur and that all DegP forms, although with distinct space-filling capabilities, can be hosted inside the DNA prisma (manuscript accepted, Nature Communications).

CXCR4 is a receptor protein of the chemokine receptor family. The CXCR4/CXCL12 signaling pair is associated with a variety of diseases like cancer cell metastasis or chronic inflammation. EPI-X4 is a peptide that specifically interacts with the receptor, thereby blocking CXCR4 (X4)-tropic HIV-1 infection and CXCL12 signaling. Our computational studies allowed us to propose binding sites of the peptide on CXCR4. The molecular environment was explicitly considered by embedding the protein in a full

atomistic membrane model and explicit water molecules. Our work revealed which residues of EPI-X4 are essential for receptor binding. On this basis, we made specific predictions for a next generation of EPI-X4 derivatives with improved binding efficiencies. These predictions were experimentally proven by the group of J. Münch (Ulm) and resulted in the generation of even more potent leads (unpublished work).

Molecular interactions on chemical reactivity

Carbenes and carbenium ions are challenging molecules and among the most important reactive intermediates in chemistry. They play key roles in a large number of reactions. In nucleophilic solvents such as alcohols, they can be extremely short-lived (lifetimes in the order of picoseconds), and it was believed that the corresponding cations could be stabilized only in super-acidic, non-nucleophilic solvents. We recently used QM MD and QM/MM MD approaches to investigate the reaction of diphenylcarbene (DPC), an archetypical triplet state carbene, with water in argon matrices and in water ice at 3 K. The combined matrix isolation (W. Sander, Bochum) and computational study allowed us to establish that, in the complex with a single water molecule, the triplet ground state of DPC is switched to its singlet state, stabilized by a strong hydrogen bond with water [109]. A similar effect was found for fluorenylidene (FY), where we also demonstrated that hydrogen bonds with protic solvents like water strongly influence the reactivity of the carbene by selectively stabilizing the singlet state and thus inverting the singlet-triplet gap [114].

The interactions between DPC and the halogen bond donor CF_3I were studied using QM and QM/MM calculations. CF_3I forms very strong complexes with the singlet state of DPC, but interacts only weakly with triplet DPC. This results in a switching of the spin state of DPC, with the singlet complex becoming more stable than the triplet complex. CF_3I forms a second complex (type II) with DPC that is thermodynamically slightly more stable. Our calculations predicted that in this second complex the DPC···I distance is shorter than the F_3C···I distance, whereas in the first complex (type I) the DPC···I distance is, as expected, larger. The type II complex could be only found as a minimum in the matrix environment (QM/MM calculations) and the interconversion was temperature-dependent. We also performed a 2-dimensional potential energy scan with the halogen bond distance and angle as reaction coordinates to explore the relative stability of these structures. The type II complex is characterized by a C-I distance of 2.3 Å. It is stable over a range of C-I-C angles while the type I structure is characterized by a nearly linear C-I-C angle and is stable over a range of C-I distances. Our study of intersystem crossing in the reaction of DPC and CF_3I indicated that it may occur when

the C-I distance is between 3.25 and 3.90 Å. The large calculated spin-orbit coupling may facilitate the intersystem crossing [67].

Unlike DPC and FY, bis(*p*-methoxyphenyl)carbene is the first carbene to be isolated in both its lowest-energy singlet and triplet states. We studied the influence of the C-C-C bond angle at the carbene center and of the conformational flexibility of the methoxy groups on the singlet-triplet gap. Unlike the carbene angle, the orientation and rotation of the methoxy groups have basically no influence on the relative stability of the conformers in the singlet or triplet state. In addition, to assess the impact of water on the singlet-triplet gap, several water complexes were computed considering not only the carbene center as a potential H-bond acceptor, but also both oxygen atoms of the methoxy groups. We found that hydrogen bonding with the methoxy groups shows a small tendency to stabilize triplet states over singlets, which is however not pronounced enough to overcome the larger effect of the interaction of water with the carbene center that strongly stabilizes the singlet [122].

In addition to the interactions with water, we were also interested in the effect of organic solvents and their mixtures on singlet-triplet gaps and carbene reactivity. In a combined broadband femtosecond transient absorption (P. Nürnberger, Bochum) and QM/MM study, we showed that for DPC the decision-maker is not the nearest solvent molecule but its neighbor. Therefore, variation of the solvent mixing ratio allows control over the reactivity of DPC. Using QM/MM molecular dynamics simulations, we also proposed two mechanisms for OH insertion into DPC by methanol [70] (Figure 17) and predicted possible side reactions.

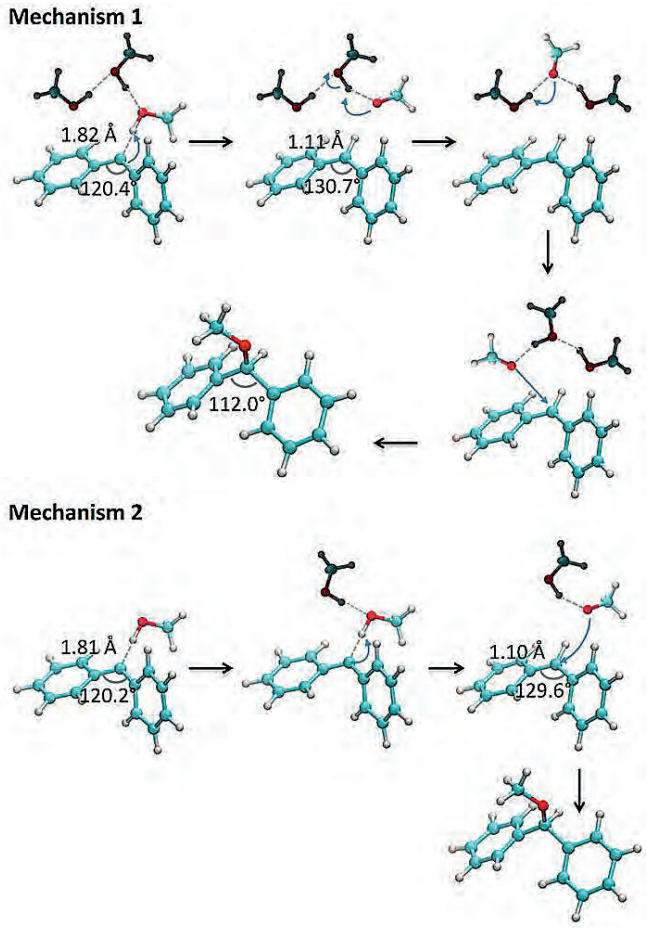

Fig. 17. Mechanisms 1 and 2 of O-H insertion for the reaction of singlet DPC with methanol, as observed in the QM/MM MD simulations. Average distances and angles are given.

Multi-scale computational approaches

Hybrid methods are at the core of our research. ChemShell is a QM/MM modular package that allows the combination of several QM and MM methods. Currently, there is considerable interest in the development of coarse-grained (CG) force fields to improve the performance and sampling in MD simulations and geometry optimizations. Although the CG methodology has been successfully applied to very large molecular systems, it does not allow the study of fine structural details due to the approximate CG representation. In this context, we have implemented a QM/MM/CG protocol in ChemShell. This approach was validated using two enzymes: chorismate mutase (CM) and p-hydroxybenzoate hydroxylase (PHBH). We also evaluated the role of CG modeling on biocatalysis. In CM, the inclusion of an atomistic MM water layer was necessary for a correct description of the energy profile. In the case of PHBH, the use of the polarizable CG model for the outer water did not affect the stabilization of the highly charged FADHOOH-pOHB transition state compared to the fully atomistic QM/MM calculations. A detailed performance analysis in a glycine−water model

system indicated that computation times for QM energy and gradient evaluations at the density functional level are typically reduced by 40−70 % for QM/MM/CG relative to fully atomistic QM/MM calculations [49].

We are currently working on the implementation of an interface to GROMACS in ChemShell and on the implementation of grid cell theory at the multiscale level. We are also implementing an approach to explore potential energy surfaces and to find thermally allowed intersystem crossings (ISC) in reactive intermediates based on QM molecular dynamics simulations.

Future directions: I plan to continue working on protein-ligand interactions. This will be extended to molecular tweezers with specific binding anchors designed to target certain regions of interest in the protein. Multivalent guanidiniocarbonylpyrrole ligands and novel peptide derivatives will also be investigated. The influence of the solvent on protein-protein interactions, enzymatic activity, and catalysis will be in the focus of our research. New reactive intermediates and their interactions with other organic molecules will be explored, and our QM MD approach for ISC will be implemented at the multiscale level to account for solvent and environmental effects.

Publications resulting from this research area: 49, 67, 70, 95, 108-123

External funding: Chemical Industry Funds (Liebig Stipend), German Research Foundation: RESOLV Cluster of Excellence (EXC 1069), Collaborative Research Center “Supramolecular Chemistry on Proteins” (SFB 1093), Boehringer Ingelheim Foundation (Plus-3 grant)

Cooperations:; P. Bayer (Essen, DE); G. Bitan (Los Angeles, US); R. Crespo-Otero (London, U.K); S. Ebbinghaus (Bochum, DE); M. Ehrmann (Essen, DE); J. Münch (Ulm, DE); P. Nürnberger (Bochum, DE); C. Ottmann (Eindhoven, NL); B. Sacca (Essen, DE); W. Sander (Bochum, DE); F. Schulz (Bochum, DE); T. Schrader (Essen, DE); W. Thiel (Mülheim/Ruhr, DE); E. Wanker (Berlin, DE)

2.5.7 Research Area "Biomolecular Solvation" (M. Heyden)

Involved: R. Persson, C. Päslack, V. Pattni, Y. Xu, B. Majumdar, A. Singh, D. Ray

Objective: Fundamental biomolecular processes involve major changes of the solvation for the involved molecular species: aggregation, folding, unfolding or conformational changes of proteins, complex formation of enzymes with their substrates, and the binding of ligand or drug molecules to receptors. Consequently, solvation free energies are a major driving force that determines thermodynamic equilibrium as well as kinetic barriers. Here, we develop novel simulation and analysis procedures to study microscopic contributions to the solvation free energy, which can be utilized for enzyme and drug design, as well as to understand a particular biomolecular system. Further, we utilize this information to improve implicit solvent simulations of concentrated biomolecular solutions on the *meso*-scale, which can describe realistic *in vivo* environments of biochemical processes.

Results: Atomistic molecular dynamics simulations with explicit solvent molecules contain, in principle, all the information required to analyze the influence of a molecular solute on the solvent energetics and structure. However, extracting this information, in particular separating energetic and entropic contributions to the total free energy, is often a challenging task. We have now developed a novel technique (3D-2PT), which provides not only total solvation energies and entropies of a given molecule, but resolves their local contributions in the three-dimensional environment of a molecule. A main challenge is the spatial resolution of the local solvent entropy, which we obtain from analyzing the local vibrational density of states (VDoS) of the solvent. The latter is obtained from time-dependent fluctuations of atomic velocities. Figure 18 shows an example analysis for a small model solute, which exhibits the chemical features of a peptide bond. Of particular importance for the analysis are low-frequency modes in the

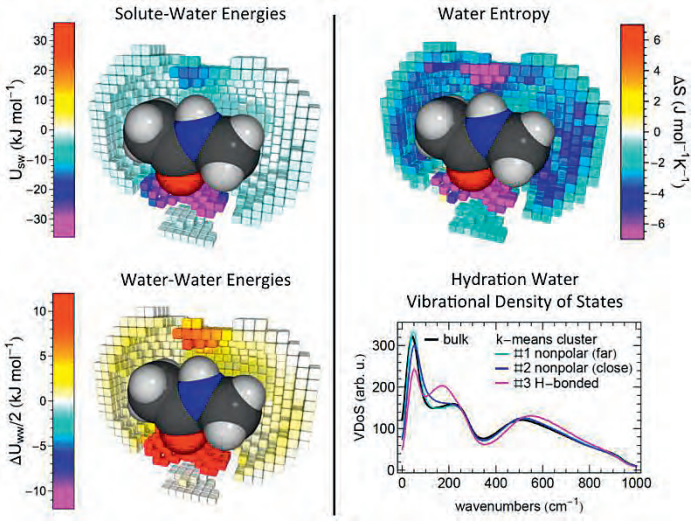

Fig. 18. Solvation free energy contributions in the hydration shell of N-methylacetamide. Local hydration water entropies are derived from spectra of thermally excited intermolecular vibrations (bottom right).

far-infrared range (0-330 cm^{-1} or 0-10 THz) of the vibrational spectrum, which are primarily characterized by intermolecular vibrations in the solvent, e.g. vibrations of the water hydrogen bond network. These vibrations are thermally accessible (k_BT/h=6 THz at 300K) and therefore carry the main part of the entropic information (Figure 19). The method can be applied for simulations of large biomolecular systems containing ~100,000 of atoms (Figure 20) and non-aqueous solvents.

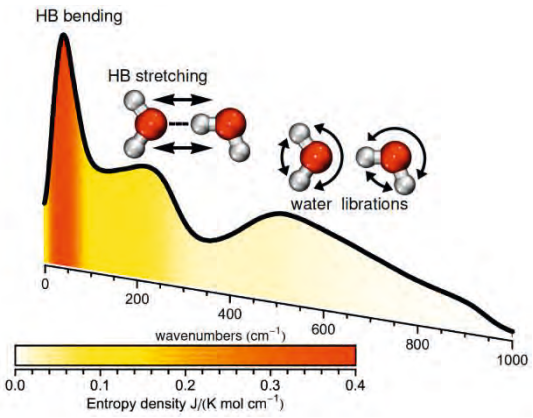

Fig. 19. Entropy information of characteristic intermolecular vibrations in the vibrational density of states of water.

A thermodynamic analysis based on the spectrum of intermolecular vibrations is particularly powerful in combination with spectroscopy experiments, which can follow changes in the solvent spectrum. This is realized by our cooperation partner Martina Havenith at the Ruhr-University Bochum, who develops time-resolved terahertz absorption spectroscopy methods. This technique allows for studies of non-equilibrium processes during a triggered reaction on a millisecond timescale, i.e. enzymatic catalysis in a stopped-flow experiment and protein unfolding/refolding after a laser-induced T-jump. Here, simulations of the biomolecular systems at different stages of the process can reproduce the observed spectral changes, in particular shifts of vibrational frequencies, and provide the microscopic information for the interpretation in terms of changes in the solvation energy, entropy and free energy.

Our analysis of spatially resolved thermodynamic properties of water in the hydration shell of proteins further allows detailed studies of the complex and non-additive effects that govern the interactions of biomolecules with their solvent, as well as their binding partners, i.e. ligands, substrates, or potential drug molecules. Biomolecular surfaces feature a heterogeneous mix of functional groups as well as various convex and concave surface curvatures. Both, surface topology and the chemical nature of solvent-accessible groups affect the solubility of a protein interface and the binding of other molecules. This results in broad distributions of hydration water properties, i.e. binding energies and local entropies.

Equally broad distributions are observed for hydration water dynamics, i.e. hydrogen bond network fluctuations, rotational relaxation and translational diffusion. These dynamic processes can be characterized in simulations via time correlation functions,

which is a routine application in our lab. A combined analysis of local thermodynamic and dynamic properties of water in the hydration shell of proteins allows us to study fundamental correlations between both. In particular, we can demonstrate that the molecular entropy of water is related to translational and rotational dynamics. Studying these correlations in detail provides the key for the thermodynamic interpretation of experimental observables that are sensitive to local hydration water dynamics at various sites of a biomolecular surface. For example, Overhauser dynamic nuclear polarization (ODNP) can be used to study local hydration water mobility in the vicinity of spin-labels attached to selected sites in the protein. These experiments are carried out in the group of our partner Songi Han at UC Santa Barbara. Our simulations are able to reproduce the observed variations in hydration water mobility, while providing at the same time a semi-quantitative ruler to translate experimentally detectable variations of local dynamics into variations in entropy.

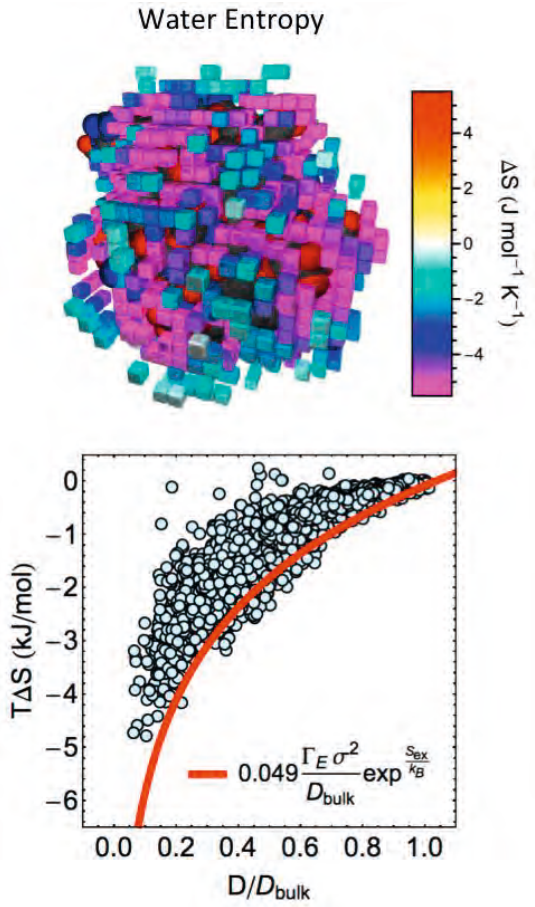

Fig. 20. Local hydration water entropies in the hydration shell of ubiquitin (top) are partially determined by local diffusion (bottom). The universal scaling law (red line), derived previously for bulk liquids, provides a lower limit for the local entropy (Dzugutov, M. *Nature* **1996**, *381*, 137-139).

A new target application of spatially resolved solvation free energies is their use as effective desolvation potentials in implicit solvent simulations of *meso*-scale systems of multiple interacting proteins and biomolecules. Together with the group of Douglas Tobias at UC Irvine, we recently developed a novel Monte Carlo simulation technique that includes efficient sampling of protein flexibility in simulations of complex protein solutions (Figure 21). We could show that this treatment significantly improves predictions of protein-protein interactions; however, the empirical treatment of (de)solvation free energies in the implicit solvation model remains a source of error. Our 3D-2PT approach enables us to derive tailored desolvation free energy potentials for the studied proteins directly from explicit solvent simulations, which then allow accurate simulations of biomolecular aggregation and molecular recognition in conditions resembling realistic biomolecular environments.

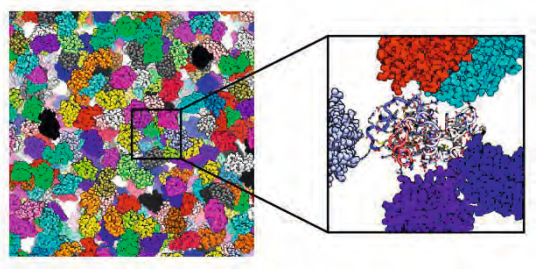

Fig. 21. Multiple-Conformation Monte Carlo simulation of a concentrated solution of lysozyme (169 mg/ml).

Future directions: We plan to extend the 3D-2PT methodology to mixed solvents, to develop a machine-learning procedure for the fast prediction of solvation free energies based on datasets generated by 3D-2PT simulations, and to derive computational tools to optimize the solvation free energy of lead compounds and ligand complexes.

Publications resulting from this research area: 124, 125, 128, 129, 132, 133, 134

External funding: Cluster of Excellence RESOLV (EXC-1069); European Research Council (via ERC Advanced Grant to M. Havenith); DAAD (stipend to D. Ray)

Cooperations: J. Dzubiella (Berlin, DE); S. Ebbinghaus (Bochum, DE); S. Han (Santa Barbara, US); M. Havenith (Bochum, DE); T. Head-Gordon (UC Berkeley, US); D. Russo (Grenoble, FR); L. Schäfer (Bochum, DE); D. J. Tobias (Irvine, US); M. Weik (Grenoble, FR)

2.5.8 Research Area “Ab Initio Quantum Chemical Methods for Complex Molecular Systems” (M. Roemelt)

Involved: A. Khedkar

Objective: A physically meaningful theoretical description of many complex molecular systems requires the usage of multireference methods. These methods treat a small part of the molecule, the so-called “active space”, exactly while the rest of the molecule is subject to approximations. In the last decade mathematical techniques such as the Density Matrix Renormalization Group (DMRG) have emerged that allow for multireference calculations with active space sizes that are out of reach for comparable standard quantum chemical methods. The objective of this research area is to develop extensions to the DMRG Ansatz that improve its accuracy and to allow the calculation of magnetic properties. Furthermore, application of these methods to transition metal compounds aims at understanding their unique physical and chemical properties.

Results: In the last decade the ab initio density matrix renormalization group (DMRG) has been shown to provide a reasonable and accurate alternative to complete active space (CAS) methods as basis for molecular multireference calculations. It can be regarded as an approximation to the exact diagonalization of the large Hamiltonian matrix in the basis of many-electron wavefunctions within the active orbital space. A great advantage of DMRG is that it approximately solves a problem whose complexity scales exponentially with increasing system size by optimizing only a polynomial number of parameters. Owing to this favorable behavior DMRG is able to treat large active spaces on the order of 20-80 orbitals. However, quantitative accuracy is only reached if dynamic electron correlation effects are considered, too. In the reporting period we have developed a novel approach to the combination of DMRG and strongly contracted second-order N-electron valence perturbation theory (SC-NEVPT2) for quantum chemical multireference calculations [138]. The main objective of this approach is to lower the cost of treating systems with large active spaces and large orbital spaces with a moderate and controllable accuracy. The complexity of the problem and the computational cost are reduced by projecting the perturber functions as well as the unperturbed Hamiltonian onto a reduced Hilbert space. The form of this reduced space is determined by a modified density matrix renormalization procedure. This procedure ensures that both the electronic ground state and the perturber functions are accurately approximated during the calculation. As a result, the total energy (DMRG + SC-NEVPT2) converges rapidly and smoothly towards the exact value with

increasing number of states in the renormalized Hilbert space as demonstrated for a dimeric Cu cluster (cf. Figure 22).

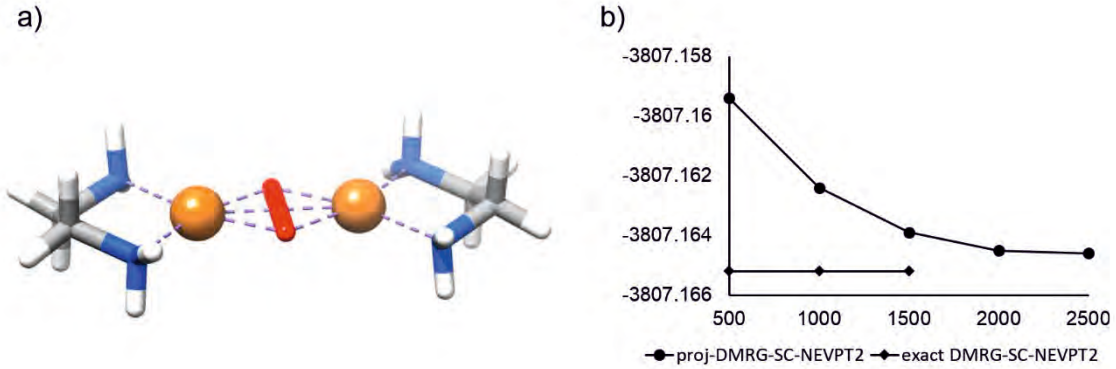

Fig. 22. Ball and stick visualization of $[Cu_2O_2(en)_2]^{2+}$ (a) and total energy calculated with the projected DMRG-NEVPT2 with respect to the bond dimension M (b).

Furthermore we have developed an approach to describe spin-orbit coupling (SOC) on top of a regular Born-Oppenheimer DMRG calculation in the framework of quasi-degenerate perturbation theory (QDPT) [136]. This approach accounts for SOC effects on the many-electron level and can thus be thought of as the molecular equivalent of atomic Russell-Saunders or LS coupling. With the spin-orbit coupled wavefunctions at hand the molecular g-tensors can be calculated in a rigorous and phenomenological way as proposed by Gerloch and McMeeking in 1975. Importantly, since the SOC matrix is fully diagonalized within a finite set of many-electron states, our approach is able to produce qualitatively and quantitatively correct results even for systems with a near-degenerate ground state. For example, the behavior of the molecular g-values of a Mo(III) trisamidoamine catalyst as it is distorted along its Jahn-Teller axis is correctly reproduced (cf. Figure 23). In contrast, regular linear-response type or single reference perturbation theory methods are bound to fail in these cases.

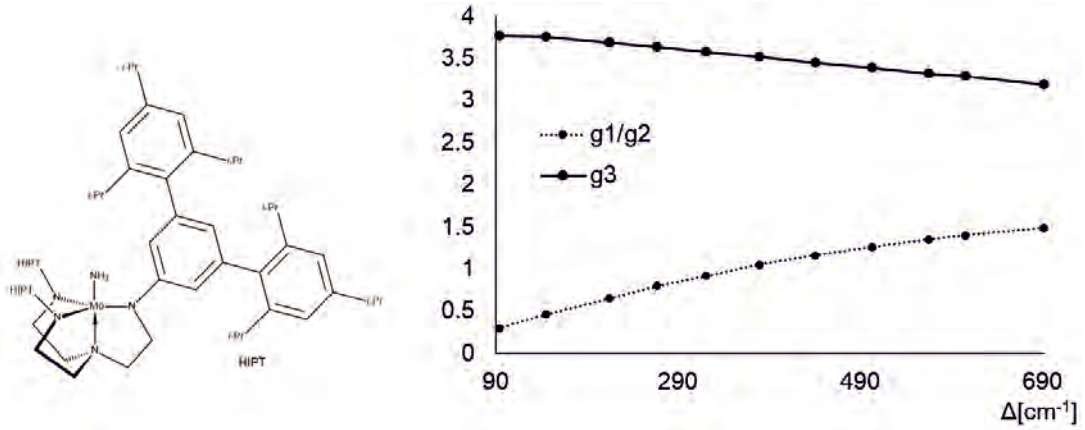

Fig. 23. Left: The chemically active Mo(III) trisamidoamine ammonia complex that is a crucial intermediate in the Yandulov/Schrock cycle. HIPT = hexaisopropylterphenyl. Right: The evolution of its molecular g-values with increasing Jahn-Teller splitting of the near-degenerate electronic ground state doublet.

During the reporting period our group has written our own standalone SCF and DMRG-SCF program from scratch. It has a variety of features including

- SCF for closed and open-shells
- DMRG-SCF (DIIS and full Newton Raphson)
- Density fitting
- Nuclear gradients
- Conventional and projected (vide supra) DMRG SC-NEVPT2
- Automated formula generation based on second quantization operator algebra
- Interfaces to the ORCA and PySCF program packages

The code is fully parallelized and utilizes the LibInt integral generation library by E. Valeev as well as the BLOCK code by G.K.-L. Chan. In the future it will be used in computational studies and moreover serve as basis for further developments in this field such as automated active orbital selection schemes and nonadiabatic coupling coefficients.

A study of the magnetic coupling constants of dimeric Mn compounds (cf. Figure 24), including a mixed-valence species, with DMRG-based methods elucidated the importance of different orbital subspaces for the description of magnetic coupling with *ab initio* techniques (manuscript in preparation). As anticipated, it could be shown that in addition to the Mn *3d* orbitals, the occupied *2p* orbitals of bridging oxo groups play an important qualitative role in magnetic coupling. In contrast, unoccupied oxo-orbitals or any orbitals that are located on bridging carboxylate groups contribute only in a minor way to the observed antiferromagnetic behavior. Moreover, the obtained results demonstrate that quantitative correct results can only be expected when dynamic electron correlation is explicitly taken into account.

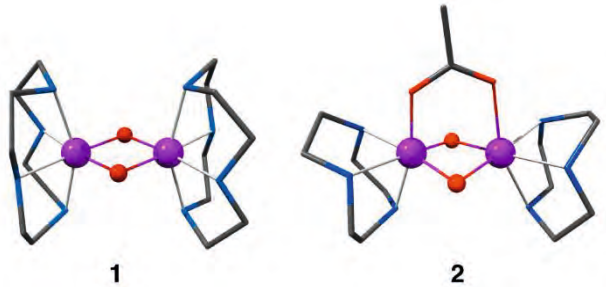

Fig. 24. Structures of the investigated Mn complexes. Color scheme: Mn purple, O red, N blue, C grey. Hydrogen atoms are omitted for clarity.

Future directions: Applications of the aforementioned theoretical methods will yield insight into the physical and chemical properties of complex molecular systems. A second scheme for the inclusion of SOC in molecular DMRG calculations will be implemented and applied. In addition, our code will be supplemented by a novel

automated selection scheme for large-scale active spaces as well as the ability to calculate nonadiabatic coupling coefficients to study chemical reactions on multiple adiabatic surfaces.

Publications resulting from this research area: 136, 138

External funding: none

Cooperations: G. K.-L. Chan (Princeton, NJ, US), V. Krewald (Wien, AT), D. Pantazis (Mülheim, DE), S. Sharma (Boulder, CO, US)

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Publications by other members of the Department (marked in bold) are included only if they carry the address of the Institute.

There are nine joint theory papers, which are listed twice but with a unique number. Joint research projects between the Thiel group and experimental groups in the Institute are documented in fifteen joint publications, which are listed both here and in the section of the experimental partner.

2.6 Biocatalysis – Emeritus Manfred T. Reetz

Emeritus:

Manfred T. Reetz (born 1943)

Curriculum Vitae: Manfred T. Reetz

1943	Born in Hirschberg (Germany) on August 13, 1943
1965	Bachelor degree, Washington University, St. Louis, USA
1967	Master degree, University of Michigan, Ann Arbor, USA
1969	Doctoral degree, Universität Göttingen with U. Schöllkopf
1971-72	Post-doc with R.W. Hoffmann at Universität Marburg
1973-1978	Assistant Professor at Universität Marburg (including Habilitation)
1978	Guest Professor at University of Wisconsin, USA
1978-1980	Associate Professor at Universität Bonn
1980-1991	Full Professor at Universität Marburg
1989-1990	Guest Professor at Florida State University, Tallahassee/USA
1991-2011	Director at the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr
1993-2002	Managing Director of the Max-Planck-Institut für Kohlenforschung
1992-2011	Honorary Professor at Ruhr-Universität Bochum
1993-2011	Chairman of Studiengesellschaft Kohle mbH (SGK)

Awards and Honors

1976	Chemical Industries Prize (Dozentenstipendium des Fonds der Chemischen Industrie)
1977	Jacobus van't Hoff Prize (The Netherlands)
1978	Chemistry Prize of the Academy of Sciences Göttingen
1986	Otto-Bayer-Prize (Germany)
1989	Leibniz Award of the Deutsche Forschungsgemeinschaft
1997-	Member of German National Academy of Sciences Leopoldina
1997	Fluka-Prize "Reagent of the Year 1997"
2000	Nagoya Gold Medal of Organic Chemistry
2001-	Member of Nordrhein-Westfälische Akademie der Wissenschaften
2003	Hans Herloff Inhoffen Medal
2005-	Foreign Member of the Royal Netherlands Academy of Arts and Sciences
2005	Karl-Ziegler-Prize (Germany)
2005	Cliff S. Hamilton Award in Organic Chemistry (USA)
2006	Ernst Hellmut Vits-Prize (Germany)

2006	Prelog Medal (Switzerland)
2007	Honorary Professor at Shanghai Institute of Organic Chemistry (China)
2007	Ruhr-Prize for Arts and Science (Germany)
2009	Lilly Distinguished Lectureship Award (Czech Republic)
2009	Arthur C. Cope Award, ACS (USA)
2009	Yamada-Koga Prize (Japan)
2011	Honorary doctoral degree of Johann Wolfgang Goethe-Universität, Frankfurt (Germany)
2011	Tetrahedron Prize for Creativity in Organic Chemistry
2011	Otto-Hahn-Prize (Germany)
2012	IKCOC-Prize (Japan)
2013	Susi and Barry Trost Lectureship
2014	Chirality Medal
2014	Paul Tarrant Lectureship (University of Florida/USA)
2015	Schulich Distinguished Lectureship (Technion/Israel)
2016	Honorary Member of the Israeli Chemical Society

1980-2016 > 165 Plenary Lectures and Name Lectureships

Other Activities / Committees

1987-1988	Chairman of Chemistry Department, Universität Marburg
1989-1992	Committee Member of Fonds der Chemischen Industrie (Engeres Kuratorium)
1990-1995	Member of the Board, German Chemical Society (GDCh)
1992-1996	Chairman of Selection Committee, August-Wilhelm-von-Hofmann-Prize (Denkmünze, GDCh)
1993-2004	Member of the Scientific Advisory Board, Institut für Katalyseforschung Rostock
1994-1998	Member of Selection Committee, Carl-Duisberg-Prize (GDCh)
1994-1999	Member of Advisory Board, *Nachrichten aus Chemie, Technik und Laboratorium*
1994-2001	Member of Selection Committee, Karl Heinz Beckurts-Prize
1995	Vice-President of German Chemical Society (GDCh)
1997	President of Bürgenstock-Conference

1997-2001	Member of Board, Katalyseverbund NRW
1997-2012	Member of Advisory Board, *Topics in Organometallic Chemistry*
1998-2005	Member of Selection Committee, Emil-Fischer-Medaille (GDCh)
1999-2007	Member of Advisory Board, Catalysis NRSC (The Netherlands)
1999-2005	Chairman of Selection Committee, Adolf-von-Baeyer-Prize /GDCh
1999-	Member of Selection Committee, Alfried Krupp-Prize
1999-2011	Member of Selection Committee, Otto Bayer-Prize (Bayer AG)
2000-	Member of Advisory Board, *Russian Journal of Organic Chemistry*
2000-2005	Member of Advisory Board, *Advanced Synthesis & Catalysis*
2001-2005	Member of Scientific Advisory Board for the School of Engineering and Science, International University Bremen
2002-2010	Member of Editorial Board, *Angewandte Chemie*
2003-2017	Member of the Kuratorium der Alfried Krupp von Bohlen und Halbach-Stiftung
2003-	Member of the International Advisory Board, *QSAR & Combinatorial Science*
2005-2013	Member of the Editorial Advisory Board, *Bulletin of the Chemical Society of Japan*
2006-2011	Member of the Advisory Board, *Topics in Stereochemistry*
2006/2007	Member of the International Advisory Board of the Chemistry Department of Nagoya University (Japan)
2007-2015	Senator of the Chemistry Section, German National Academy of Sciences Leopoldina
2008-2010	Member of Advisory Board of the Karl Ziegler-Foundation (German Chemical Society)
2008-	Member of Ethics Committee of the Max Planck Society
2009-	Associate Editor of Chemistry and Biology
2009-2010	President of BOSS XII
2009-2010	Coordinator of ORCHEM 2010
2011-2013	Speaker of Class I of the German National Academy of Sciences Leopoldina
Since 1980	Member of Advisory Committees of numerous scientific conferences

Research in Biocatalysis: External Emeritus Group of M. T. Reetz

Following formal retirement as Director of the Department of Synthetic Organic Chemistry in August 2011 at age 68, Manfred T. Reetz continued research as the first Hans-Meerwein-Research-Professor in the Chemistry Department of Philipps-University in Marburg. As part of a 5-year contract with participation of the Max-Planck-Society, the MPI für Kohlenforschung and the Philipps-University, the Max-Planck-Society pledged to support 5-6 postdocs with stipends in addition to funds for consumables. The Mülheim MPI offered access to its infrastructure and some additional support for consumables, while Marburg provided lab space, infrastructure and likewise some support for consumables. During this time Reetz was also a member of the LOEWE network SynChemBio, financed by the state of Hessen.

On August 31st 2016 the 5-year contract terminated. Two of the four remaining postdocs with stipends are now financed by the Mülheim MPI until the summer and winter of 2017, respectively. The other two postdocs receive salary support from Reetz third party funding (A. C. Cope Fund/USA) until the summer and fall of 2017, respectively.

The primary topic in the Biocatalysis Group is directed evolution of stereo- and regioselective enzymes as catalysts in organic chemistry and biotechnology. Following proof-of-principle by the Reetz group in 1997, this Darwinian approach to asymmetric catalysis has been generalized, and indeed today numerous academic and industrial groups around the world are actively using the technology. During the last three years, the group has focused on four major projects:

- Methodology development with the aim of making directed evolution more efficient, faster, and therefore highly reliable.
- Applications in synthetic transformations that are problematic or even impossible using state-of-the-art transition metal catalysts or organocatalysts, thereby demonstrating complementarity of the three approaches.
- De novo design of one-pot cascade reactions enabled by directed evolution.
- Learning from directed evolution by performing mechanistic, structural and theoretical studies of selected mutants.

2.6.1 Research Area "Methodology Development in Directed Evolution of Selective Enzymes in Organic Chemistry" (M. T. Reetz)

Involved: C. G. Acevedo-Rocha, R. Agudo, S. Hoebenreich, A. Li, G. Li, A. Ilie, R. Lonsdale, Z. Sun, J. Wang, F. E. Zilly

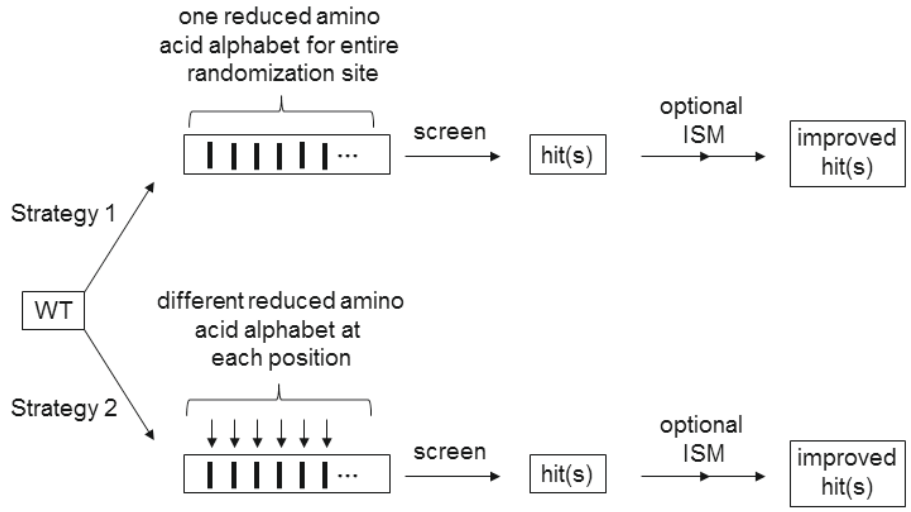
Objective: As part of our intensified continuation of methodology development in directed evolution, new methods and strategies were devised which enable the generation of highest-quality mutant libraries requiring minimal screening (traditionally the bottleneck of directed evolution). The ultimate goal is to develop a "mature" directed evolution in which screening is no longer the slow step in the overall process.
Results: Two fundamentally different approaches to methodology development were considered: 1) Advanced techniques for beating the numbers problem in directed evolution; and 2) Exploring the possibility of solid-phase gene synthesis in mutant library construction as an alternative to the usual molecular biological (genetic) approach.

Beating the numbers problem:
We have previously developed the *C*ombinatorial ***A***ctive-Site ***S***aturation ***T***est (CAST) in which sites comprising 1, 2, 3 or more residues lining the enzyme binding pocket are randomized using codon degeneracies ranging from NNK encoding all 20 canonical amino acids to those that encode reduced amino acid alphabets down to 5-6 amino acids as combinatorial building blocks for the whole site. Application of our CASTER computer aid, based on the Patrick/Firth-algorithm, shows that when using NNK codon degeneracy for saturation mutagenesis, the degree of oversampling for ensuring 95% library coverage rapidly reaches astronomical numbers. These numbers can be reduced sharply upon applying, for example, NDT codon degeneracy encoding only 12 representative amino acids, *but randomizing sites larger than 4-5 residues still requires excessive screening* (Table 1).[2,18,26,27,30]

	NNK (20 aa)		NDT (12 aa)	
number of amino acid positions at one site	codons	transformants needed	codons	transformants needed
1	32	94	12	34
2	1028	3066	144	430
3	32768	98163	1728	5175
4	1.05×10^6	3.14×10^6	20736	62118
5	3.36×10^7	1×10^8	2.49×10^5	7.45×10^5
6	$>1 \times 10^9$	$>3.2 \times 10^9$	$>2.9 \times 10^6$	$>8.9 \times 10^6$
7	3.4×10^{10}	1×10^{11}	3.5×10^7	1.1×10^8
8	1×10^{12}	3.3×10^{12}	4.2×10^8	1.3×10^9

Table 1

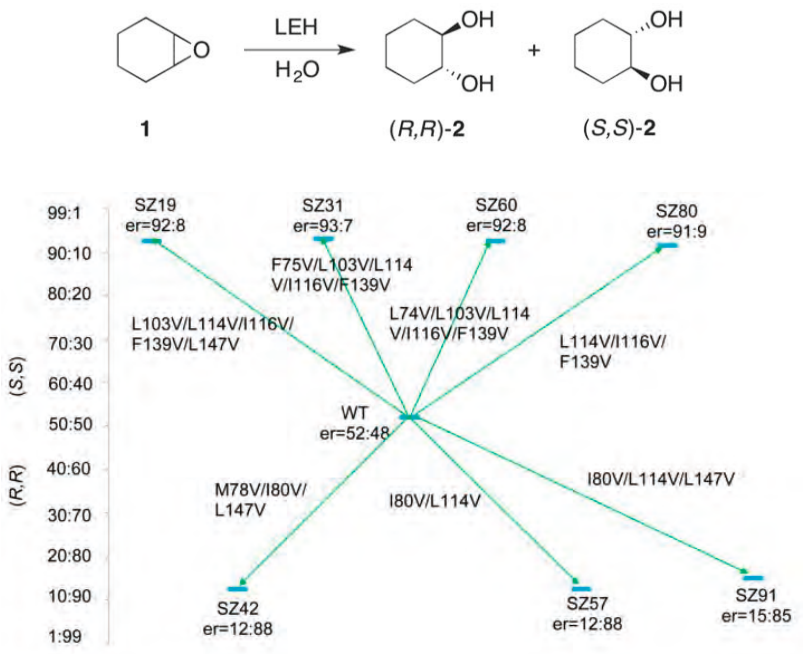
We systematized saturation mutagenesis according to the principle shown in Scheme 1 which features two different strategies.[30,40] Criteria for rationally choosing reduced amino acid alphabets were also developed using *1) Crystal structures, revealing the electronic and steric nature of CAST residues*[18,37]*; 2) bioinformatics consensus information derived from multiple sequence alignment in the CAST region* [18,26,27,37]*; 3) exploratory NNK-based saturation mutagenesis at individual positions at CAST sites requiring in each case only one 96-format microtiter plat*e, revealing which single mutations may be crucial in subsequent combinatorial mutagenesis at large randomization sites.[28,38] The most frequently "occurring" amino acids are then used as reduced amino acid alphabets.



Scheme 1

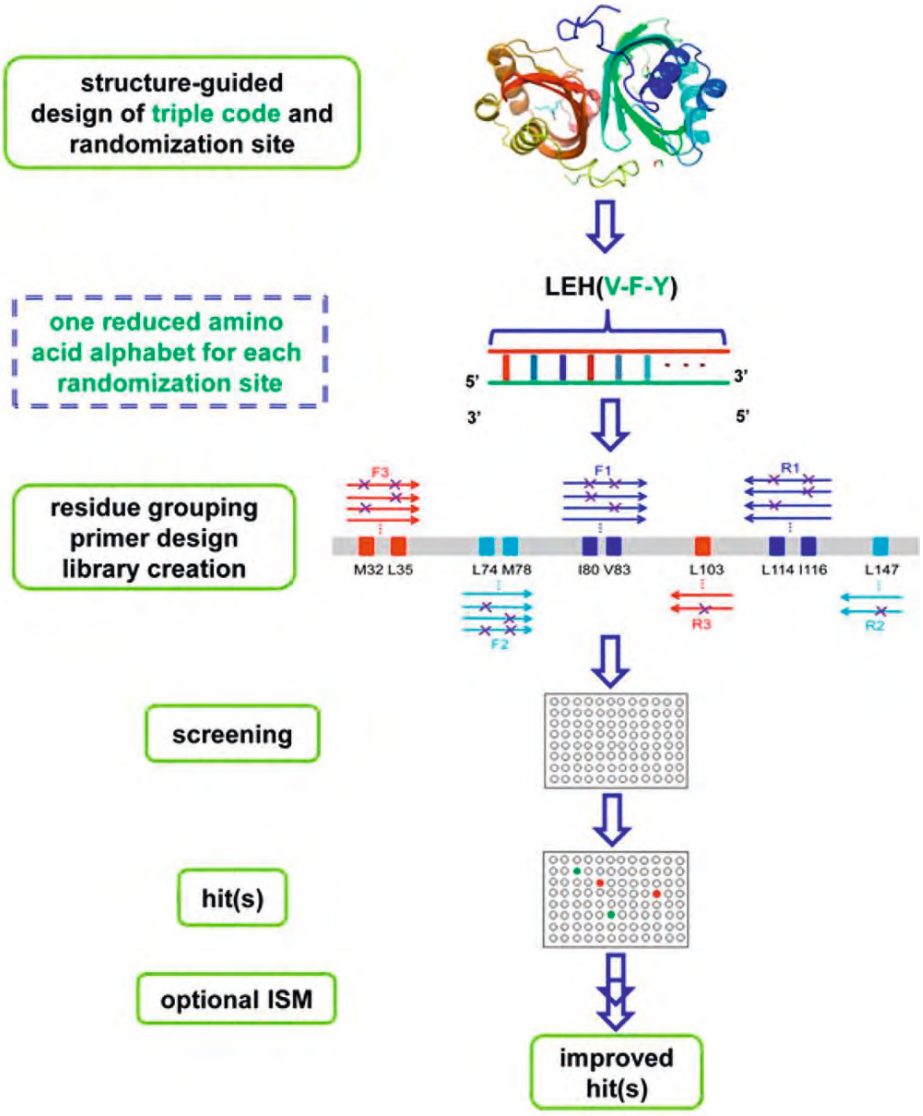
An example of strategy 1 (Scheme 1), in which a single amino acid was used to randomize 10 CAST positions in a single saturation mutagenesis experiment requiring only 3,000 transformants for 95% library coverage concerns the hydrolytic desymmetrization of cyclohexene oxide catalyzed by the limonene epoxide hydrolase (LEH) with formation of the (*R*,*R*)- and (*S*,S)-diols,[18] (Scheme 2). *NNK or NDT would*

have required the screening of $3x10^{15}$ or $2x10^{11}$ transformants, respectively! Since the crystal structure of wildtype (WT) LEH shows essentially only hydrophobic residues surrounding the binding pocket, *valine as a bulky hydrophobic amino acid was chosen as the sole building block.* Scheme 2 shows that excellent results were obtained in one and the same small library generated by single code saturation mutagenesis (SCSM). [18] In the case of the best (*R,R*)-selective mutant (er = 12:88), only one round of iterative saturation mutagenesis (ISM) boosted stereoselectivity to er = 2:98. [18] Typically 3 or 4 valines were introduced at different CAST positions in a given improved mutant, which causes notable changes in the shape of the binding pocket, thereby inducing a specific orientation as the reactive pose of the substrate. The best mutants were also tested in the reaction of other structurally different epoxides.



Scheme 2

Although the extreme case of SCSM proved to be successful,[18] we do not recommend it as a general guide. Instead, *triple code saturation mutagenesis (TCSM) involving three rationally chosen amino acids appears to be a viable compromise between structural diversity and screening effort*, provided appropriate choices of reduced amino acid alphabets are made.[27,28,38] Using the same LEH-based platform, but this time with valine/phenylalanine/tyrosine (V-F-Y) as building blocks in TCSM (Scheme 3), even better results were obtained with less screening.[27]



Scheme 3

Importantly, TCSM was also tested using two other enzyme types in reactions of synthetically challenging substrates, again requiring only small libraries screened by automated chiral GC:

• *ADH as catalyst in the reduction of difficult-to-reduce prochiral ketones.*[28]

• *P450-BM3 as catalyst in the multi-step transformation of cyclohexane into (R)- and (S)-2-dihydroxycyclohexanone.*[38]

On the basis of these developments, we conclude that TCSM, *being step-economical,* is currently the best strategy. It is superior to SCSM,[18] double code saturation mutagenesis (DCSM)[37] and binary patterning.[39] It should be noted that primer design is a rational molecular biological exercise,[1,2,40] but when making decisions in CAST-based directed evolution, the cost of primers also deserves attention, as delineated in our study focusing on techno-economical analyses.[20]

Finally, *an efficient technique for multi-parameter optimization of thermostability, enantioselectivity and activity was developed,* in which saturation mutagenesis was performed at CAST sites for enantioselectivity and activity and simultaneously at remote residues displaying the highest flexibility as judged by B-factors (B-FIT technique) for stability.[31]

Solid-phase gene synthesis in mutant library construction:
Driven by international technological developments, the cost of gene syntheses has dwindled in recent years, but synthesizing a thousand potentially enantioselective mutants may appear to be unreasonable. However, if this is done combinatorially, it proves to be feasible. We chose a mechanistically complex enzyme and first designed P450-BM3 CAST libraries for selective hydroxylation of a model compound, and generated them by the usual genetic manner. In parallel, the design schemes were sent to a company which applied their chemical technology called *Sloning, which involves solid-phase gene synthesis.* Subsequently we compared the libraries. *We discovered that the Sloning libraries are superior in terms of quality and diversity (less amino acid bias, less repetition of wildtype, etc.).* If the prices of such libraries continue to tumble, then the usual molecular biology applied in saturation mutagenesis will be replaced by such a *chemical approach*. Other companies are now offering commercial libraries prepared by solid-phase gene synthesis on chips which promise to have significantly higher library quality and diversity. Library design based on CASTing, ISM, reduced amino acid alphabets, etc. will then play the key role when applying such a chip-technology. *The future of directed evolution?*

Future directions: Proving the generality of TCSM is necessary, especially when combined with simultaneous multi-parametric optimization of stereoselectivity, activity and thermostability. (one of the remaining challenges in directed evolution). Particularly exciting would be the implementation of an alternative to Sloning-mediated gene synthesis, namely solid-phase based generation of mutant gene libraries on microchips, possibly in combination with microfluidic devices.

Publications resulting from this research area: 1, 2, 7, 14, 17, 18, 20, 26- 28, 30, 31, 37-40.

External funding: LOEWE Research Cluster SynChemBio (Hessen, DE); Arthur C. Cope Fund (US)

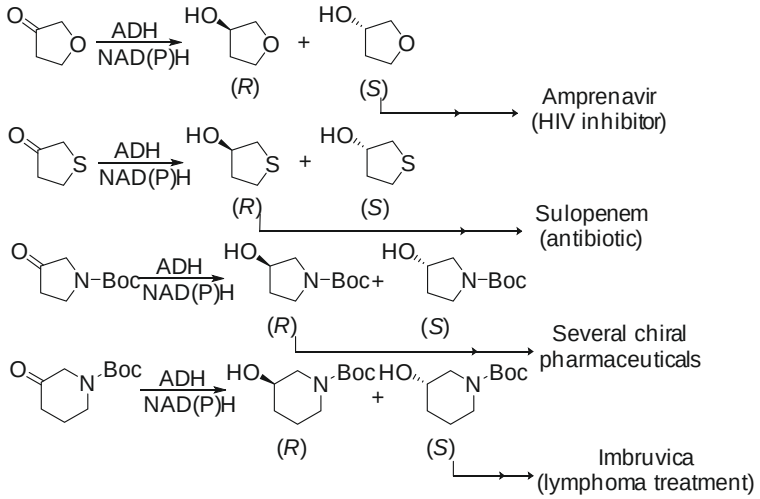
Cooperations: Y. Nov (Statistics Department, Haifa University/IL), M. Zilly (Physics Department, Duisburg-Essen University/DE), J. Zhou (Shanghai Institute of Organic Chemistry/CN); J.-H. Xu (East China University of Science and Technology, Shanghai/CN), J.-E. Bäckvall (Stockholm University/SE)

2.6.2 Research Area "Applications of Advanced Directed Evolution Methods" (M. T. Reetz)

Involved: C. G. Acevedo-Rocha, R. Agudo, A. Ilie, A. Li, R. Lonsdale, G.-D. Roiban, J. Sanchis, Z. Sun, J. Wang, Z.-G. Zhang

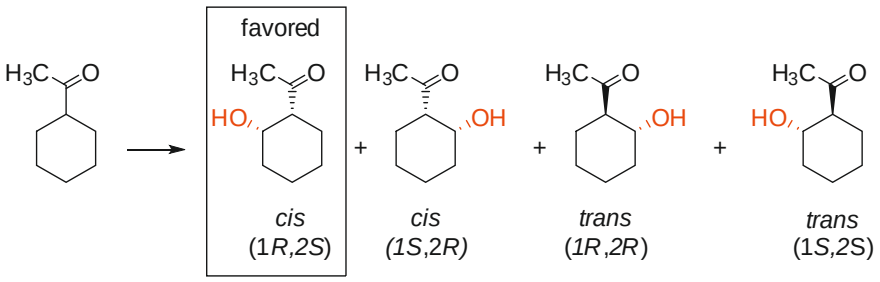
Objective: Application of newly developed directed evolution methods to selected stereo- and regioselective reactions in synthetic organic chemistry with primary emphasis on those transformations that are not readily possible using state-of-the-art transition metal catalysts or organocatalysts.

Results: Directed evolution generally involves a model substrate, the evolved mutant(s) being highly stereoselective for that particular compound. However, organic chemists need catalysts that are active and selective not just for a single compound (unless a pharmaceutical company is interested in only one specific transformation).[34,40] We have therefore tested our mutants not just for model substrates, but also for additional compounds. Typical examples follow: Upon applying triple code saturation mutagenesis (TCSM) as an advanced form of CASTing to the robust alcohol dehydrogenase from *Thermoethanolicus brockii* (TbSADH) using 3-oxo-tetrahydrofuran as substrate, *both (R)- and (S)-selective mutants were evolved step-economically (95-99% ee at full conversion) in a single library*.[28] *Commercial chiral Ru-catalysts failed to provide acceptable levels of enantioselectivity.* The mutants were also applied to other difficult-to-reduce ketones[28] (Scheme 1) and to structurally very different substrates,[35] likewise leading to 94-98% ee.

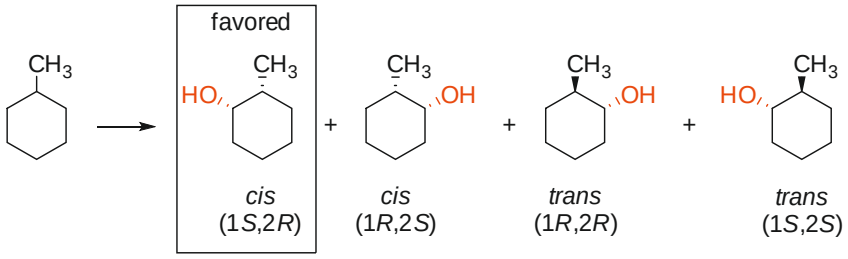


Scheme 1

Extensive work with P450-BM3 was performed in various applications.[6,9,11,12,15,17,21,38] An example is simultaneous control of regio-, enantio- and diastereoselectivity in the hydroxylation of achiral compounds with concomitant creation of two chirality centers, catalyzed by mutants evolved by applying CASTing based on the use of a 6-membered reduced amino acid alphabet. Scheme 2 shows two substrates, six others reacted similarly.[6] *Notice that the potentially most reaction positions with the weakest CH-bonds were not attacked!*



Best mutant: Regioselectivity: 78 : 22
Diastereoselectivity: 98 : 2
Enantioselectivity: 98 : 2
Conversion: >85%



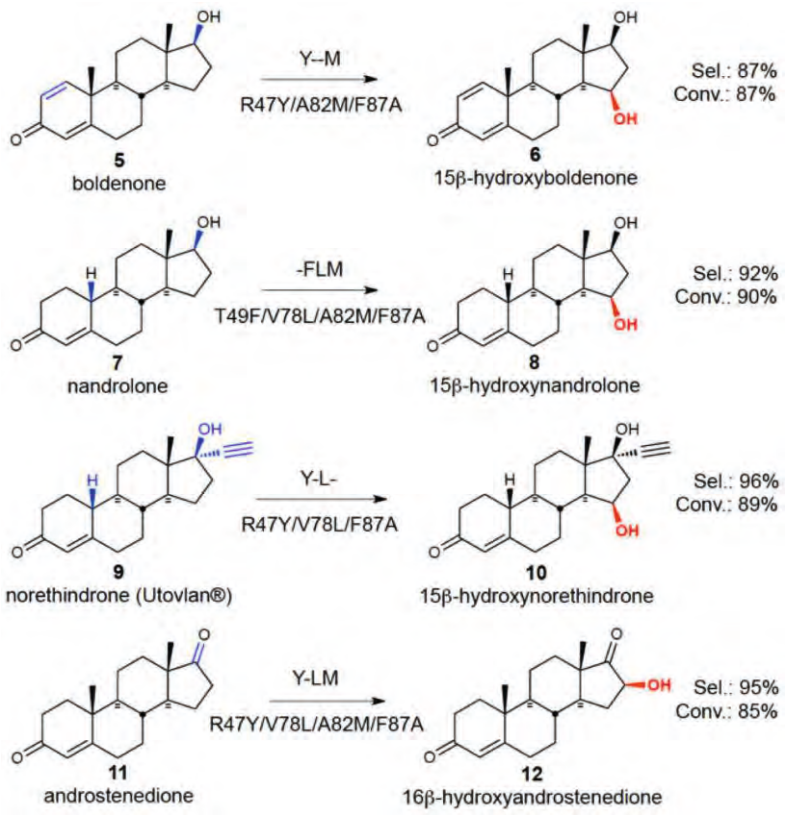
Best mutant: Regioselectivity: 71 : 29
Diastereoselectivity: 97 : 3
Enantioselectivity: 96 : 4
Conversion: >85%

Scheme 2

Enantioselective α-hydroxylation of ketones can be performed in many cases with transition metal catalysts or organocatalysts. Nevertheless, we performed P450-CASTing with a rationally chosen reduced amino acid, which provided small mutant libraries harboring hits with 96-99% ee for (*R*)- and inverted (*S*)-selectivity (Scheme 3).[17] *The mutants were also tested with 19 other substrates,* often (but not always) leading to >90% ee.

Scheme 3

In the last 3-Year Report (2011-2013) we described the first case of P450 directed evolution for controlling regioselective hydroxylation of testosterone at the 2ß- and 15ß-positions on an optional basis as part of "late-stage hydroxylation". Since then the CAST-approach has been improved significantly as part of methodology development (see Reetz report 1), also with the aim of targeting other positions in steroids. Typical examples are featured in Scheme 4, the first three cases involving 15ß-selectivity of further steroids, *the last one illustrating an evolved switch to hydroxylation at position C16*.[41] We have since investigated a total of 15 structurally different steroids, which is of significance for the pharmaceutical industry.

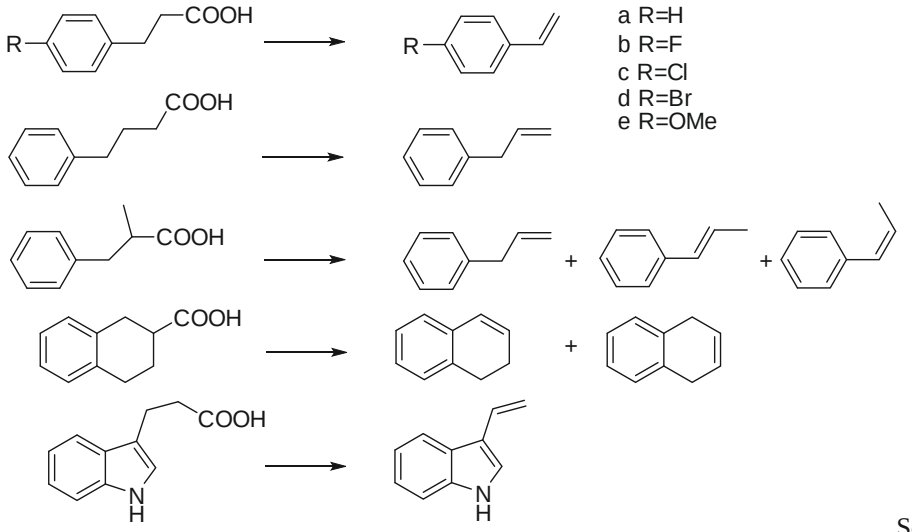


Scheme 4

Further work with P45-BM3 in selective oxidation reactions involved:

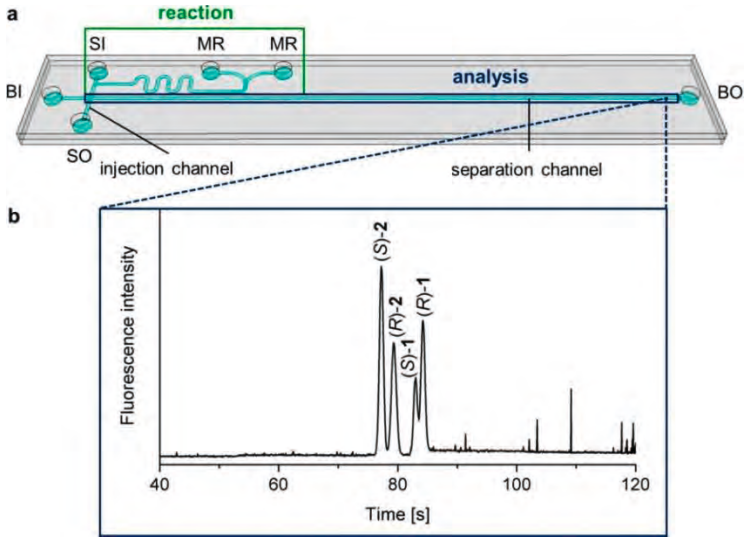
- *Regio- and enantioselective hydroxylation of substituted 1-tetralones at the 4-position with formation of alcohols that are chiral components of prominent Chinese folk medicines.*[9]
- *Regio-, diastereo- and enantioselective hydroxylation of achiral alkanes with formation of alcohols having three centers of chirality in a single CH-activation event. (The principle was illustrated, but in the absence of further mutagenesis, the degree of overall selectivity remains low to moderate in this case).*[11]
- *Diastereoselective epoxidation of cyclic alkenes involving anti- versus syn preference.*[12]
- *Chemo- and regioselective hydroxylation as a means to perform bioorthogonal activation of caged compounds in living cells.*[21]

Further projects involved altogether different goals. Inspired by the recently reported P450-peroxydase $OleT_{JE}$, which in nature catalyzes the oxidative decarboxylation of fatty acids $RCH_2CH_2CO_2H \rightarrow RCH{=}CH_2$, a directed evolution study was initiated in which structurally very different carboxylic acids were tested at room temperature using air as the oxidant (Scheme 5).[32] Since practical problems were encountered in setting up optimal expression and screening systems, only very small rationally designed libraries were generated. Increased activity in broadening substrate acceptance as well as high regioselectivity but moderate diastereoselectivity favoring trans-olefins were observed. This is the *first time that such an enzyme has been used to produce di-substituted olefins from branched carboxylic acids*.[32] It is a mild alternative to the Pd-mediated Gooßen-method at 120 °C (best chemical method).



Scheme 5

Other projects focused on the substrate range of mutants of epoxide hydrolases,[18,27,30,37,39] of promiscuous Baeyer-Villiger monooxygenases as sulfoxidation catalysts,[10] and in the practical one-step transformation of cyclohexanone into caprolactone.[16] A phosphotriesterase was evolved iteratively as a robust degrader of the widely used pesticide malathion,[36] which can probably be used for the detoxification of other more dangerous phosphorous-based compounds. In a different type of application, *Aspergillus niger* epoxide hydrolase mutants were applied to a hydrolytic kinetic resolution and *used for the first time in an integrated microfluidic device in which only a few hundred cells were necessary for enantioselectivity quantification* (Scheme 6).[29]



Scheme 6

Future directions: Late-stage P450 hydroxylation in a natural products synthesis would be one interesting topic, as is advanced directed evolution of $OleT_{JE}$ for generalizing oxidative decarboxylation of structurally different carboxylic acids as a mild olefin synthesis. Evolving desaturases for introducing double bonds regioselectively in any given organic compound is yet another challenging goal. Also of interest, an alcohol dehydrogenase such as TbSADH could be subjected to directed evolution so that it becomes a transaminase with ammonia being the amine source (ketones exist in equilibrium with small amounts of the ketimine), with significant advantages over transaminases. Directed evolution of cascade sequences is another "hot" topic.

Publications resulting from this research area: 6, 9, 10-12, 15-18, 21, 27-29, 32, 35-38, 40

External funding: LOEWE Research Cluster SynChemBio (Hessen, DE); Arthur C. Cope Fund (US)

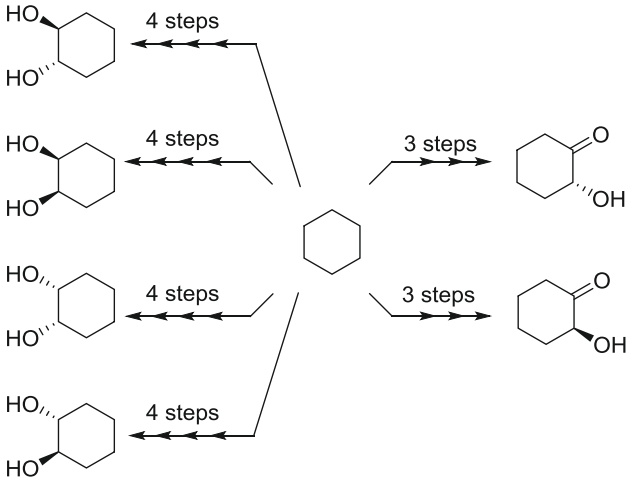
Cooperations: E. Meggers (Marburg, DE); I. Korendovych (Syracuse, US), D. Belder (Leipzig, DE); J. Zhou (Shanghai Institute of Organic Chemistry, CN); J-H. Xu (East China University of Science and Technology, Shanghai, CN); J. Sanchis (Monash University, AU)

2.6.3 Research Area "Creation of Designer Cells for Redox-based Enzymatic Cascade Reactions Enabled by Directed Evolution" (M. T. Reetz)

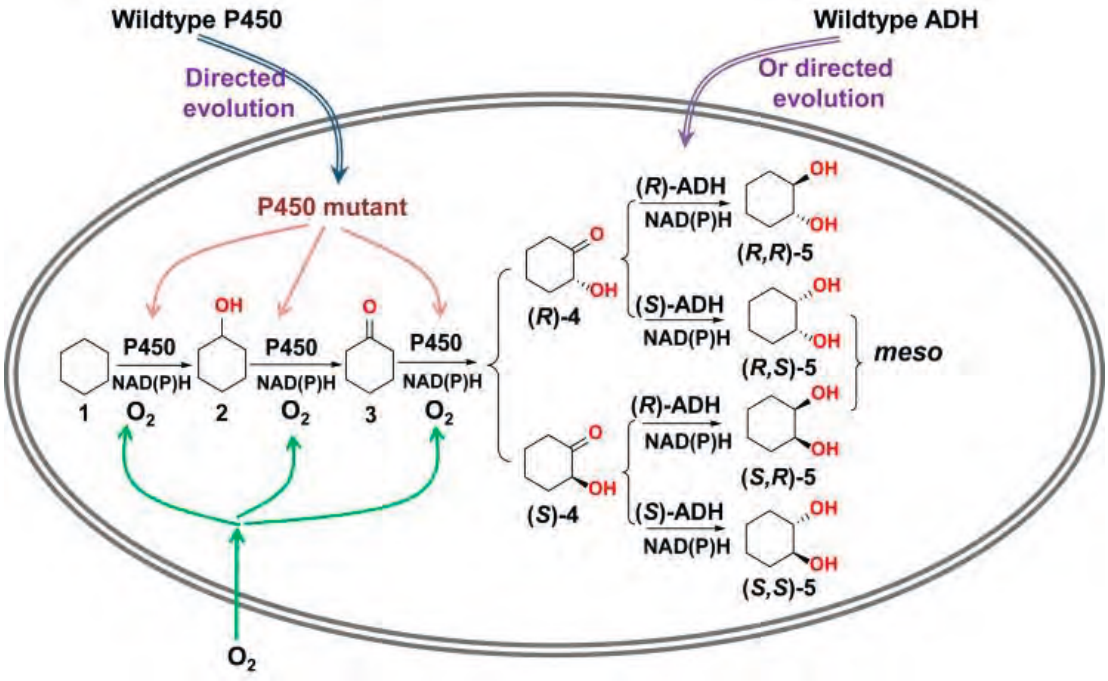
Involved: A. Ilie, A. Li, R. Lonsdale, Z. Sun, J. Wang

Objective: The purpose was the use of directed evolution in the construction of *E. coli* designer cells that enable one-pot regio- and stereoselective multi-step redox reactions in cascade sequences not possible by transition metal catalysts or organocatalysts.

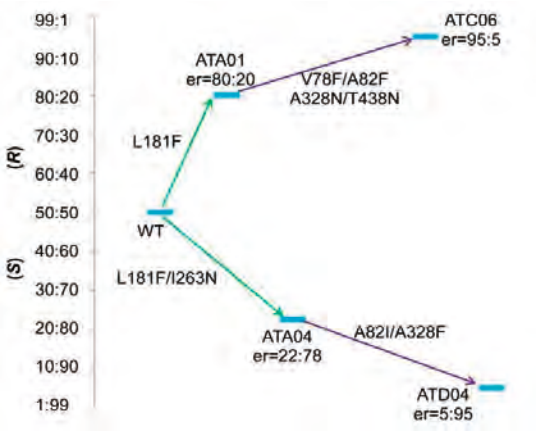
Results: Nature orchestrates the buildup of structural complexity stepwise *in vivo* in the cytosol of cells in which a multitude of enzymes function as selective catalysts. In contrast to metabolic pathway engineering which is based on renewable feedstocks such as glucose as the starting material for accessing special compounds of interest (derivatives), we are interested in the creation of designer cells which enable one-pot multi-step reaction sequences based on cheap petrochemicals. *The de novo construction of designer cells with the aim of realizing any given reaction sequence that an organic chemist might envision is a different type of problem not covered by metabolic engineering*. Particularly challenging are those cases of cascade reactions in designer cells that involve several sequential redox steps, especially when the control of regio-, chemo- and stereoselectivity is required which is impossible using wildtype enzymes. Indeed, very few examples have been reported to date, and only one utilized directed evolution (our own study highlighted in the 2011-2013 Report). We envisioned several cascade sequences utilizing cyclohexane (**1**) as the starting material: Two designed *E. coli* cells that consume cyclohexane as an energy source with formation of the acyloins (*R*)- and (*S*)-2-hydroxycyclohexanone, respectively, as well as more complex cells that take cyclohexane all the way to (*R*,*R*)-, (*S*,*S*)- or *meso*-cyclohexane-1,2-diols:



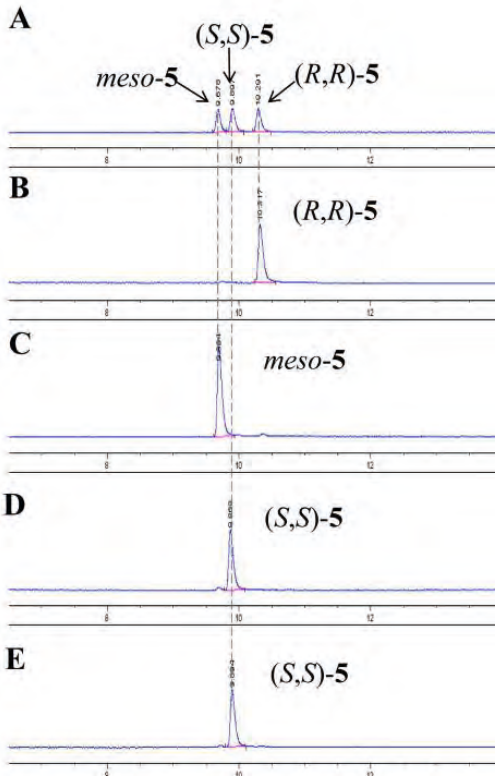
In order to reach both goals, a flexible unified concept was devised according to[38]:



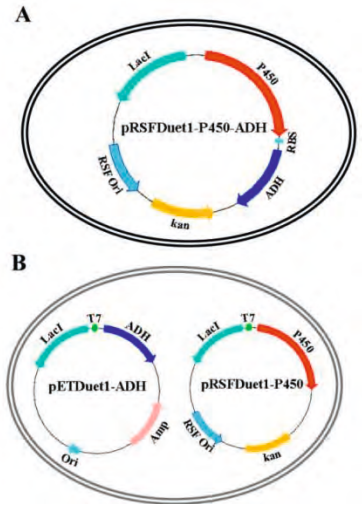
P450-BM3, a well-known monooxygenase having a fused reductase domain, was chosen as the enzyme for the first three CH-activating steps, followed by appropriate alcohol dehydrogenases (ADH)s for the final step(s) on the way to the diols. P450-BM3 does not accept cyclohexane (**1**), nor cyclohexanol (**2**) or cyclohexanone (**3**), probably due the small size of these substrates in the large binding pocket of the enzyme. The difficult part was evolving single P450-BM3 mutants which catalyze all three steps starting from cyclohexane (**1**), one leading to (*R*)-**4**, the other to (*S*)-**4**. This was achieved by applying triple code saturation mutagenesis (TCSM) in iterative form (ISM) (see Reetz Report 1), initially using cyclohexanone (**3**) as substrate. Enantioselectivities of er = 95 : 5 were achieved in the formation of (*R*)- and (*S*)-**4**. These two mutants also catalyzed the two first steps **1**→ **2**→**3**, thereby *making the one-pot conversion of cyclohexane (1) into the acyloins (R)- and (S)-4 possible.*[38]



The remaining goal was the production of the three stereoisomeric diols **5** in a one-pot process starting from cyclohexane (**1**). Using a bioinformatics approach, ADHs as appropriate enzymes in the reduction of C4-acyloins were readily identified. Gratifyingly, they also proved to be excellent catalysts in the diastereoselective reduction of the acyloins (*R*)- and (*S*)-**4**, with formation of (*R*,*R*)-, (*S*,*S*)- and *meso*-**5**, respectively, as shown by the GC plots of the crude products resulting from the different designer cells (*top chromatogram A: standard mixture of the three stereoisomers; B, C, D and E: crude products from E. coli designer cells using cyclohexane as starting material.*):



Thus, in the case of the ADHs, directed evolution was not necessary, since the wildtypes did the job. The best plasmid configuration, important for minimizing cell stress, inter alia, was also explored by testing two versions: Putting both P450 and ADH genes in one plasmid led to significantly better results than placing two separate plasmids in a designer cell[38]:



This work demonstrates that directed evolution is highly useful in the construction of designer cells which enable redox-based multi-step cascade sequences. Such one-pot processes requiring only a single workup are not possible using state-of-the-art transition metal catalysts or organocatalysts.

Future directions: This study opens the door for many synthetically novel possibilities, e.g., testing in one-pot processes other starting materials as substrates, utilizing (evolved) transaminases in the last step in order to obtain all four stereoisomeric amino-alcohols, and extending the directed evolution concept to include other enzymes such as mutants of Baeyer-Villiger monooxygenases.

Publications resulting from this research area: 22, 38

External funding: LOEWE Research Cluster SynChemBio (Hessen, DE)

Cooperations: Jian-He Xu (East China University of Science and Technology, Shanghai, CN)

2.6.4 Research Area "Learning from Directed Evolution" (M. T. Reetz)

Involved: C. G. Acevedo-Rocha, A. Ilie, A. Li, G. Li, R. Lonsdale, J. Sanchis, Z. Sun, J. Wang

Objective: a) Examine the mechanistic details of an ene-reductase by QM/MM; b) Uncover the reasons for enhanced or inverted stereoselectivity or altered regioselectivity of selected evolved enzymes; c) Explore additive versus cooperative or deleterious mutational effects by constructing and analyzing multidimensional fitness landscapes, showing when epistasis is crucial in directed evolution.

Results:

QM/MM study of the ene-reductase YqjM

Ene-reductases catalyze the conjugate reduction of α/ß-unsaturated ketones and other activated alkenes, but stereoselectivity is often poor, or reversal is necessary. We have previously applied directed evolution to the ene-reductase YqjM for enhancing and inverting enantioselectivity of several prochiral substrates, but were unable to postulate sound interpretations because crucial mechanistic details of this class of enzymes were lacking. We performed the first QM/MM study of this class of enzymes, cyclohexenone serving as the model substrate.[24] Figures 1a and 1b show the highest ranked poses of the "normal" and "flipped" orientations, respectively, and Fig. 1c features the QM region used in QM/MM computations.

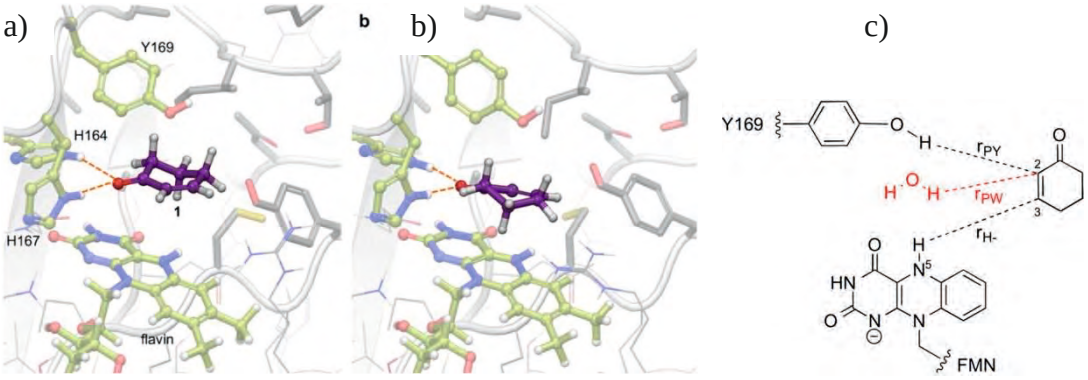


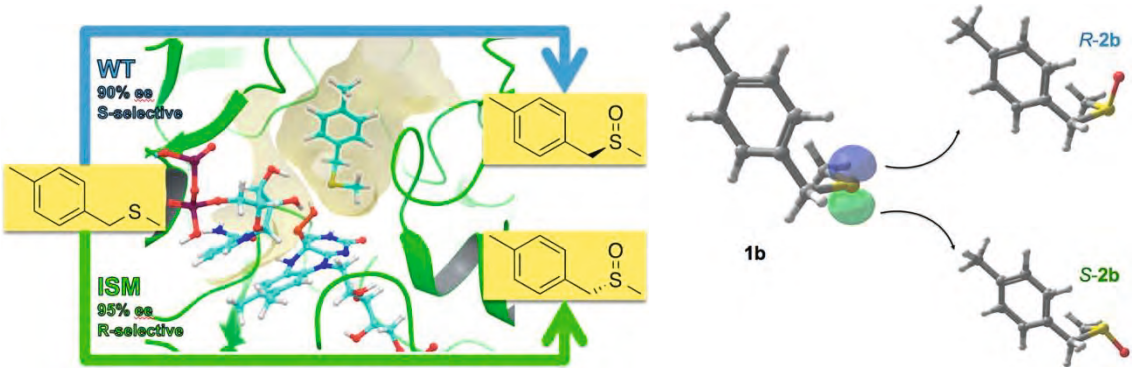
Fig. 1

Reaction pathways at B3LYP-D/OPLS2005 level suggest that *the hydride from FMN and the proton are added in distinct steps, not concertedly* as often postulated. The substrate is bound weakly, two active site histidines inducing polarization of the

carbonyl function (not LUMO-lowering by strong H-bonds to the carbonyl O-atom!), with Tyr196 providing the proton in the final fast step. This study not only provides *detailed insights into the mechanism of an ene-reductase as generated by QM/MM, the results can also be used to interpret the enantioselectivity of evolved mutants as catalysts in the reduction of prochiral substrates*.[24]

Shedding light on the origin of enhanced and inverted stereoselectivity of enzyme mutants

In most of our experimental studies of directed evolution of stereo- and regioselective enzymes, we apply docking and molecular dynamics simulations (MD) simulations in order to shed light on the reasons for altered catalytic profiles. The lessons from directed evolution flanked by such theoretical studies enable fundamental mechanistic insights. Typical examples are featured here, beginning with the Baeyer-Villiger monooxygenase PAMO which we used in an asymmetic promiscuous sulfoxidation reaction employing *p*-methylbenzyl methyl thioether as substrate.[10] WT PAMO favors formation of the (*S*)-sulfoxide (90% ee), while CAST-based iterative saturation mutagenesis (ISM) led in two steps to the quadruple mutant I67Q/P440F/A442N/L443I showing complete reversal of enantioselectivity (95% ee in favor of the (*R*)-sulfoxide (Fig. 2a). This switch entails an energy change of $\Delta\Delta G^{\neq} = 16.4$ kJ/mol !



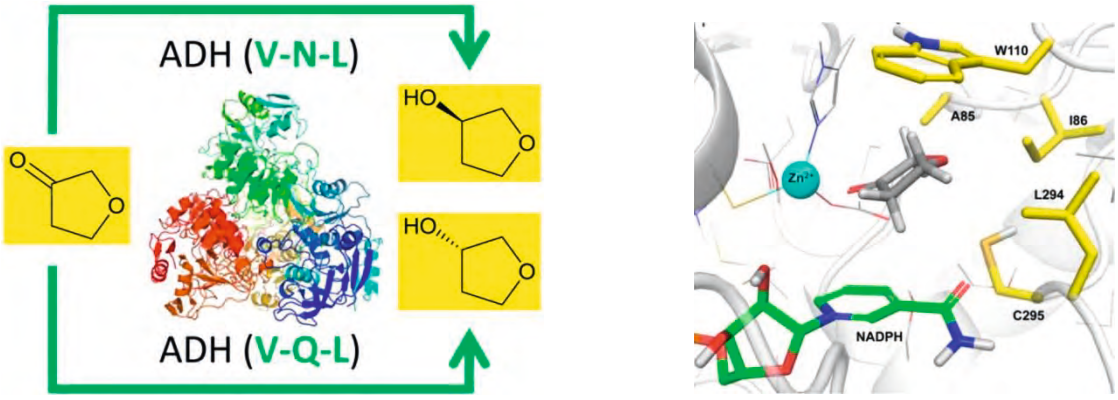
a) b)

Fig. 2

A previous QM/MM study (W. Thiel, M. T. Reetz, et al, *JACS* **2012**) focused on the mechanism of enzymatic Baeyer-Villiger oxidations, showing that the flavin anion Fl-OO^- is the oxidant. In the sulfoxidation reaction, Fl-OOH is the active electrophilic species.[10] the closest of the two sulfur lone electron pairs to the –OOH moiety will be the one that undergoes oxidation preferentially (Fig. 2b). Highest docking scores were computed, leading to a plausible model. *In this way the intricacies of binding were illuminated for the quadruple mutant I67Q/P440F/A442N/L443I, in line with the observed (R)-selectivity.*[10] Similar calculations were performed at all evolutionary steps

in the upward climb within all 24 pathways of the fitness landscape (see next section below).

Mutants of the alcohol dehydrogenase TbSADH, evolved by TCSM with 3-oxo-tetrahydrofuran as substrate (Fig. 3a) were also analyzed.[28] Mutant SZ2074 (I86N/C295N) shows 99% ee/(*R*) and mutant SZ2172 (I86V/W110L) ensures 95% ee/(*S*); WT 23% ee (*R*). The Prelog-rule, a model referring to a large binding cavity for the carbonyl α-group and a small one for the α'-group, cannot be applied, since in the present case steric differences are hardly discernible. TbSADH is a Zn-dependent ADH in which the carbonyl O-atom binds to the Lewis acid with concomitant activation for hydride attack by NADPH (Fig. 3b).[28]



a) b)

Fig. 3

The furan ether O-atom undergoes *different H-bonding interactions which positions the substrate in opposite orientations with respect to NADPH as hydride source* (Figure 4). [28]

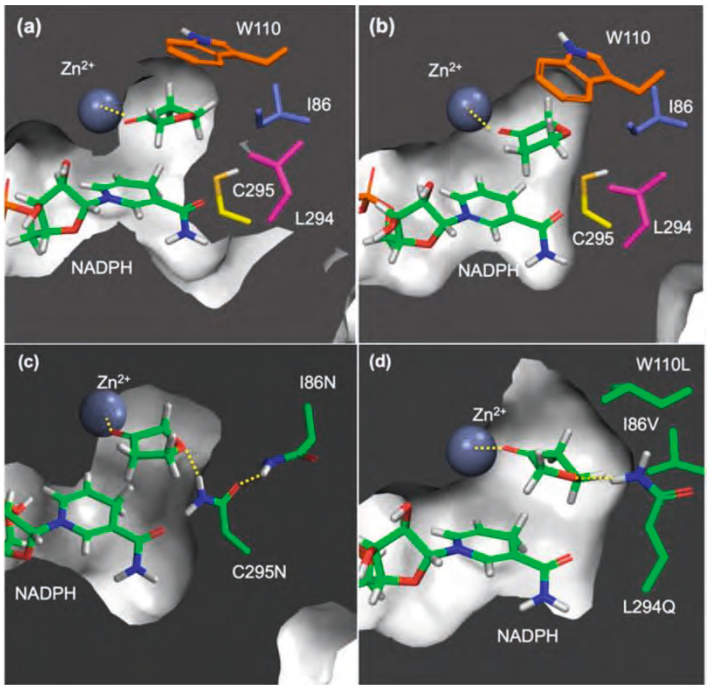


Fig. 4. (Docking poses of 3-oxo-tetrahydrofuran: a) WT (*S*)-selective pose; b) WT (*R*)-selective pose; c) SZ2074 (*R*)-selective pose; d) SZ2172 (S)-selective pose) [28]

Docking and MD computations were also performed in other directed evolution studies, focusing on enantioselective epoxide hydrolase,[27,31,39] regio- and stereoselective P450 enzymes,[6,9,12,17,21,38,41] and a P450-peroxydase as a diastereoselective catalyst in oxidative decarboxylation.[32] In the case of single code saturation mutagenesis (SCSM) of limonene epoxide hydrolase (LEH) with evolution of (*S*,*S*)-selective mutant SZ92 (95% ee) and reversed (*R*,*R*)-selective mutant SZ338 (96% ee) in the desymmetrization of cyclohexene oxide with formation of the respective diols, crystal structures harboring the (*S*,*S*)- and (*R*,*R*)-products were obtained (Fig. 5).[18] The *reshaped binding pockets* are clearly visible (see binding cavities located above D101), which were analyzed by docking/MD computations. *This is the first case of crystal structures of both enantiomeric mutants produced by directed evolution, thereby nicely illustrating Emil Fischer's lock-and-key hypothesis.*

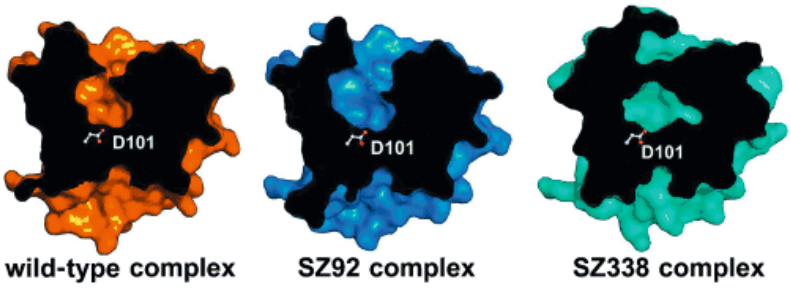
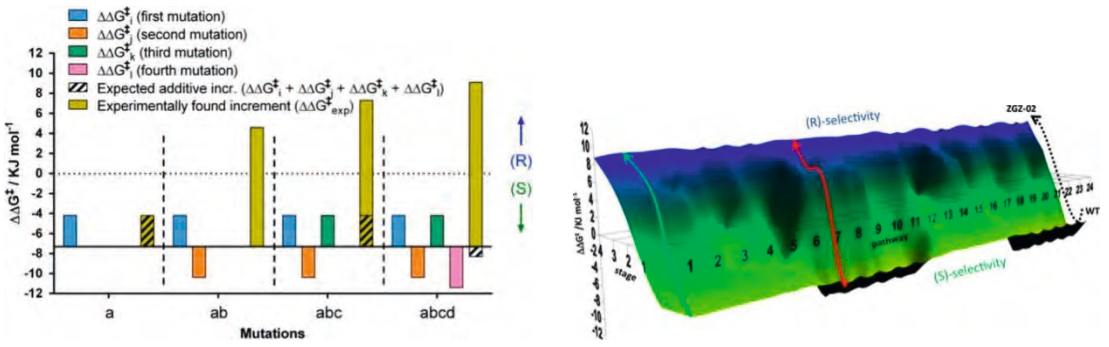


Fig. 5.

Fitness landscapes for exploring additive versus cooperative mutational effects

Additive mutational effects are those in which the respective point mutations do not influence each other, whereas non-additive mutational effects can be cooperative (more than additive) or deleterious (less than additive). Fitness landscapes needed to identify such effects are accessible by deconvoluting a multi-mutational variant produced by directed evolution. This requires formidable lab work (which explains why such studies are rare), but the results are illuminating. *We find cooperative (more than additive) and deleterious effects (less than additive) to be the rule, not the exception!* Two deconvolution studies were performed during the past three years: The first concerned reversal of enantioselectivity of PAMO in the sulfoxidation of *p*-methylbenzyl methyl thioether via two ISM steps WT (*S*) → P440F/A442N/L443I → I67Q/ P440F/A442N/L443I (*R*) (Fig. 2a).[10] As a first deconvolution step of the (*R*)-selective quadruple mutant, all four point mutations were prepared and tested in the asymmetric sulfoxidation reaction along 24 pathways, one trajectory defined by a→ b→c→d being shown in Scheme 1a.[10] *Surprisingly, all four point mutations proved to be (S)-selective, but in concert they are highly (R)-selective!* Alternatively speaking, the combination of four (*S*)-selective mutations results in a highly (*R*)-selective mutant. The same pattern was discovered in the other 23 evolutionary pathways. These and other trends at various evolutionary stages were explained by induced docking pose computations. A fitness landscape comprising 4! = 24 pathways was constructed experimentally (Scheme 1b), [10] which revealed that 6 trajectories lack local minima, 18 being characterized by local minima but with built-in escape events and continuous upward climbs to the same (R)-selective quadruple mutant. *In all cases strong cooperative (not just additive) mutational effects proved to be pervasive.*



a) b)

Scheme 1

Obviously, Scheme 1b features a fitness landscape based on a single catalytic trait in the upward climb. In a second eye-opening project utilizing P450-BM3 as catalyst in the oxidative hydroxylation of steroids, *part of the first multiparametric fitness landscape was constructed by considering both regioselectivity and activity as the definition of fitness*. Even at this early stage of the project it was observed that the two catalytic traits are interrelated.

Future directions: A QM/MM study of the (*R*)- and (*S*)-selective TbSADH mutants would strengthen the present qualitative model. Complete multiparametric fitness landscapes coupled with theoretical analyses of dynamic effects in enzymes also constitute future research topics.

Publications resulting from this research area: 6, 9, 10, 12, 15, 17, 18, 21, 24, 27, 28, 31-33, 37, 38

External funding: LOEWE Research Cluster SynChemBio (Hessen, DE); Arthur C. Cope Fund (US)

Cooperations: J. Sanchis (Monash University, AU), Y. Nov (Statistics Department, Haifa University, IL), M. Zilly (Physics Department, Duisburg-Essen University, DE), J. Zhou (Shanghai Institute of Organic Chemistry, CN); J.-H. Xu (East China University of Science and Technology, Shanghai, CN)

2.6.5 Publications 2014-2016 from the Emeritus Group Biocatalysis M. T. Reetz

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2.7 Technical Chemistry

External scientific member:

Walter Leitner (born 1963)

Group leader:

Nils Theyssen (born 1974)

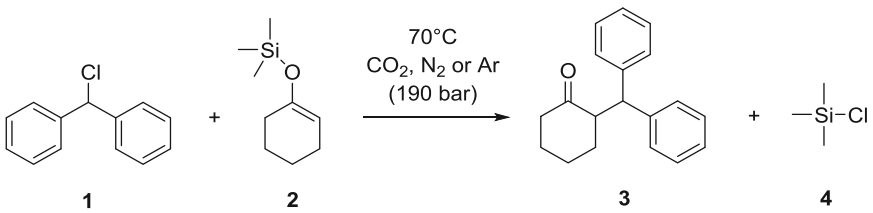
2.7.1 Research Area "Concerning the Role of $scCO_2$ in S_N1 Reactions" (W. Leitner, M. T. Reetz, N. Theyssen)

Involved: Y. Qiao

Objective: From 2013 onwards *González-Núñez* and co-workers reported the use of supercritical carbon dioxide ($scCO_2$) being an activating solvent for a variety of S_N1 reactions. However, our results do not support the claimed activating effect of this media *via* enhanced S_N1 ionization.

Results: Inspired by the intriguing literature reports, we attempted to perform alkylations of enolsilanes with formation of α-alkylated ketones. If successful, the use of $scCO_2$ was hoped to eliminate the need for stoichiometric amounts of strong Lewis acids such as $TiCl_4$ and allow for a "green" version of these synthetically important transformations. Although we failed in the case of 1-chloro-1-phenylethane, the more S_N1-active benzhydryl chloride (**1**) reacted smoothly with the enolsilane **2** to give the alkylation product **3** and the chlorosilane by-product **4** in 86-90% conversion (Scheme 1).

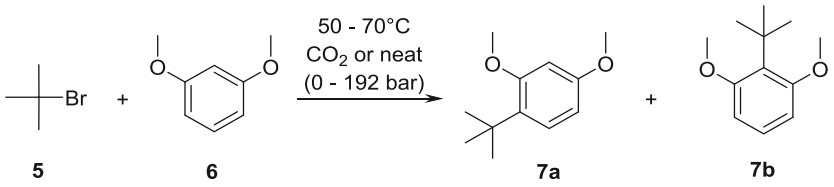
In order to check whether the use of $scCO_2$ plays a decisive role in this transformation, we performed the same reaction under identical conditions by replacing CO_2 with compressed nitrogen or argon. Surprisingly, high conversions were observed in both cases (93-97% and 93-99%, respectively) after 5 h in a stainless steel reactor, with product selectivities between 95 and 99%. We therefore conclude that an "activating effect" of $scCO_2$ can be ruled out for this particular reaction.



Scheme 1. Lewis acid free alkylation of enolsilane **5**.

These observations prompted us to re-investigate the effect of $scCO_2$ on the S_N1-type Friedel-Crafts reaction using the alkylation of 1,3-dimethoxybenzene (**6**) with *tert*-butyl bromide (**5**) as chemical probe (Scheme 2). We chose this particular reaction because it

was reported to proceed quite smoothly to give quantitative conversion under the conditions of *González-Núñez* and co-workers. In a series of experiments, including an design of experiment approach and conversion time profiles with different CO_2 amounts, our data demonstrate a retarding rather than activating effect of CO_2.



Scheme 2. Lewis acid free Friedel-Crafts alkylation.

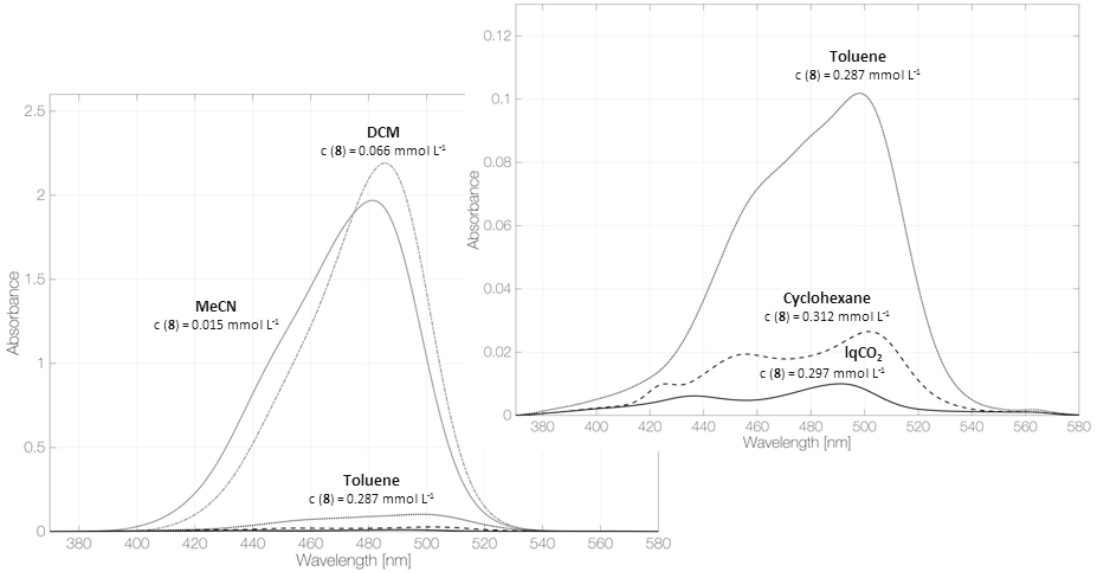


Fig. 1. Visible region of the UV/Vis spectra for 4,4',4''-trimethoxytrityl chloride (**8**) in liquid CO_2, cyclohexane, toluene, dichloromethane and acetonitrile at 25°C.

In order to gain further evidence for the questionable ionizing potential of carbon dioxide, we investigated the degree of ionization as a function of the applied reaction medium by high-pressure UV/Vis spectroscopy at 60 and 25 °C. For this purpose, compound **1** and 4,4',4''-trimethoxytrityl chloride (**8**) were used, which is an particularly sensitive indicator molecule for ionization in the visible regime (Figure 1). The presence of the 4,4',4''-trimethoxytrityl cation could be detected both in supercritical and liquid CO_2, but in marginal amounts only. The relative carbocation concentration derived from peak integration is a factor of about 3500 lower than the one obtained in acetonitrile. The degree of carbocation formation decreases in the order

$$MeCN > DCM >> toluene >> cyclohexane > scCO_2 \sim \textit{liq.}CO_2$$

following typical solvent polarity scales such as Reichhardt's $E_T(30)$ in an almost perfect manner (Table 1).

Table 1. Quantification of the relative ionization degrees of **8** in different media by peak integration of spectra shown in Figure 1. $E_T(30)$ values are given for comparison.

Solvent	Concentration of **8** in mmol / L	normalized ratio of carbocation formation	$E_T(30)$ in kcal / mol
$scCO_2$	0.2974	1	28.5
cyclohexane	0.3122	2.8	30.9
toluene	0.2872	11.3	33.9
dichloromethane	0.0663	768	40.7
acetonitrile	0.0151	3467	45.6

Our findings demonstrate that there is no enhanced dissociation of compound **8** in supercritical or liquid CO_2 at all. Overall, our study disproved an *activating effect* of compressed carbon dioxide on alkyl halide ionization for S_N1 type reactions.

Publications resulting from this research area: 14

External Funding: Cluster of Excellence "Tailor-Made Fuels from Biomass" (Excellence Initiative by the German Federal and State Governments)

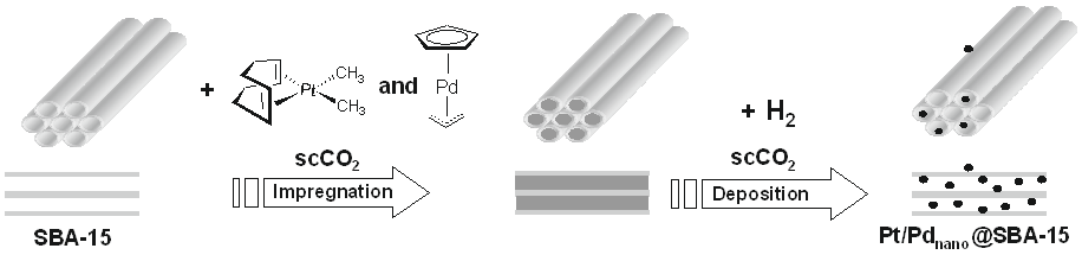
Cooperations: T. Eifert, M. A. Liauw, G. Franciò, K. Schenk (RWTH Aachen University, DE)

2.7.2 Research Area "Nanocatalyst Preparation via Supercritical Fluid Reactive Deposition" (W. Leitner, N. Theyssen)

Involved: Y. Qiao, N. Said, M. Rauser

Objective: Supercritical fluid reactive deposition (SFRD) was employed to generate mono- and bimetallic Pt and Pd nanoparticles (NPs) on SBA–15 as mesoporous support material. The choice of solvent during preparation was reflected in the catalytic hydrogenation of levulinic acid (LA) to γ–valerolactone (GVL).

Results: The principle of the applied SFRD process is illustrated in Scheme 1. The support material, the metal complexes and the reaction media were filled into a stainless-steel high pressure reactor and heated to 50 °C under continuous stirring. After 2 h, hydrogen was added in a controlled manner, which led to the formation of nanoscale metallic deposits, preferentially inside the pores of the SBA-15.



Scheme 1. Synthesis of SBA–15 supported bimetallic Pt/Pd NPs by supercritical fluid reactive deposition (SFRD) using $scCO_2$ as transport and reaction medium.

The influence of the different reaction media on the structure of the NPs was very pronounced as shown by TEM. The materials obtained from $scCO_2$ were found to contain well–dispersed spherical NPs of small size with a quite uniform distribution. The mean diameters were determined to 5.0 ± 1.1 nm. Particles of similar shape and size (4.3 ± 1.0 nm) were obtained by liquid phase impregnation using *n*–pentane as solvent. In sharp contrast, the micrographs of materials obtained by use of toluene or THF revealed the presence of much larger agglomerates. The metal ensembles are not spherical anymore, but rod–shaped structures of substantial length. In particular with THF, these wire-type structures reach up to 100 nm in length.

Moreover, the internal structure of the spherical bimetallic particles obtained from $scCO_2$, *n*–pentane and THF was analyzed with a combination of EDX and STEM (Figure 1). Whereas the particles obtained from *n*-pentane show a Pd-rich core and a Pt-rich shell, the particles produced by the SFRD method have an almost perfectly random distribution of the two metals in an alloy-type structure. THF behaves again quite differently, resulting preferentially in a separated structure with monometallic domains.

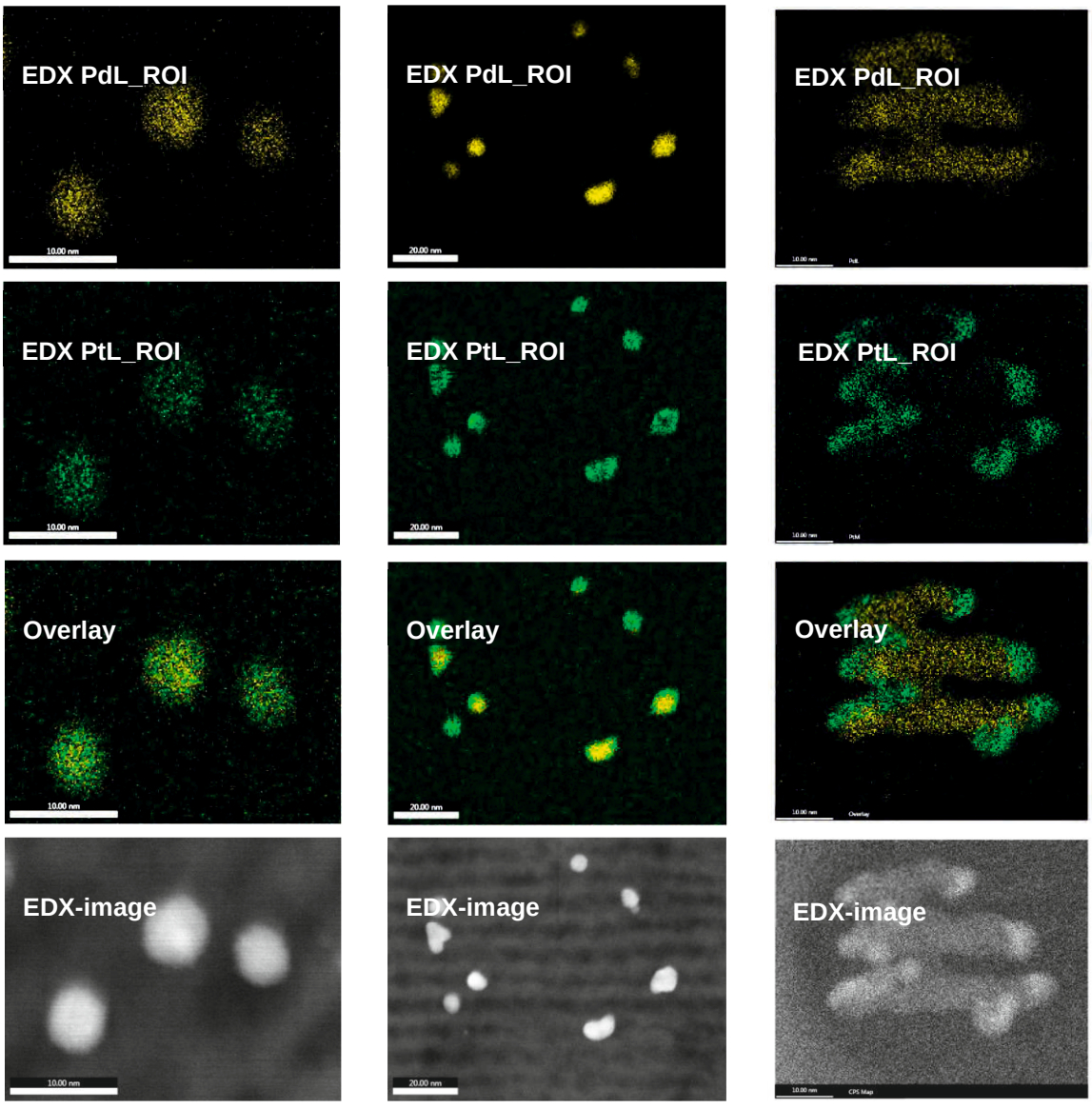


Fig. 1. STEM-EDX analysis of 3%Pt_1–Pd_3/SBA–15 synthesized in $scCO_2$ (left), *n*–pentane (middle) and THF (right).

The obtained materials were tested in the catalytic hydrogenation of LA to GVL. Compared with literature data, the materials prepared in *sc*CO_2 showed favorable activity, achieving total TON values up to 7200 and total TOF values up to 3600 h^{-1}. The influence of the Pt/Pd-ratio on the catalytic performance is depicted in Figure 2. Doping the Pt-catalyst with 25% Pd showed almost no effect. At higher Pd-ratios, however, the bimetallic systems showed significantly higher conversion and yields. Pure Pd, in contrast, was again less effective. Most significantly, the differences in material properties resulting from the use of different solvents were also clearly reflected in the catalytic performance (Figure 3). Only 30% yield could be achieved with the catalyst materials synthesized using toluene or THF, all other factors being identical. In contrast, the catalysts synthesized in *sc*CO_2 and *n*–pentane gave ca 80% yield after 2 h reaction time with very little – if any – difference in activity.

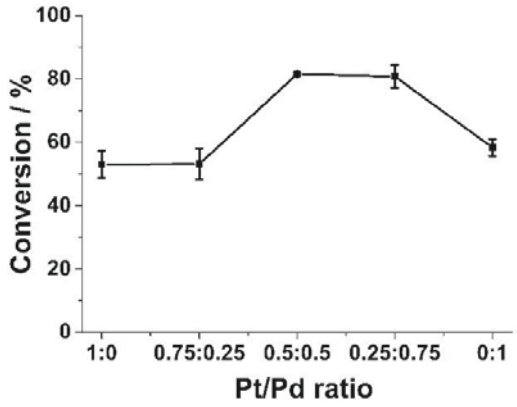


Fig. 2. Activity tests of LA to GVL using different metal compositions supported on SBA-15.

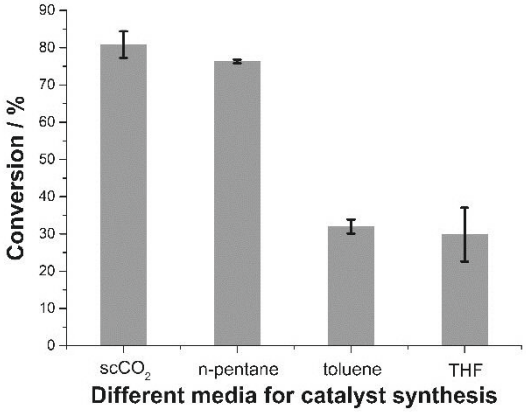


Fig. 3. Activity tests of LA hydrogenation to GVL using 3% Pt_1–Pd_3/SBA–15 synthesized in different media.

Publications resulting from this research area: 13

External Funding: Cluster of Excellence ‘‘Tailor–Made Fuels from Biomass’’ (Excellence Initiative of the German Federal and State Governments)

2.7.3 Publications 2014-2016 from the External Scientific Member

Leitner

(1) Yan, Q.; Miazek, K.; Grande, P. M.; Domínguez de María, P.; Leitner, W.; Modigell, M. *Energy Fuels* **2014**, *28*, 6981-6987.
(2) Luska, K. L.; Julis, J.; Stavitski, E.; Zakharov, D. N.; Adams, A.; Leitner, W. *Chem. Sci.* **2014**, *5*, 4895-4905.
(3) Vom Stein, T.; Meuresch, M.; Limper, D.; Schmitz, M.; Hoelscher, M.; Coetzee, J.; Cole-Hamilton, D. J.; Klankermayer, J.; Leitner, W. *J. Am. Chem. Soc.* **2014**, *136*, 13217-13225.
(4) Beydoun, K.; Ghattas, G.; Thenert, K.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2014**, *53*, 11010-11014.
(5) Luska, K. L.; Migowski; Leitner, W. *Green Chem.* **2015**, *17*, 3195-3206.
(6) Vom Stein, T.; den Hartog, T.; Buendia, J.; Stoychev, S.; Mottweiler, J.; Bolm, C.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2015**, *54*, 5859-5863.
(7) Grande, P. M.; Viell, J.; Theyssen, N.; Marquardt, W.; Domínguez de María, P.; Leitner, W. *Green Chem.* **2015**, *17*, 3533-3539.
(8) Zhang, Z.; Franciò, G.; Leitner, W. *ChemCatChem* **2015**, *7*, 1961-1965.
(9) Dominguez de Maria, P.; Grande, P. M.; Leitner, W. *Chem. Ing. Tech.* **2015**, *87*, 1686-1695.
(10) Poliakoff, M.; Leitner, W.; Streng, E. S. *Faraday Discuss.* **2015**, *183*, 9-17.
(11) Luska, K. L.; Migowski, P.; El Sayed, S.; Leitner, W. *Angew. Chem., Int. Ed.* **2015**, *54*, 15750-15755.
(12) Francio, G.; Hintermair, U.; Leitner, W. *Philos. Trans. R. Soc., A* **2015**, *373* (2057).
(13) Qiao, Y.; Said, N.; Rauser, M.; Yan, K.; Qin, F.; Theyssen, N.; Leitner, W. *Green Chem.* DOI 10.1039/C6GC02490D.
(14) Beydoun, K.; Thenert, K.; Streng, E. S.; Brosinski, S.; Leitner, W.; Klankermayer, J. *ChemCatChem* **2016**, *8*, 135-138.
(15) Rohmann, K.; Hölscher, M.; Leitner, W. *J. Am. Chem. Soc.* **2016**, *138*, 433-443.
(16) Klankermayer, J.; Leitner, W. *Philos. Trans. R. Soc., A* **2016**, *374* (2061).
(17) Luska, K. L.; Bordet, A.; Tricard, S.; Sinev, I.; Grünert, W.; Chaudret, B.; Leitner, W. *ACS Catal.* **2016**, *6*, 3719-3726.
(18) Klankermayer, J.; Wesselbaum, S.; Beydoun, K.; Leitner, W. *Angew. Chem., Int. Ed.* **2016**, *55*, 7296-7343.
(19) Rohmann, K.; Kothe, J.; Haenel, M.; Englert, U.; Hölscher, M.; Leitner, W. *Angew. Chem., Int. Ed.* **2016**, *55*, 8966-8969.

CHAPTER 3

Scientific Service Units

3 Scientific Service Units

The Institute's Scientific Service Units are integral parts of our research efforts. The highly interdisciplinary approach to catalysis requires immediate and direct access for all groups to a large and diverse pool of reaction engineering techniques ("Technical Laboratories"), analytical methods (Chromatography, Mass Spectrometry, Nuclear Magnetic Resonance, Chemical Crystallography, Electron Microscopy), and information or data handling systems (Library, Computer Group). A maximum standard of safety, reliability, and flexibility is essential for these units to respond to the needs of modern basic research in catalysis and related areas of chemistry.

In addition to providing the appropriate infrastructure and know-how, several service facilities are actively involved in specific projects, generally in cooperation with the scientific groups of the five Departments. For example, new techniques have been developed over the years in the fields of high-throughput screening, microfluidics, and chip-electrophoresis, to name just a few representative cases.

In order to make this approach truly successful, a long term strategy is essential for maintaining and developing the know-how and experience of the staff. This includes the active role of the Scientific Service Units in specific research projects, participation in conferences and the hosting of postdoctoral fellows with the aim of introducing new techniques.

In line with the rules stipulated by the MPG, all data recorded in the analytical departments or directly in one of the experimental groups are securely archived in electronic and/or hardcopy format for a minimum of ten years (usually much longer). A user-friendly electronic laboratory notebook (ELNA) has been developed and further extended during the reporting period, which ensures secure data storage and retrieval. At the same time, ELNA provides a constantly growing searchable in-house database.

3.1 Technical Laboratories and Central Occupational Safety (N. Theyssen)

Involved: P. Attaei Far, N. Fuhrmann, N. Sadlowski, M. Schalk, L. Winkel

The technical laboratory comprises a large central high pressure laboratory. Moreover, it houses appropriate distillation equipment for solvent purification and drying (turnover ~ 18.000 L per year), large scale synthesis facilities, the necessary infrastructure for receiving and sorting different types of chemical waste (about 29 tons per year), two research laboratories and office space. The workshop hall has been thoroughly renovated in 2014.

At the beginning of 2016 a new rotary evaporator of 20 L scale was purchased which is used as a central unit for drying and distillation of dichloromethane. It allows the throughput to be increased and ensures a higher degree of automatization and self-monitoring.

In the last two years, the quality control of the distributed solvent batches was improved. The residual water content is determined by coulometric Karl Fischer titration. Moreover, the content of each purchased barrel of diethyl ether, ethyl acetate, hexane isomers, n-pentane, MTBE, THF and toluene is analyzed via standardized GC prior to drying and distillation/rectification. In case of significant changes in the contaminations, individual barrels can hence be reclaimed; alternatively, the distillate is analyzed again and the recorded chromatograms are published on the Intranet sites of the technical laboratories. If unusual contaminants are detected, the scientific research groups are informed via email or telephone.

A more elaborated wiring (star instead of ring architecture) and a new software was installed in 2016 in all 22 small and medium sized high pressure boxes that improves the recording rate of pressure/temperature curves by a factor of hundred.

A new centrifuge was purchased for common usage with accelerations of up to 26.000 g. It can be used for centrifuge tubes of 2 to 500 mL size, the temperature can be adjusted between –20 and +40 °C, and flushing with inert gas is possible. Therefore it can be used for the centrifugation of combustible liquids (in accordance with the Guidelines for Laboratories, DGUV Information 213-851)

In the reporting period a new central disposal site for liquid chemical waste was built outside the technical laboratories. The disposal is realized in a scalable manner and uses chemically resistant Intermediate Bulk Containers (IBCs, more precisely ASF containers) of 1 m^3 size. The site is designed such as to minimize exposure of the operator to any chemical vapours.

Dr. Theyssen, who is in charge of the Technical Laboratories, is also the Safety Commissioner of the Institute. His work is supported by N. Sadlowski, an occupational safety engineer, M. Schalk (responsible for the supervision of external companies and periodic equipment tests) and, temporarily, by P. Attaei Far. In 2016, the team started implementing an electronic safety and health management system (ASi) that is already used by other MPG institutes.

Publications resulting from this research area:

(1) Kennema, M.; Theyssen, N. In *Catalytic Hydrogenation for Biomass Valorization*; Royal Society of Chemistry: London, 2015; pp 282-298.
(2) Qiao, Y.; Theyssen, N.; Hou, Z. *Recycl. Catal.* **2015**, *2* (1), 36-60.

For scientific contributions of the local joint working group of W. Leitner and N. Theyssen please see chapter 2.7.

3.2 Chromatography and Electrophoresis (P. Schulze)

Involved: S. Begoihn, G. Breitenbruch, A. Deege, V. Dietl, L. Gitlin, N. Haupt, C. Heidgen, S. Henze, H. Hinrichs, S. Kestermann, D. Klütt, F. Kohler, M. Massanek, J. Rosentreter, S. Ruthe, M. S. Sterling

This department provides central analytical services for in-house scientists, including qualitative and quantitative analysis, ee determinations, and preparative separations of chemical mixtures using modern chromatographic and electrophoretic methods as well as hyphenated techniques. Part of the group is involved in the development of detection technology.

Gas chromatography

The GC team applies a variety of modern capillary gas chromatographic techniques for routine analysis such as high temperature GC, GC x GC, SPME or KAS-TDU. Most analytes are detected via flame ionization or thermal conductivity detection. Unknown substances are identified using mass spectrometric detection (GC-MS). The team also develops analytical methods, e.g. the quantification of analytes in samples with complex or aqueous matrices.

Liquid chromatography and electrophoresis

The liquid chromatography and electrophoresis laboratory applies liquid phase separations e.g. high pressure liquid chromatography and capillary electrophoresis. In 2014-2016 the HPLC-group focused on increasing the separation efficiency and selectivity. For this reason several new achiral sub 2 µm and chiral 3 µm stationary phases were tested and applied. Likewise, the application and the development of 2D-HPLC were extended.

Two HPLC-systems for column switching and backflush techniques have been installed for analysis and simultaneous determination of saccharides and their reduction products. These systems are also in use for the analysis of oxidation products of glucose, glycerin and 5-(hydroxymethyl)furfural.

In January 2015 a 2D-system for comprehensive and heart cutting HPLC has been installed. It was the first commercial system for multiple heart cutting techniques and allows separations of complex mixtures at up to 120 MPa operation pressure.

With a combination of 2 µm achiral and 3 µm chiral reversed phase columns, the separation of diastereomers or enantiomers were performed for more than 50 samples.

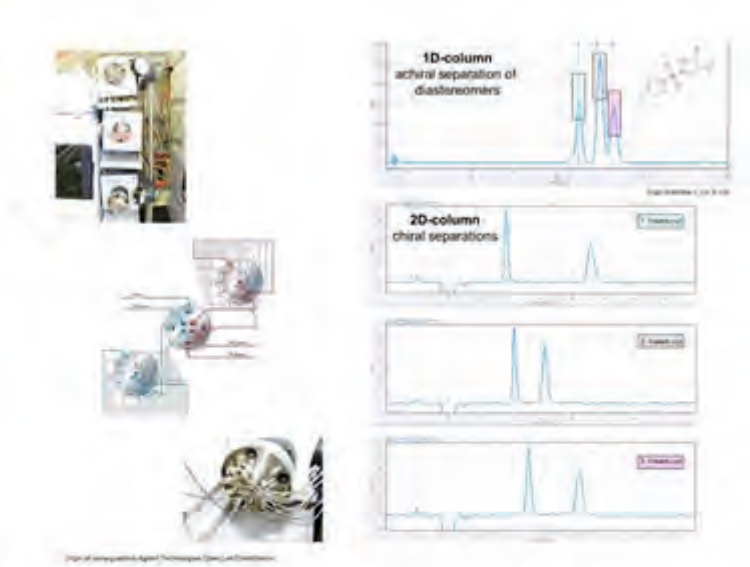


Fig. 1 Chiral separation of three diastereomers in a single run. Achiral separation of the diastereomers in the 1st dimension with the multiple heart cuts and corresponding chiral separations in the 2nd dimension.

Additionally, the LC group was involved in the following projects:

- Development of 372 new chiral HPLC methods; installation of method scouting systems for chiral separations.
- Micro preparative separation of a huge number of reaction products for NMR and MS.
- Separation and identification of peptides by multi charge HPLC/MS analysis.
- Separation and identification of steroids by LC/MS/MS.
- Separation and HPLC/MS identification of 65 different catalysts of the IDPi-project with molecular weights of up to 2800 on special 300 Å C3- and C8-stationary phases.
- Trace analysis of methanol and 2-propanol by ion chromatography.
- Achiral and chiral separations of several helicene derivatives using 2D-HPLC.

Preparative liquid chromatography

In the preparative HPLC, mainly reaction batches of up to 20 grams total amount are separated using upscaled HPLC methods. Different stationary phases such as NP-, RP- or chiral stationary phases are utilized in separation columns with inner diameters

between 10 and 50 mm. Most samples are detected *via* UV absorbance. Analytes lacking UV absorbing double bonds are detected by differences in refractive index.
To increase the separation efficiency of i.e. constitutional aromatic isomers, peak recycling is applied by fractionating the pure parts of each peak and redirecting the remaining peaks to the beginning of the column (Figure 2).

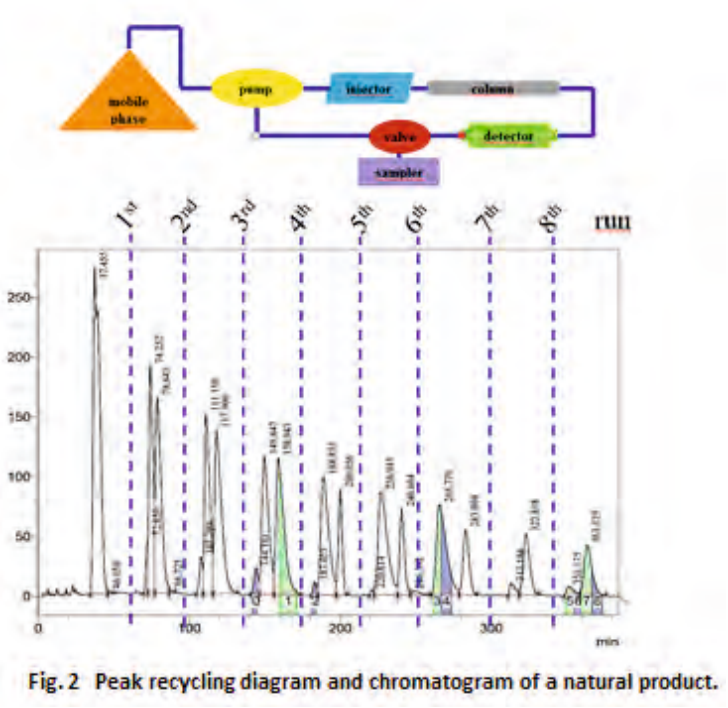


Fig. 2 Peak recycling diagram and chromatogram of a natural product.

Column switching in preparative HPLC increases the separation speed of lately eluting substances.

Pre-purification of the sample is conducted on a short column and the elution area of interest is transferred on the second dimension applying a longer column which is used to purify the target analytes.

Independent research projects

A low fluidic volume fluorescence detection cell was developed and built based on UV LED excitation and an alternative optical design. Its configuration facilitates high signal-to-noise detection and allows for up to three excitation sources to be used either simultaneously or in sequence resulting in potentially higher selectivity.

In another project, a manufacturing process for capillary-based liquid core waveguides (LCW) based upon a low refractive index polymer coating was developed. Due to its large path length, low volume and small emitting cross-section, this design is advantageous for spectrally resolved detection setups in HPLC i.e. analyte characterization via Raman.

Publications resulting from this research area:

(1) Gitlin, L.; Schulze, P.; Ohla, S.; Bongard, H.-J.; Belder, D.; *Electrophoresis* **2015**, *36*, 449-456.

(2) Gliemann B. D.; Petrovic A.G.; Zolnhofer E. M.; Dral P. O.; Hampel F.; Breitenbruch G.; Schulze P.; Raghavan V.; Meyer K.; Polavarapu P. L.; Berova N.; Kivala M.; *Chem. Asian J.* **2016**, DOI: 10.1002/asia.201601452R1.

External funding: ZIM-AiF (2 projects)

Cooperations: D. Belder (Leipzig, DE), M. Kivala (Erlangen, DE)

3.3 Mass Spectrometry (W. Schrader)

Involved: M. W. Alachraf, M. Blumenthal, B. Dietrich, Z. Farmani, A. Gaspar, C. Grundmann, W. Joppek, D. Kampen, H.W. Klein, A. Kondyli, S. Lababidi, I. Lim, R. Luo, J. Machado Santos, S. Marcus, D. Margold, L. Molnarne Guricza, D. Richter, M. Scheppat, A. Stavitskaya, A. Vetere, X. Wang

During the last three years the MS group had to integrate four new technicians who replaced four retired co-workers with – combined – more than 130 years of experience. Fortunately, the positions could be filled in advance which allowed for some overlap. The training of the new members in all aspects of mass spectrometry therefore was and will be a major part of the internal work.

Additionally, older instruments such as two 30 years old sector field mass spectrometers were replaced by more powerful new instrumentation. These old machines had been used for standard measurements using Electron Ionization (EI) on thermally stable compounds. We now use another sector field instrument for this task while a new high resolution Orbitrap Mass Spectrometer coupled to a gas chromatograph was purchased for high resolution and high accuracy EI measurements.

Likewise, an older FT-ICR MS was decommissioned after the vendor took it out of support (with expensive repairs necessary to keep it running after the magnet had quenched). A new Q-Exective Orbitrap was purchased in 2014 with an Electrospray Ionization (ESI) source as replacement.

Modern analytical methodologies need to be available in order to solve the analytical problems of the synthetic laboratories. The group is offering full support for all groups at both institutes on campus concerning the identification of unknown and new components using all available ionization methods. Rapid turn-over is a strong priority that allows the synthetic chemists to obtain the results as soon as possible. The institute’s own database and software package (MassLib) is constantly modernized to meet new requirements, and the different new atmospheric pressure ionization and high resolution methods have found a greater emphasis.

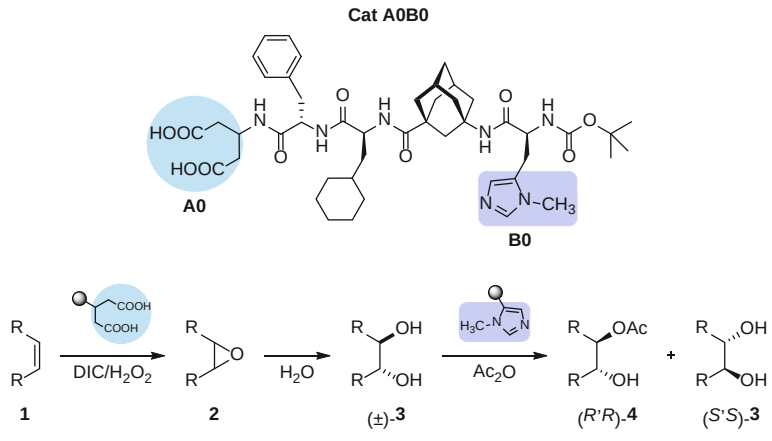


Fig. 1. Reaction sequence using a multicatalyst.[8]

The **research interests** are ranging from the development of analytical techniques to studying complex chemical reactions, often in energy-related materials such as biofuels or fossil fuels. Additional studies focus on the investigation of unusual reactions to gain information about their mechanisms. One example is a cooperation with the group of Peter Schreiner at the University Giessen. The group has developed a new approach to cascade reactions in organocatalysis, where the different catalytic moieties are attached to a spacer molecule. Each moiety needs activation prior to its reaction in the sequence. We studied the mechanism of one of those reaction sequences, involving a multi-catalyst with a chiral peptide backbone and an adamantane spacer separating two catalytically active centers. One catalytic moiety, a dicarboxylic acid is responsible for the first reaction step, an epoxidation, while an *N*-methyl imidazole moiety catalyzes the terminal acylation step (see Figure 1).[8]

This triple cascade sequence constituted of an epoxidation, an epoxide opening, and an enantioselective acylation reaction catalyzed by an oligopeptide multicatalyst was studied in detail using electrospray ionization mass spectrometry. The key reaction intermediates were successfully characterized. Additional side reactions were discovered that were not known before. During the activation of the first catalytic moiety by DIC (di*iso*propylcarbodiimid) and H_2O_2 a side reaction takes place on the catalytic moiety for the second reaction step to form a partially oxidized methyl imidazole moiety, which reduces the activity of the second catalytic moiety. These results allow for an optimized reaction planning.

Another project deals with the investigation and characterization of complex crude oil mixtures. Despite the continuous development of renewable energy sources, energy supplies will be dependent upon the availability of fossil materials for at least the next 2-3 decades.

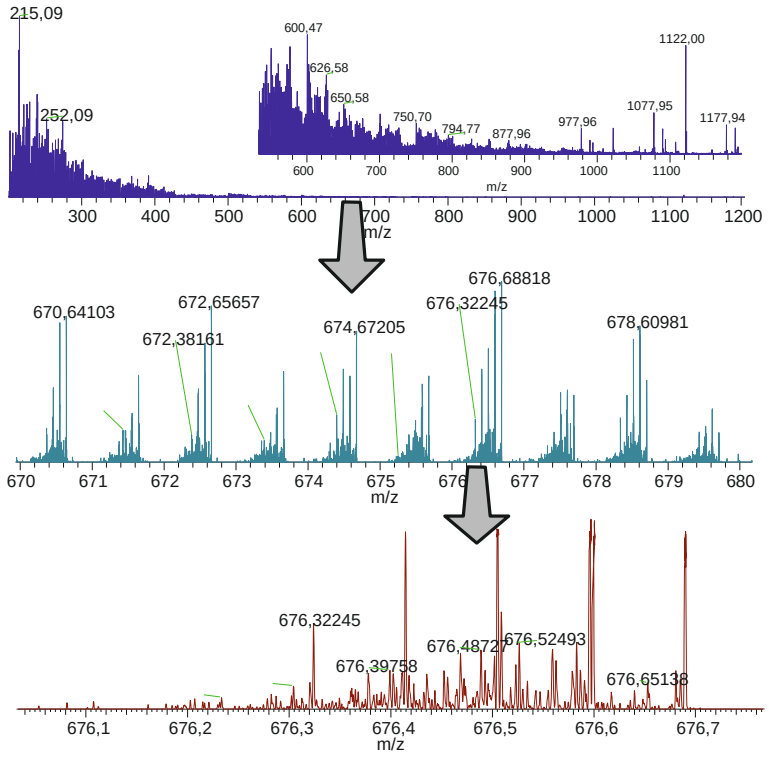


Fig. 2. Mass spectrum with different zoom factors showing the complexity of a crude oil sample.

Even now, as more sustainable resources are mixed with fossil oils, the chemistry in such mixtures still remains a big mystery. One of the reasons is that chemical changes within a mixture of more than one million distinct chemical compounds are almost impossible to follow. Here, ultrahigh resolution mass spectrometry is the only method that allows different components to be distinguished. An example is shown in Figure 2, where a mass spectrum with different zoom factors is shown. It can be seen that up to 200 different signals can be detected and assigned with an elemental composition within one nominal mass unit, describing the complexity of such materials. Since mass spectrometry only gives detailed data of the elemental composition of each signal, chemical diversity such as structural differences of the same elemental formula are not detected. To be able to do this, different hyphenated methods have been developed during the reporting period. These include the online-coupling of ligand exchange chromatography (LEC), size exclusion chromatography (SEC) and ion mobility spectrometry (IMS) to mass spectrometry.

The LEC columns are synthesized and packed in our lab and allow running different separation applications from heavy asphaltenes to full crude oils. Ion mobility spectrometry is a method that separates ionized compounds according to their collisional cross section in an electric field and therefore enables isomeric compounds to be distinguished. Different ion sources for atmospheric pressure photo and laser ionization (APPI and APLI) have been constructed for ionization with an IMS unit coupled to a mass spectrometer. These methods allow isomers within the distinct elemental compositions to be distinguished.

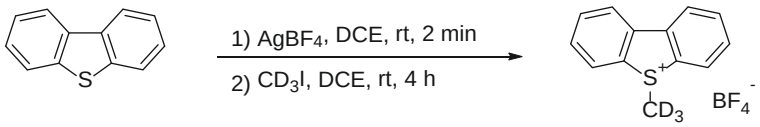


Fig. 3. Alkylation of sulfur heterocycles.

In addition to the development of analytical methods for the analysis of complex mixtures, the chemical reactivity of individual compounds within such complex mixtures has been studied. Estimates show that crude oil contains more than one million chemical compounds which often have some type of aromatic core with a number of different, mostly aliphatic side chains. We have studied the reactivity of the different aromatic cores, specializing on polyaromatic heterocycles and their reactivity towards alkylation. The use of a deuterated alkylating agent allows differentiation of alkylated and non-alkylated compounds on the molecular level using mass spectrometry.[9]

Publications resulting from this research area:

(1) Schrader, W. *Eur. J. Mass Spectrom.* **2014**, *20*, 0-0.
(2) Schrader, W.; Xuan, Y.; Gaspar, A. *Eur. J. Mass Spectrom.* **2014**, *20*, 43-49.
(3) Lababidi, S.; Schrader, W. *Rapid Commun. Mass Spectrom.* **2014**, *28*, 1345-1352.
(4) Molnárné Guricza, L.; Schrader, W. *J. Mass Spectrom.* **2015**, *50*, 549-557.
(5) Lim, I.; Schrader, W.; Schüth, F. *Chem. Mater.* **2015**, *27*, 3088-3095.
(6) Vetere, A.; Schrader, W. *Anal. Chem.* **2015**, *87*, 8874-8879.
(7) Molnárné Guricza, L.; Schrader, W. *Energy Fuels* **2015**, *29*, 6224-6230.
(8) Alachraf, M. W.; Wende, R. C.; Schuler, S. M. M.; Schreiner, P. R.; Schrader, W. *Chem.-Eur. J.* **2015**, *21*, 16203-16208.
(9) Wang, X.; Schrader, W. *Int. J. Mol. Sci.* **2015**, *16*, 30133-30143.

External funding: Deutsche Forschungsgemeinschaft (DFG); BMWi/ZIM (KF3121303SK4); SABIC Industries; Ivan Gubkin Program of the Deutsche Akademische Auslandsdienst (DAAD) (Scholarship for A. Stavitskaya), São Paulo Research Foundation Brazil (FAPESP) (Scholarship for J. Machado Santos)

Cooperations: J. T. Andersson (Münster, DE), B. List (Mülheim/Ruhr, DE), P. R. Schreiner (Marburg, DE), F. Schüth, (Mülheim/Ruhr, DE), M. N. Eberlin (Campinas, BR), R. Safieva (Moscow, RU)

3.4 Nuclear Magnetic Resonance (C. Farès)

Involved: W. Endler, B. Gabor, M. Kochius, J. Lingnau, M. Leutzsch, P. Philipps, C. Wirtz, B. Zibrowius

Service Activities

The NMR department provides a broad range of specialised NMR techniques and analytical service. During the reporting period, approximately 50,000 NMR spectra have been recorded on a wide range of samples, from natural products, active enzymes and metal complexes in solution to valorised wood, porous silicas and zeolites in solids. To meet demands, the department is equipped with six NMR spectrometers with field strengths corresponding to ^{1}H frequencies of 300, 400, 500 and 600 MHz for analyses in solution and of 300 and 500 MHz for analyses in solid state. The department is also staffed with technical and scientific co-workers, skilled in NMR set-up and interpretation as well as in related software and hardware maintenance. The department is organised in three broad areas of service.

(1) Open-Access and Routine NMR: Basic NMR measurements in liquid state can be carried out in high-throughput mode on a dedicated "open access" 300-MHz NMR spectrometers at room temperature. With minimal set-up, scientific personnel from the entire institute can access this instrument around the clock to obtain rapid NMR data automatically. The selection of available experiments is limited to those with high sensitivity, high information content and rapid execution with predefined parameters (e.g. 1D spectra of ^{1}H and common heteronuclei, simple 2D correlation experiments). Liquid samples requiring special set-up or treatment can be submitted for measurement to our operators on a 400-MHz spectrometer. The most common requests are: (a) unusual experiments or nuclear frequencies not available in the automatic mode, (b) experiments at high or low temperature, (c) advanced techniques requiring optimisation of acquisition parameters, and (d) spectroscopy of chemical reactions and kinetics followed in real time directly in the NMR tube. These services cover nearly 90% of all experiments run in our department.

(2) Advanced NMR Analyses Particularly challenging NMR studies of solution compounds are accepted for advanced analysis. For these samples, our experienced staff members provide full measurement, analysis and interpretation assistance in close collaboration with the chemical research groups. The advanced techniques are carried out on one of our two dedicated spectrometer: (a) a 600-MHz system, equipped with a

cryogenically-cooled probehead, which provides exquisite sensitivity and resolution for ^{1}H, ^{13}C and ^{15}N measurements near room temperature and which is ideally suited for sub-milligram quantities of 50+ carbon organic molecules; (b) a more versatile modern 500-MHz instrument which provides the possibility to measure at high and low temperature, to cover a broad range of NMR-active isotopes, and to run advanced triple-resonance experiments. A large part of the analytical work is dedicated to determine or confirm structures, stereochemistries, conformations and dynamics.

(3) Solid-State NMR Solid-state NMR spectroscopy remains one of the most important techniques for the characterisation of solid catalysts and other new materials synthesised in the institute (Schüth group). Both dedicated 300- and 500-MHz spectrometers are equipped with magic-angle spinning (MAS) probeheads to obtain high resolution signals from a wide range of NMR active nuclei. In continuation of work performed in previous years, solid-state NMR spectroscopy has particularly been applied for the characterisation of the following solids:

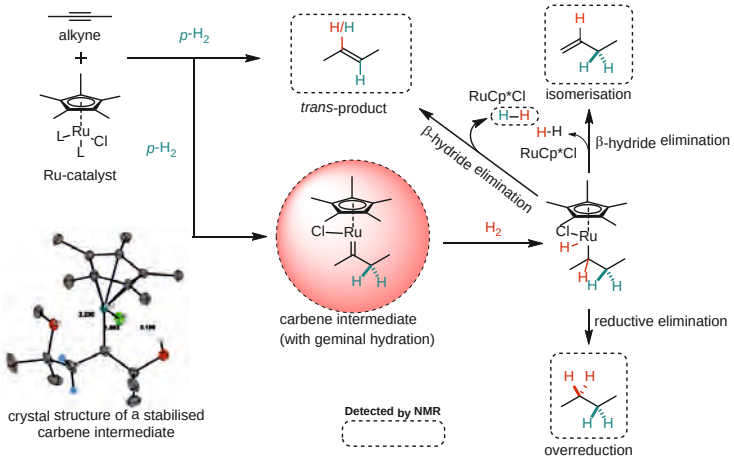
- Catalysts prepared from mesoporous silicas or zeolites (^{29}Si, ^{13}C and ^{27}Al)
- Complex aluminium hydrides and boron hydrides (mainly by ^{27}Al and ^{11}B NMR, respectively)
- Alkylaminoalanes (^{13}C and ^{27}Al)
- Products obtained in valorisation processes of wood and lignin (^{13}C).

Research Area "*Characterisation of reaction intermediates using PHIP*"

Objective: Using PHIP-NMR experiments, we aimed to provide a mechanistic interpretation of a novel *trans*-hydrogenation reaction by detecting and following its reaction intermediates.

Results: The group of A. Fürstner recently described a *trans*-selective hydrogenation reaction of internal alkynes using a ruthenium catalyst. To better understand the non-intuitive one-step *trans*-hydrogenation mechanism, as well as to identify the pathways leading to the unwanted over-reduced and isomerised side products, a mechanistic study based on NMR was instigated using *para*-hydrogen induced polarisation (PHIP). This specialised NMR method releases the "stored" polarisation of dihydrogen in its *para*-state (p-H_2) to boost its signals by a factor up to 10000 above the "thermal" NMR sensitivity and is ideally suited to detect the low-concentrated intermediates in hydrogenation reactions. Indeed, a distinctive carbene intermediate, unambiguously

formed *via* a "geminal hydrogenation" step, could be exposed for the first time. This unusual species was later stabilised through chemical modification and its structure could be confirmed by NMR and x-ray crystallography. In further PHIP-selective exchange correlation experiments (OPSY-EXSY), the fate of this intermediate could also be clearly identified, namely to the unwanted isomerised and reduced products as well as to the desired *trans*-product. With the support of DFT-calculations from the Thiel group, a detailed reaction pathway was inferred, whereby the involvement of a second hydrogen molecule was identified and which showed that the carbene intermediate plays a major part in the reaction, as a gateway to unwanted by-products (Scheme 1). A thorough understanding of the mechanism will hopefully help with the development of a second-generation *trans*-hydrogenating catalyst.



Scheme 1. PHIP-NMR observed species and their role in the catalytic hydrogenation of internal alkynes.

Other research activities

The NMR department continues to develop and to establish advanced NMR methodologies as part of their collection of routine applications. A number of state-of-the-art methods have been explored and used in the NMR department during the current reporting period.

- Residual dipolar couplings (RDC) to determine stereochemistries, to differentiate enantiomers and to provide complementary conformational and dynamic information.
- Rapid injection NMR (RINMR) for tracking catalytic transformations in "real time".
- Paramagnetic NMR to study the reaction mechanism of the FeFe-hydrogenase HydA1 (collaboration with the Lubitz Group, MPI-CEC)

Publications resulting from this research area:

(1) Käldström, M.; Meine, N.; Farès, C.; Rinaldi, R.; Schüth, F. *Green Chem.* **2014**, *16*, 2454-2462.

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External funding: none

Cooperations: Prof. Lubitz (Max Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, DE), Dr. Ulrich Sternberg (Jena, DE)

3.5 Electron Microscopy and Chemical Crystallography (C. W. Lehmann)

Introduction: The EmRay-Group combines all electron microscopy activities of the institute and selected areas of crystallography, namely crystal structure determination from single crystals and polycrystalline organic materials. The present research fields encompass electron density studies, crystal engineering and sub-nanometre EDX analysis. In addition to operating in-house facilities, the group is part of a team building the dedicated chemical crystallography beamline P24 at PETRA III in Hamburg.

Service Activities, *i) Crystallography:* The service activities focus on single crystal structure analysis and offer powder diffraction of organic compounds as an alternative method for crystal structure determination. The recent acquisition of a MetalJet X-ray source employing a gallium-indium alloy is a major step towards extremely brilliant X-rays.

For single crystal structure analysis state-of-the-art technology is employed, comprising three area detector systems. A Cu-rotating anode equipped with a four circle goniometer and a large surface area CCD-detector is used for the determination of the absolute configuration of enantiopure light atom compounds. Inorganic and organometallic compounds are investigated using either a Mo-rotating anode or a molybdenum micro focus X-ray source, both equipped with four circle goniometers. All diffractometer systems employ graded multilayer optics to maximise X-ray intensities and are equipped with liquid nitrogen low temperature devices for sample cooling and stabilisation. A total of approximately 500 data sets are collected annually, however an increasing number of samples yield only very small crystals with dimensions of less than 20 μm. These samples will benefit most from the MetalJet X-ray source after its completion. Until then, selected samples are analysed using synchrotron radiation. In the past the single crystal beamline at ANKA Karlsruhe was employed, however following termination of the general user operation at ANKA successful applications were made to the protein beamline P11 at the Petra III synchrotron operated by DESY in Hamburg. Since September 2013 we have measured 199 datasets at DESY. Currently we investigate crystals in the 10-50 μm diameter range at the synchrotron facilities. Routine crystal structure determination of crystals with a diameter in the range of 1-10 μm still remain a challenge.

ii) Electron Microscopy: The instrumentation for electron microscopy has seen the addition of a dedicated scanning transmission electron microscope equipped with a spherical aberration corrector, cold field emission gun operating at up to 200 kV and an

EDX detector covering more than one steradian of solid angle. The self-service facilities were extended further by means of a 15 kV desktop SEM. Presently available electron microscopes in the group comprise further a 200 kV TEM with cold field emitter gun, able to obtain micrographs with atomic resolution. Two 120 kV TEMs supplement the set-up. One of these 120 kV transmission electron microscopes has been dedicated for self-service by trained PhD students and Post-Docs. Scanning electron microscopy is performed with an ultra-high resolution microscope, which gives a line resolution better than 0.34 nm (graphite lattice spacing). For qualitative and quantitative chemical analysis of solid samples a further 30 kV SEM is in operation. An important aspect of the electron microscopy service is the sample preparation, which forms a crucial part of the activities in the group. In addition to established coating and cutting methods, in particular ultra-microtomes, the group is constantly honing its methods and is introducing new techniques in particular argon ion sample thinning for the new STEM.

Research Projects, *Electron Density Studies:* New collaborations with W. Frank (Düsseldorf) and J. Ellena (Sao Paulo, Brazil) have been started in this area. One project concerns the structural chemistry and chemical bonding in dispirocyclic λ3,λ5-tetraphosphetes like $(Me_2Si(NtBu)(NtBu)P_2)_2$. These tetraphosphetes are remarkably stable in air and show unexpected molecular properties related to the unique bonding situation of the central four-π-electron four-membered phosphorus ring. The extent of rhombic distortion of the central P4 ring is remarkable due to an unusually acute angle at the σ2-phosphorus atoms. All of the P—P bonds are approximately equal in length. Static deformation density and topological analysis reveal a unique bonding situation in the central unsaturated P4 fragment characterized by polar σ-bonding, pronounced out-of-ring non-bonding lone pair density on the σ2-phosphorus atoms, and an additional non-classical three-center back-bonding contribution.

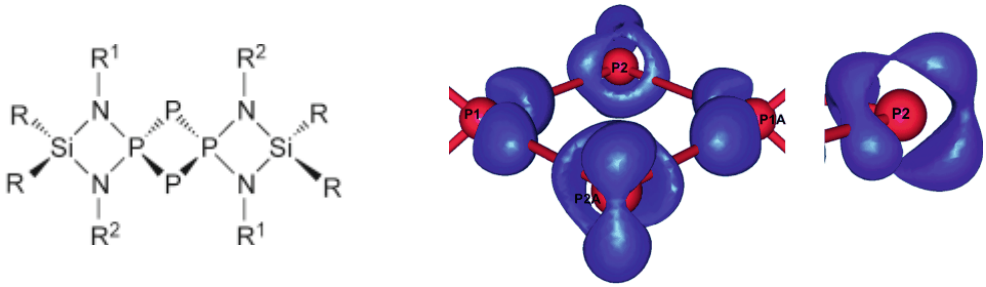

Fig. 1. Molecular diagram of the tetraphosphete (left) and isosurface representation of the static deformation density (0.17 e $Å^{-3}$) in the P4 unit and for atom P2 (right).

Crystal Engineering (N. Nöthling): In this area our interest in diastereomeric and chiral co-crystals has been extended to ternary systems including a component which is liquid at ambient conditions. While lactic acid was not included in the co-crystal, it induced a

new polymorph of the previously studied system (*R*)-proline amide – (*R*)-mandelic acid (Master thesis N. Nöthling). Lately we have focussed our efforts to grow single crystals of small molecules, which are liquids at room temperature and are common place chemicals like anisole, 2-methylfuran, furfural and, as shown below, acetic anhydride. Electron diffraction studies and theoretical calculations on the gas phase indicate that acetic anhydride exists as a mixture of planar and non-planar rotamers. All H atoms undergo hydrogen bonding, but only with the O atoms of the carbonyl groups.

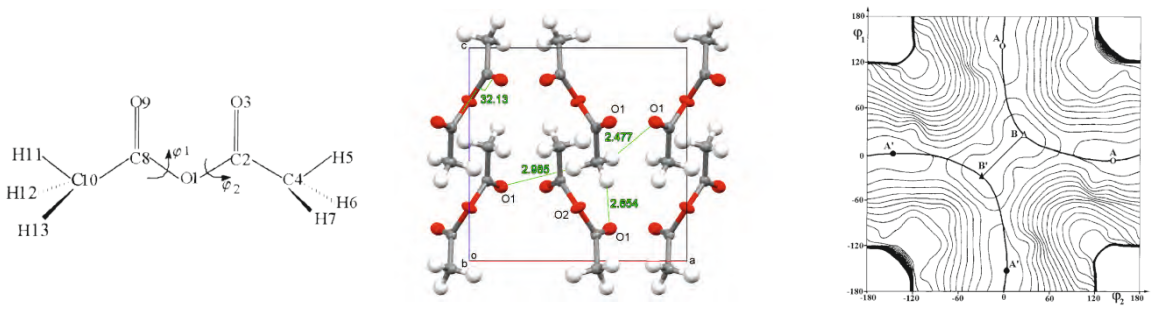

Fig. 2. Molecular diagram of acetic anhydride, showing the critical dihedral angles (left), the hydrogen bonding and molecular conformation in the crystal (centre) and the conformational energy map at 4-21G level, the minimum is along BB' and the contour level 1 kcal/mol. The conformational ratio A:B is 63:37% (right).

Chemical Crystallography Synchrotron Beamline: The extension to the PETRA III synchrotron laboratory at DESY in Hamburg is almost completed. The process has been delayed by about 18 month related to the civil engineering activities at DESY. However, in Hall East the hutch and infrastructure have been installed for the dedicated chemical crystallography beamline P24 meanwhile. Together with MPI Chemische Physik fester Stoffe (J. Grin) funding for additional components for this beamline, in particular the detector and a liquid nitrogen cooled monochromator has been secured. Specific emphasis is being placed on handling reactive and sensitive samples in a state-of-the-art diffraction set-up. Very successful proof-of-principle experiments at the macromolecular beamline P11 have prompted us to install a sample changing robot at our beamline P24 in order to achieve data collection and turn-around times of less than 2 minutes.

High resolution EDX analysis of Pt-Ni particles embedded in hollow graphitic spheres (A.-C. Swertz): Pt-Ni particles embedded in hollow graphitic spheres have been proven as highly active catalyst for the oxygen-reduction reaction in fuel cell application. The analysis of these particles with an average size of 3.5 nm was performed using the ultrahigh-resolution Hitachi HD-2700 scanning transmission electron microscope. EDX line scans with a high spatial resolution (≤ 0.2 nm) allow the characterization of individual nanoparticles. Before the electrochemical degradation the structure of these

particles could be identified as alloy with a homogenous distribution of Pt and Ni throughout the particles. After electrochemical degradation the line profiles clearly evidence the formation of a core-shell like structure with a Pt-Ni alloy core surrounded by a 0.5-1 nm thin Pt-rich shell.

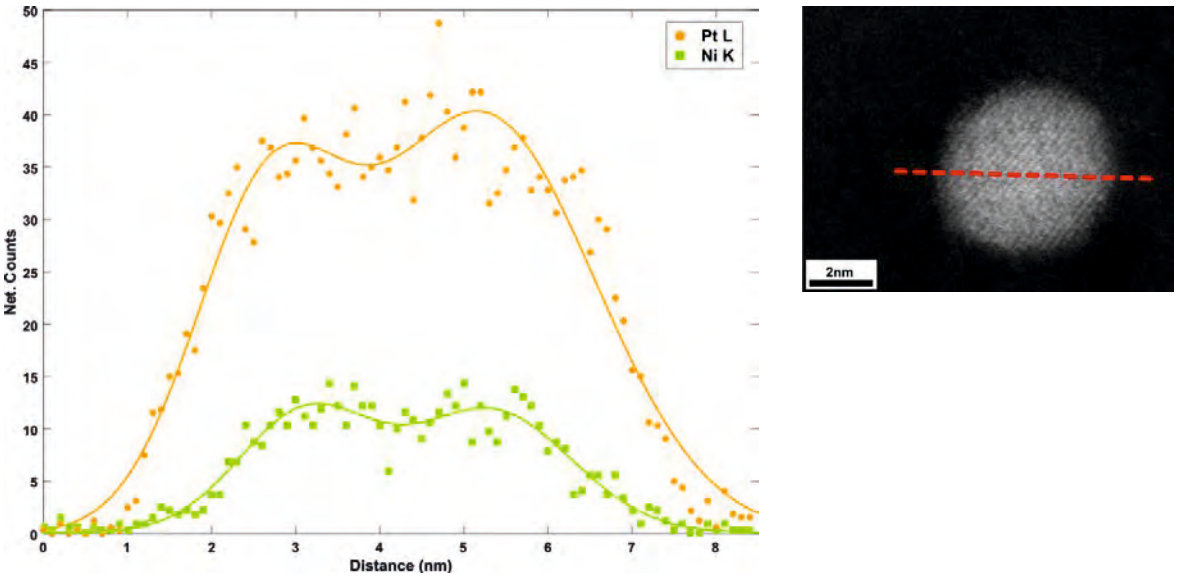

Fig. 3. HAADF image and EDX line scan of one Pt-Ni particle after electrochemical degradation. The elemental distribution of Pt and Ni show the formation of a core-shell like particle.

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Cooperations: U. Englert (Aachen, DE), W. Grünert (Bochum, DE), F. Mohr (Wuppertal, DE), J. J. Schneider (Darmstadt, DE), O. Terasaki (Stockholm, SE), W. Frank (Düsseldorf, DE), J. Ellena (Sao Paulo, BR), D. Enders (Aachen, DE), S. Barcikowski (Essen, DE), S. Huber (Bochum, DE), J. Grin (Dresden, DE).

3.6 Library and Information Management (P. Fischer, R. Lohmer)

Our one-person library is responsible for providing all library-services for our Institute. It serves the five chemical departments by buying, collecting and archiving books and journals. The focus of the collection is on organic, organometallic, theoretical, polymer and coal chemistry as well as on materials science. More than 17000 books and monographs and over 670 theses cover all aspects of catalysis; an inventory was carried out in 2014. All media are electronically catalogued and searchable by the ALEPH program. The library also contains a large collection of recent and historic print-journals. The 75+ subscribed journals and book series are electronically catalogued and most of them can be accessed as digital media.

Furthermore our library participates in the "Max Planck Digital Library (MPDL)" which covers the digital activities of the Max Planck Society. Since 2008 all required processes for collaboration between MPDL and local libraries are established and work well.

The "MPDL basic service" of the Max Planck Society provides online access to most of the key journals needed by our scientists. A list of the relevant publishers is part of the library intranet page of our institute. In 2015 we have set up a new Intranet presentation that covers the library services, with a special focus on the available contents and a user-friendly design.

The "MPDL basic service" also allows us to get print journals for deep discount prices, e.g. the products from the American Chemical Society, the Royal Society of Chemistry, the deGruyter Group and the Wiley group. Therefore, we continue purchasing a selected number of such journals until the electronic long term archive problem is resolved either by the publishers themselves or by the Max Planck Society. Additionally we subscribe to 70 print journals that are not included in the MPDL basic service.

Scientific papers not available in our or any other MPG library can be ordered and accessed via SUBITO, Fernleihe, IFLA, etc.

We have not yet introduced e-books because there were no clear license modes that convinced us to switch from printed books. However, we share all relevant information with other institutes and the MPDL and make preparations for archiving and indexing e-books. It is expected that we are in the position to introduce e-books by 2017.

Printed books, however, remain integral part of our library; their number is constantly growing by ca. 120 titles per year. In addition, many books are borrowed from other libraries.

Since 2012 we administer all publications from our institute in the publication repository “Pubman (Pure)” of MPDL. This allows us to prepare publication lists as needed for the internet portal or for various presentations (MPG Jahrbuch, the Report for the Scientific Advisory Board etc). Because Pubman is constantly evolving, the librarian carries out trainings to familiarize our (new) employees with the opportunities that the system provides.

3.7 Computer Group (P. Fischer)

The IT group is responsible for the IT infrastructure of our Institute. It supports the following areas:

- Electronic Laboratory Notebook with connected Archive (ELNA).
- Operation and enhancement of the common local area network (LAN).
- Acquisition, operation, and system management of central servers and attached devices.
- Selection and installation of new hardware and software in general.
- Computerization of experiments.
- Development of application software and its adaptation to new requirements.
- Administration of web pages and data bases.
- Information and education of computer users.
- Trouble shooting in case of failures.

Electronic Laboratory Notebook with connected Archive (ELNA):
The rollout of the system continued in 2014 with the Department of Prof. List. Continuous feedback by the group members resulted in requests for new features, which were implemented. Major changes in 2014:

- A new screening functionality
- Collection of analytic requests

In 2015 the members of the new Department of Prof. Ritter started immediately using ELNA. All members of Prof. Schüth's Department and of the Technical Laboratories adapted the electronic lab notebook by 2016. Required changes by these departments:

- Multi-level synthesis of up to twenty steps
- Single structures without reaction equations
- Timestamp-based text registration with added image
- Locally editable images of text entries

ELNA is now in operation in all experimental research groups of the Institute. Analytical requests can now completely be administered in ELNA for all co-workers of the Institute. Therefore, the former system to place and process analytical requests will be shut down at the end of 2016.

The architecture of the electronic archive was modified due to license policies. ELNA was extended to replace the Oracle WebLogic Content Management System mentioned in the previous report.

Local area network:
The network core infrastructure was newly designed, and old components were replaced to meet the growing and changing requirements for bandwidth, security, and availability and to provide the flexibility for future expansions. Furthermore a centrally administered WLAN solution with guest account management was implemented. The first video conferencing system of the Institute was installed as an additional collaboration platform for our scientists. Currently, the certificate-based authentication of end-point devices (according to standard IEEE 802.1x) is in the process of implementation.

Computer hardware:
The IT group operates the central UNIX and Windows servers of the Institute, and also manages the applications and the compute and file servers of the Department of Theory. The jobs from the Department of Theory are handled by a “grid engine queue system”.

The UNIX virtual machines that host central services (external and internal logins, internal email, internet and intranet web pages, DNS, DHCP, RADIUS, KERBEROS, etc.) were migrated to a new three-node ESX cluster with a VSAN for the disk of the VMs. The Windows Active Directory was updated to Windows Server 2012R2.

For the Department of Theory, the IT group maintains ca. 250 Linux servers based on Intel XEON and AMD Opteron CPUs, which are equipped with different amounts of memory and storage (small/medium/large) to support different computational applications. Currently there are a total of

- 384 cores for small computations,
- 2608 cores for medium-sized computations, and
- 1024 cores for large computations.

In addition, two servers are equipped with NVIDIA GPUs and 5 servers have 112 Gbit Infiniband interconnect.

Workstations and PCs:
PCs represent the largest number of work-place computers. There are ca. 700 PCs in our Institute. Most of them run Windows 7. In the Department of Theory as well as in several other service and research groups, there are Linux- or UNIX-based workstations for more demanding applications.

E-Mail:
The E-Mail-System (with almost all mailboxes and mailing lists) was migrated to the GWDG to a Microsoft Exchange 2010 Cluster. The E-Mail-System is linked by the IdM (Identity Management) of the GWDG to the Active Directory of our Institute to provide data synchronization.

Application software:
Safety data sheets for all chemical compounds used in our laboratories can be retrieved conveniently by a web browser from our in-house data base system. The underlying data is kept up to date according to current legal regulations. Analyses can be ordered electronically for gas chromatography, X-ray crystallography, and mass spectrometry. The IT group maintains an elaborate book-keeping system for gas-chromatography samples that had previously been designed and implemented in-house. Raw data and reports from mass spectrometry and gas chromatography are archived automatically.

The IT group continues to provide support to the library of the Institute through the Aleph 500 integrated library system. It also supports the Beilstein CrossFire database and the SciFinder interface to the Chemical Abstracts Service. OwnCloud, a file hosting service provided by the GWDG, was established for the new Department of Prof. Ritter to replace the formerly used Dropbox software. Finally, the IT group provides support for the travel-expenses reporting system, the flexitime logging system, and the new session desk Archimedes.

Development projects:
As already pointed out, the upgrade of features in the electronic laboratory notebook is an ongoing process that is driven by the needs of the scientists.
To provide a redundant Hyper-V-Infrastructure and to virtualize as many Windows-Server-systems as possible, a new Hyper-V-Cluster is planned.
Concerning the necessary renewal of our telecommunication system, the IT group plans to install a commercially available system that offers Voice-over-IP functionality.

CHAPTER 4

The Training of Young Scientists

4 The Training of Young Scientists

The Institute considers the training of **young scientists** (**master** and **doctoral students**, **post-docs**) a highly important task. Overall, their number amounts to more than 160 persons (Figure 1).

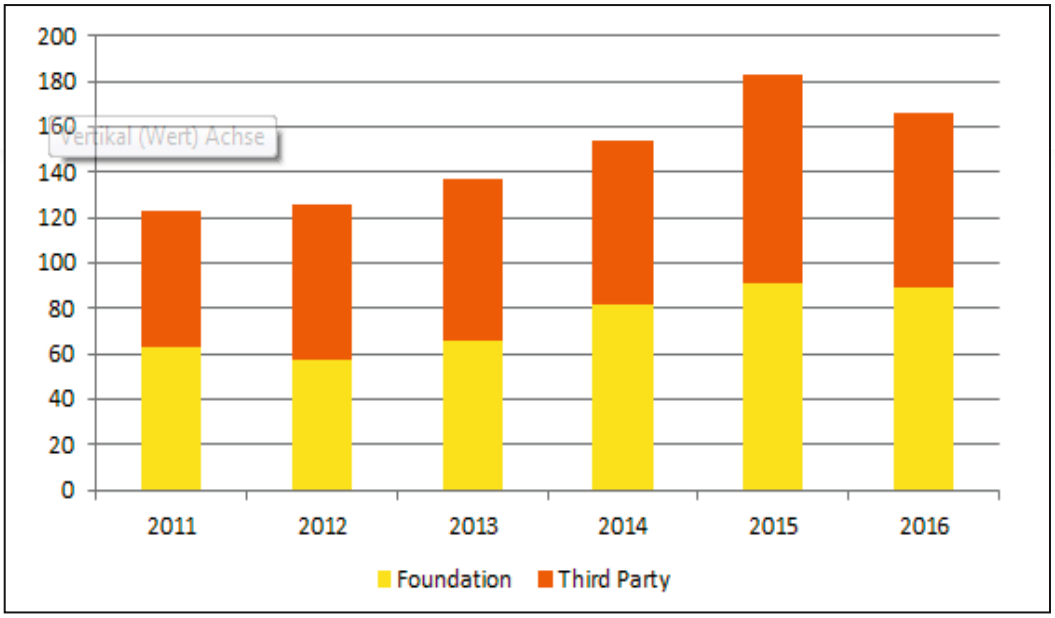


Fig. 1. Support for young scientists (reporting date: 09/30/2016)

The financial resources of the Institute allow for the support of about 50–60 such positions in the five departments of the scientific members (including the sub-groups). In addition, the independent junior research groups have a separate budget for such positions. Further positions are financed by third-party funds and by support grants awarded to individual scientists. From 2014 to 2016, the latter category included a series of scholarship awardees (Heisenberg, Alexander von Humboldt, Deutscher Akademischer Austauschdienst, Kekulé, Liebig) and similar awards from abroad (Austria, Belgium, China, Denmark, Japan, Mexico, Portugal, Spain, Switzerland, Turkey).

Status Dec 31, 2014	Total	MPG and Found. Funds.	Third-Party Funds	Male	Female	National	Intern.
Master students	5	2	3	2	3	4	1
PhD students	91	36	55	68	23	44	47
Post-docs	58	44	14	46	12	1	57
	154	82	72	116	38	49	105
Status **Dec 31, 2015**							
Master students	3	0	3	2	1	2	1
PhD students	105	48	57	83	22	45	60
Post-docs	75	43	32	58	17	3	72
	183	91	92	143	40	50	133
Status **Sept 30, 2016**							
Master students	5	3	2	2	3	5	0
PhD students	94	52	42	74	20	43	51
Post-docs	67	34	33	51	16	2	65
	166	89	77	127	39	50	116

Table 1. Young Scientists

The vast majority of the master and doctoral students come from German and European Universities. This includes the Universities with which the Institute's group are affiliated (Aachen, Berlin, Bochum, Cologne, Dortmund, Duisburg/Essen, Düsseldorf, Münster, Wuppertal).

The following table specifies the geographical origin of the postdocs.

Post-docs	**2011**	**2012**	**2013**	**2014**	**2015**	**Sept 30, 2016**
Europe	27	29	21	38	41	39
USA / Canada	1	-	4	5	7	5
Latin & South America	5	3	2	5	7	5
Asia	20	18	21	38	47	44
Africa / Australia	-	-	1	-	1	-
Total	**53**	**50**	**49**	**86***	**103***	**93***

Table 2. Postdocs: countries of origin

* since 2014, including staff members who have had a scholarship before

The training of the young scientists is supplemented by regular seminars within their department or group and by interdisciplinary Institute-wide colloquia including poster sessions. Furthermore, every year we organize the Karl Ziegler Guest Professorship, which consist of a 3-day long workshop for young scientists held by an internationally renowned scientist. The daily lectures are supplemented by discussions. Special emphasis is placed on the active participation of the young scientists.

The Institute participates in the International Max Planck Research School (IMPRS) for Surface and Interface Engineering in Advanced Materials since 2004 (Speaker: Prof. Jörg Neugebauer, MPI für Eisenforschung, Düsseldorf), and in the IMPRS Reactive Structure Analysis for Chemical Reactions (RECHARGE) since 2015 (Speaker: Prof. Frank Neese, MPI for Chemical Energy Conversion).

The Institute also contributes to the training of young scientists in the framework of several collaborative large-scale research projects. An important such project during the current report period was “SusChemSys” financed by the State of Nordrhein-Westfalen. In addition to the NRW Universities, several groups from our Institute were involved in this project aiming at the development of sustainable catalytic chemistry (Alcarazo, Fürstner, List, Maulide, Rinaldi, Schüth, Thiel).

In addition, selected young scientists from the Institute participate every year in workshops on catalysis organized by the chemical industry such as the Catalysis Research Laboratories (BASF together with the University of Heidelberg) and the BASF or Bayer PhD Student Courses.

34 PhD students graduated during the report period. Special emphasis is put on the support of young scientists at the outset of their independent academic careers. In the last years, 10 scientific group leaders worked at the Institute (2 independent research group leaders, 1 Heisenberg-Scholar, 1 RESOLV scholar, 1 Boehringer-Ingelheim Awardee), and 10 junior scientists from the Institute received calls from universities since 2008.

Name	**Year**	**University**
Mukherjee	2008	Bangalore, India
Trapp	2008	Heidelberg University
Yang	2009	Sungkyunkwan University, South Korea
Lu	2009	Dalian University, China
Palkovits	2010	RWTH Aachen
Zhang	2010	Dalian University, China
Maulide	2013	University of Vienna, Austria
Alcarazo	2015	Georg-August-University Göttingen
Barbatti	2015	Aix-Marseille Université
Rinaldi	2015	Imperial College London

Table 3. Calls from Universities

Dissertations 2014–2016

2014

Bock, Dominique Anna: Chirale Co-Kristallisation und Kristallstrukturen von Prolin-Enaminen. Wuppertal 2014.

Boulanger, Eliot: Development and Application of Hybrid Quantum Mechanical/Molecular Mechanical Methods with an Emphasis on the Implementation of a Fully Polariuable Model. Düsseldorf 2014.

Brewitz, Lennart: Die Verknüpfung von Ringschluss-Alkin-Metathese mit Transannularen Postmetathetischen Reaktionen in der Naturstoffsynthese. TU Dortmund 2014.

Gulzar, Naeem: C-H Functionalization Via Photochemically Generated Peroxides: Method Development and Mechanistic Studies. Cologne 2014.

Lehr, Konrad: Entwicklung einer alkylierenden Eliminierung zur Synthese interner Alkine und deren Anwendung in der Totalsynthese von Muscenon und Tulearin C. TU Dortmund 2014.

Neudeck, Carolina: Design of Nano-Sized Model Systems for Multi-Functional Materials with Hierarchical Structure. Bochum 2014.

Schweitzer-Chaput, Bertrand: Organocatalytic Oxidative Couplings: From Mechanistic Studies to New Radical Reactions. Cologne 2014.

Van Gemmeren, Manuel: Asymmetric Counteranion-Directed Lewis Acid Organocatalysis. Cologne 2014.

2015

Hilgert, Jakob: Mechanocatalytic Depolymerization of Cellulose and Subsequent Hydrogenation. Ruhr-Universität Bochum 2015.

Hoffmeister, Laura: Formale Totalsynthese von Kendomycin & Totalsynthese eines Marinen 4-Pyrons. TU Dortmund 2015.

Immohr, Sarah Maria: Mechanokatalytische Prozesse in der Kugelmühle. Ruhr-Universität Bochum 2015.

Karasulu, Bora: Computational Investigations of the Biocatalytic, Photophysical and Spectroscopic Properties of Flavins and Flavoproteins. Heinrich-Heine Universität Düsseldorf 2015.

Kim, Ji Hye: Brönsted Acid Catalyzed Asymmetric Acetalizations. Cologne 2015.

Kozma, Ágnes: Synthesis and Reactivity of Mono- and Polycationic Phosphines and Amines. TU Dortmund 2015.

Leutzsch, Markus H.: NMR Spectroscopic Investigations of Catalyzed Reactions – Mechanisms, Kintetics & Unexpected Intermediates. Cologne 2015.

Loerbroks, Claudia: Acid Hydrolysis of Cellulose and the Anomeric Effect: a Computational Study. Heinrich-Heine Universität Düsseldorf, 2015.

Mezzavilla, Stefano: Nanostructured Catalysts for the Application in Proton Exchange Membrane Fuel Cells. Bochum 2015.

Monaco, Mattia Riccardo: Activation of Carboxyclic Acids *via* Self-Assembly Organocatalysis. Cologne 2015.

Nunes de Oliveira, Heitor Fernando: Organic Solutions of Ionic Liquids and Aqueous Solutions of Electrolytes as Solvents for Cellulose Chemistry. Ruhr-Universität Bochum 2015.

Walter, Berit: Theoretical Investigations on Chemical Structures and Reaction Mechanisms Using Semi-empirical and Density Functional Methods. Heinrich-Heine-Universität Düsseldorf 2015.

Willwacher, Jens: Ringschluss-Alkin-Metathese/ Semihydrierung von Eninen: Total-synthesen von Leiodermatolide und Mandelalide A. TU Dortmund, 2015.

Zimmermann, Tobias: Selective Oxidation of Methane in Sulfuric Acid: Understanding and Improving Catalyst Activity, Stability, and Selectivity in the Periana System. Bochum 2015.

2016

Ferrini, Paola: Catalytic Upstream Biorefining of Lignocellusoses to Lignin Oils and Hydrosysable Holocelluloses. Ruhr-Universität Bochum 2016.

Gebauer, Konrad: Synthese von makrozyklischen, propargylischen Alkoholen durch ringschließende Alkinmetathese und deren postmetathetische Transformation. TU Dortmund 2016.

Grewe, Tobias: Nano-Engineered Tantalum-Based Materials for Photocatalytic Water Splitting. Ruhr-Universität Bochum 2016.

Gu, Lianghu: Synthesis von α-Cationic Phosphines and their Applications as Ligands. TU Dortmund 2016.

Kötzner, Lisa: Studies on the Catalytic Asymmetric Fischer Indolization. Cologne 2016.

Krech, Daniel: Die komplexen Aluminiumhydride des Cäsiums und Rubidiums: (Mechano-) Chemische Synthese und Strukturuntersuchungen. Ruhr-Universität Bochum 2016.

Linowski, P. M.: Synthesis and Applications of biscyclopropenium phosphines as ancillary ligands in catalysis. TU Dortmund 2016.

Preindl, Johannes: Totalsynthesen von 5,6-Dihydrocineromycin B, Radicinol und 3-*epi*-Radicinol sowie Synthesen der vermeintlichen Strukturen von 3-Methoxy-3-*epi*-Radicinol und Orevactaene. TU Dortmund 2016.

Rummelt, Stephan: Ruthenium-Katalysierte trans-Hydrostannierung von Alkinen und Verwandte Reaktionen. TU Dortmund 2016.

Schaubach, Sebastian: Advances in Alkyne Metathesis: Catalysts with Multivalent Siloxy Ligands & Formal Total Synthesis of (+)-Aspicilin & Stabilization of an alpha-Helical Peptide Structures. TU Dortmund 2016.

Sommer, Heiko: Transformations of Alkenylmetalloids. TU Dortmund 2016.

Spörkel, Lasse: Application and Development of Semiempirical Quantum Chemical Methods for the Investigation of the Dynamics of Electronically Excited States. Heinrich-Heine Universität Düsseldorf 2016.

Ungeheuer, Felix: Ringschluss-Alkin-Metathese von 1,3-Diinen: Totalsynthese von Ivorenolide A und B & Studien zur Totalsynthese von Rhizoxin D. TU Dortmund 2016.

Wang, Xuxiao: Development of Selective Analytical Methods for the Characterization of Complex Crude Oil Mixtures. Universität Duisburg-Essen 2016.

Master Theses 2014 - 2016

2014

Dierks, Michael: Microwave-assisted Hydrolysis of Carbohydrates. Münster 2014.

Hullermann, Abigail: Zeitaufgelöste Untersuchungen an farbstoffsensibilisierten Solarzellen. Duisburg-Essen 2014.

Pichler, Christian Marco: Studies Towards the Synthesis of Nanostructured Nickel Phosphide and Tungsten Carbide Materials. Graz 2014.

Rainko, Denis: Stabilitätsuntersuchung von Farbstoffsolarzellen. Duisburg-Essen 2014.

2015

Schreyer, Hannah: Mechanokatalytische Propenoxidation. München 2015.

Seifferth, Daniela.: Investigation of Photooxidative Degradation of Crude Oil by Ultra High Resolution Mass Spectrometry. Duisburg-Essen 2015.

Hastürk, Emrah: Design and Synthesis of New Bidentate Isocyanide Ligands for Application in Asymmetric Catalysis. Bochum 2015.

2016

Bilke, Jens Marius: Selektive Oxidation von Alkanen in Schwefelsäure. Garching 2016.

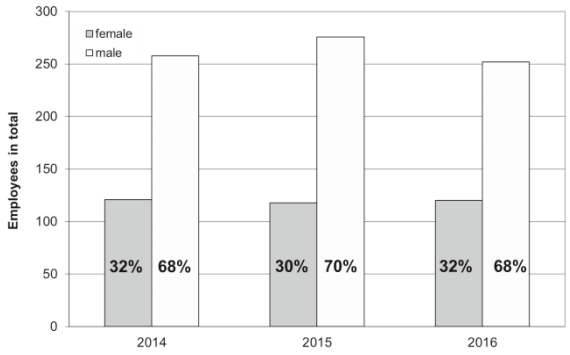
Puthenkalam, Sissy: Zeolith-geträgerte nanoskalige Hydrodesulfurierungs-Katalysatoren zur Entfernung von Schwefelverunreinigungen aus Flüssiggas-Strömen. Duisburg-Essen 2016.

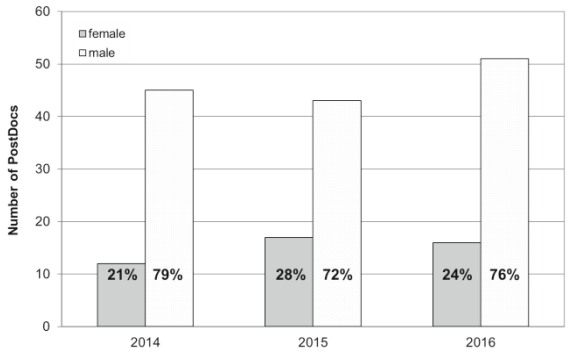
CHAPTER 5

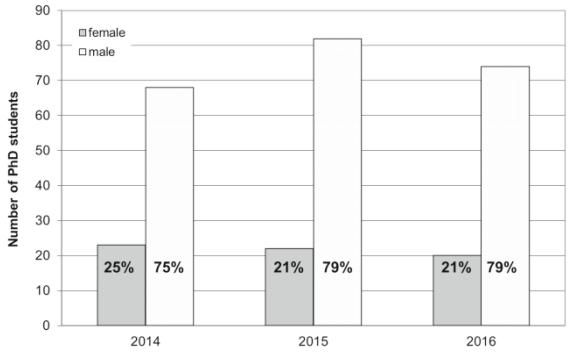
Equal Opportunities

5 Equal Opportunities (C. Weidenthaler)

In line with the general policy of the Max-Planck-Society, the Institute is committed to increase the number of female employees in all sectors of its work force. Compared to 2013, the total number of female employees has slightly decreased from 2013 to 2014 from 36 % to 32 % but remained stable over the report period. The fraction of women with postdoctoral positions fluctuated between 21 and 28 % within the report period.



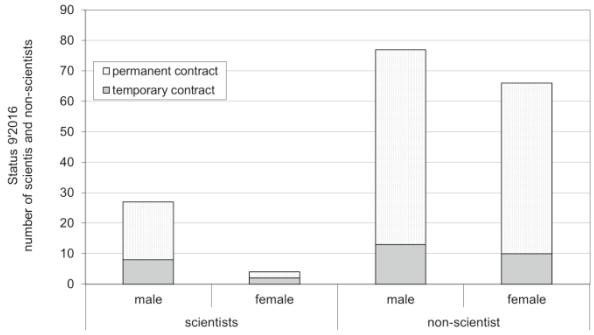




Over the last years we observe a significant and continuous decrease of female PhD students from 39% in 2013 to 21% in 2016. This development needs a critical evaluation

and strategies need to be developed to make the Institute more attractive for women in science and to encourage female students to apply for a PhD project.

Currently, four female scientists (TVöD 13 or better) are working at the Max-Planck-Institut für Kohlenforschung, two of them on a permanent position: Dr. Claudia Weidenthaler (group leader in the Department of Heterogeneous Catalysis) and Dr. Monika Lindner (Department of Homogeneous Catalysis). The two other female scientists work on temporary positions: in 2015, Dr. Elsa Sánchez-García became group leader in the Department of Theoretical Chemistry, Kateryna Peinecke is working in the Department of Heterogeneous Catalysis.



Currently, the equal opportunities representatives of the Institute are entrusted to implement a day care center for 9 children under the age of three for a minimum of 35 h per weak each in collaboration with a certified partner institution. The Institute will subsidize 4 of the childcare places according to the child care allowances stipulated by the MPG and cover the risk in case these positions remain vacant.

Dr. C. Weidenthaler was re-elected as the “equal opportunities representative” (“Gleichstellungsbeauftragte”) of the Institute in October 2016, with S. Holle as her deputy. Her rights and duties correspond to those previously defined by the MPG.

CHAPTER 6

Technology Transfer

6 Technology Transfer - Studiengesellschaft Kohle mbH (SGK)

The Max-Planck-Institut für Kohlenforschung has a long tradition in transferring the results of basic research in chemistry into industrial applications:

In the 1920's the Fischer-Tropsch process for the synthesis of gasoline from coal was developed and is still in use today. The economical impact of the Ziegler catalysts for the production of polyethylene and polypropylene, discovered in 1953/54, as well as of the process for the decaffeination of coffee beans by extracting the caffeine with supercritical carbon dioxide resulted in almost four decades of economical independence for the Institute.

In order to exploit the research results of the Institute a company acting as its trustee was founded decades ago (Studiengesellschaft Kohle mbH, SGK).

The purposes of Studiengesellschaft Kohle are

- patenting of inventions based on the research results
- licensing of the technology to industrial partners
- enforcing intellectual property rights
- negotiating research co-operations with industrial partners.

5 new patent applications were filed in 2014, 7 in 2015 and 5 in 2016 (see list of patent applications). For 30 applications from earlier years, patents were issued in 2014 to 2016 in Canada, China, Europe, India, Japan, Mexico, South Korea and USA.

License agreements exist in the reporting period for: Method for decarboxylating C-C bond formation of carboxylic acids with carbon electrophiles, Chiral Disulfonimides; Catalysts for the alkyne metathesis; Molybdenum and Tungsten Metal Complexes and use thereof as precatalysts for olefin metathesis; Multiplexing-Gaschromatographie, and for the use of different software.

Over the period 2014 to 2016 14 direct co-operations with industrial partners were in operation. Such cooperative projects are partially financed by the partner, who in return is granted an option to a license for patents resulting from the project.

The Studiengesellschaft also assists researchers of the Institute who want to start up companies based on results and know-how from the Institute. The Heidelberg-based hte

AG was co-founded by Professor Dr. F. Schüth several years ago but has now been sold to BASF SE.

Oliver Trapp, who was a group leader in the Department of Heterogeneous Catalysis until 2008, founded – after discussions with SGK – a company Trapp ChemTech GmbH & Co. KG which exploits the high-throughput multiplexing gas chromatography methods developed by him at the institute. A non-exclusive license agreement with the Trapp ChemTech was entered into in 2014.

General Manager ("Geschäftsführer") of the Studiengesellschaft is Professor Dr. Ferdi Schüth. Operational functions are performed by Dr. Matthias Nobbe, a patent lawyer, who works for the Institute for about 6 days/month on a freelance contract, and who has a power of attorney for SGK. To foster the licensing activities, the Institute signed a contract in 2009 with Max Planck Innovation, Munich, as the central technology transfer agency of the Max Planck Society. This contract was extended in 2011, whereby it automatically extends for a further year, if none of the parties terminates it at least three months before the end of the year.

Patent Applications 2014

1. Novel diazabicyclohydrocarbon-PT complexes and the use thereof as pharmaceuticals
   (Klaus-Richard Pörschke, Huiling Cui)

2. Process for production of non-pyrolytic bio-oil from lignocellulosic materials
   (Roberto Rinaldi, Paola Ferrini)

3. Process for preparing catalyst loaded polyphenylene particles, the obtained polyphenylene particles and their use as catalysts
   (Alois Fürstner, Ferdi Schüth, Feng Wang)

4. N-substituted pyridiniophosphines, processes for their preparation and their use
   (Manuel Alcarazo, Hendrik Tinnermann, Christian Wille)

5. Process for preparing leiodermatolide derivatives and their use
   (Alois Fürstner, Damien Maihol, Jens Willwacher)

Patent Applications 2015

1. Low Temperature Radical Initiator System and Processes making use thereof
(Martin Klußmann, Bertrand Schweitzer-Chaput, Hasselt University Inventors: Thomas Junkers, Joke Vandenbergh)

2. Process for preparing product oil from peat, coir or peat-like substances
(Robert Rinaldi, Marco Kennema)

3. Substituted Imidazolium sulfuranes and their use
(Manuel Alcarazo, Javier Gonzalez Pena, Garazi Talavera Urquijo)

4. Chiral Phosphoramidimidates and Derivates thereof
(Benjamin List, Philip Kaib)

5. Neue anionische Tenside und Waschmittel, welche diese enthalten (Applicants are Studiengesellschaft Kohle and Henkel)
(Roberto Rinaldi, Hebert Jesus Estevez Rivera, Henkel-Inventors: Christian Kropf, Alexander Schulz, Hendrik Hellmuth)

6. Neue anionische Tenside und Waschmittel, welche diese enthalten (Applicants are Studiengesellschaft Kohle and Henkel)
(Roberto Rinaldi, Hebert Jesus Estevez Rivera, Henkel-Inventors: Christian Kropf, Alexander Schulz, Hendrik Hellmuth)

7. Process for the Catalytic Reversible Alkene-Nitrile Interconversion
(Bill Morandi, Peng Yu, Xianjie Fang)

Patent Applications 2016

1. Process for preparing mesoporous carbon loaded with catalytically active metal and/or metal oxide nanoparticles for the transfer hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols
(Ferdi Schüth, Guang-Hui Wang)

2. Process for Removing Radioactive Isotopes from Aqueous Fluids by Fluorine Containing Reagents, Fluorine Containing, Water-insoluble Salts of the Radioactive Isotopes, and their Use as Therapeutic Agents
(Klaus-Richard Pörschke, David Pollak)

3. Process for preparing a substituted aromatic or heteroaromatic hydrocarbon and its use (Applicants are Studiengesellschaft Kohle and Harvard University)
(Tobias Ritter, Gregory Boursalian, Fabien Serpier)

4. Direct Palladium Catalyzed Aryl Fluorination (The application was filed by Harvard University)
(Tobias Ritter)

5. Process for the Oligomerization of Acetylene in the Presence of Hydrogen and a Solid Catalyst
(Ferdi Schüth, Iona-Teodor Trotus)

CHAPTER 7

Appendices

7.1 List of Publications 2014-2016

During the period 2014-2016 the Institute has published scientific contributions in total of 507 articles and book sections. For individual publication lists see the corresponding sections.

2014

Acevedo Rocha, C. G.; Reetz, M. T. Assembly of Designed Oligonucleotides: A Useful Tool in Synthetic Biology for Creating High Quality Combinatorial DNA Libraries. In *Directed Evolution Library Creation*; Gillam, E. M. J., Copp, J. N., Ackerley, D. F., Eds., 2nd ed.; Springer+Business Media: New York, **2014**; pp 189-206.

Acevedo Rocha, C. G.; Hoebenreich, S.; Reetz, M. T.; Iterative Saturation Mutagenesis: A Powerful Approach to Engineer Proteins by Systematically Simulating Darwinian Evolution. In *Directed Evolution Library Creation*; Gillam, E. M. J., Copp, J. N., Ackerley, D. F., Eds., 2nd ed.; Springer+Business Media: New York, **2014**, pp 103-128.

Acevedo-Rocha, C. G.; Agudo Torres, R.; Reetz, M. T. Directed Evolution of Stereoselective Enzymes Based on Genetic Selection as Opposed to Screening Systems. *J. Biotechnol.* **2014**, *191*, 3-10.

Alcarazo, M. α-Cationic Phosphines: Synthesis and Applications. *Chem.–Eur. J.* **2014**, *20*, 7868-7877.

Alcarazo, M. Frustrated Lewis Pairs: An Elegant Concept for Catalysis. *Synlett* **2014**, *25*, 1519-1520.

Altun, A.; Breidung, J.; Neese, F.; Thiel, W. Correlated Ab Initio and Density Functional Studies on H_2 Activation by FeO^+. *J. Chem. Theory Comput.* **2014**, *10*, 3807-3820.

Antol, I.; Glasovac, Z.; Crespo-Otero, R.; Barbatti, M. Guanidine and Guanidinium Cation in the Excited State—Theoretical Investigation. *J. Chem. Phys.* **2014**, *141*, 074307/1-10.

Asahina, S.; Suga, M.; Takahashi, H.; Jeong, H. Y.; Galeano Nunez, D. C.; Schune, F.; Terasaki, O. Direct Observation and Analysis of York-Shell Materials Using Low-Voltage High-Resolution Scanning Electron Microscopy: Nanometal-Particles Encapsulated in Metal-Oxide, Carbon, and Polymer. *APL Mater.* **2014**, *2*, 113317/1-7.

Baldizzone, C.; Mezzavilla, S.; Carvalho, H. W. P.; Meier, J. C.; Schuppert, A. K.; Heggen, M.; Galeano, C.; Grunwaldt, J.-D.; Schüth, F.; Mayrhofer, K. J. J. Confined-Space Alloying of Nanoparticles for the Synthesis of Efficient PtNi Fuel-Cell Catalysts. *Angew. Chem., Int. Ed.* **2014**, *53*, 14250-14254.

Barbatti, M.; Ruckenbauer, M.; Plasser, F.; Pittner, J.; Granucci, G.; Persico, M.; Lischka, H. Newton-X: A Surface-Hopping Program for Nonadiabatic Molecular Dynamics. *WIREs Comput. Mol. Sci.* **2014**, *4*, 26-33.

Barbatti, M. Computational Reference Data for the Photochemistry of Cyclobutane Pyrimidine Dimers. *ChemPhysChem* **2014**, *15*, 3342-3354.

Barbatti, M. Photorelaxation Induced by Water-Chromophore Electron Transfer. *J. Am. Chem. Soc.* **2014**, *136*, 10246-10249.

Bazula, P.; Arnal, P.; Galeano Nunez, D. C.; Zibrowius, B.; Schmidt, W.; Schüth, F. Highly Microporous Monodisperse Silica Spheres Synthesized by the Stöber Process. *Microporous Mesoporous Mater.* **2014**, *200*, 317-325.

Bellani, S.; Fazzi, D.; Bruno, P.; Giussani, E.; Canesi, E. V.; Guglielmo, L.; Antognazza, M. R. Reversible P3HT/Oxygen Charge Transfer Complex Identification in Thin Films Exposed to Direct Contact with Water. *J. Phys. Chem. C* **2014**, *118*, 6291-6299.

Bellussi, G.; Caro, J.; Kärger, J.; Schüth, F.; Stöcker, M.; Weitkamp, J. Obituary Hellmut G. Karge (1931-2013). *Microporous Mesoporous Mater.* **2014**, *184*, 70-71.

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7.2 List of Invited Talks Given by Members of the Institute (2014–2016)

2014

Alcarazo, M.

- University of Frankfurt, DE, January 2014
- University of Cardiff, UK, February 2014
- Bayer Healthcare, Wuppertal, DE, March 2014
- Steinheimer Meeting, Bad Homburg, DE, June 2014
- University of Dublin, IE, June 2014
- Phosphorus Conference, Dublin, IE, July 2014
- University of Bonn, DE, July 2014
- Georg August University of Göttingen, DE, July 2014
- TU Munich, DE, July 2014
- Chirality Meeting. Prague, CZ, July 2014
- ACS Meeting, San Francisco, US, August 2014
- Euro-Asian Meeting in Catalysis, Cesme, TR, September 2014
- University of Zaragoza, ES, December 2014

Barbatti, M.

- Workshop: Nonadiabatic Dynamics and Excited States, University of Jeddah, Jeddah, SA, February 2014
- Conference “Light in Chemistry, Materials and Biology”, Kharagpur, IN, February 2014
- III Interdisciplinary Symposium in Physics + Bioinformatics 2014, Uberlandia, BR, April 2014
- Conference “Promoting Female Excellence in Theoretical and Computational Chemistry II”, Oslo, NO, June 2014
- 10th Congress of the World Association of Theoretical and Computational Chemists (WATOC), Santiago de Chile, CL, October 2014
- Université Aix-Marseille, Marseille, FR, October 2014

Farès, C.

- Sino-German Symposium on Novel NMR-based Methods for Organic Structure Determination, Wenzhou, CN, November 2014

Fazzi, D.

- Universidad de Malaga, ES, March 2014
- E-MRS, Lille, FR, May 2014
- Heinrich Heine University Düsseldorf, DE, December 2014

Felderhoff, M.

- Interdisciplinary Nanoscience Center iNano, University of Aarhus, DK, January 2014
- Rockwood-Lithium, Frankfurt, DE, May 2014
- MH2014, Manchester, UK, July 2014
- South China University of Technology SCUT, Guangzhou, CN, October 2014
- BASF, Ludwigshafen, DE, October 2014

Fürstner, A.

- Day of Chemistry, TU Dortmund, DE, February 2014
- Inhoffen Medal, TU Braunschweig, DE, March 2014
- Gay-Lussac/Humboldt Prize, Paris, FR, April 2014
- International Green Chemistry Symposium, University Rennes, FR, April 2014
- Siegfried-Hünig Lecture, University of Würzburg, DE, May 2014
- GDCh Lecture, University of Marburg, DE, May 2014
- XXIII International Symposium on Medicinal Chemistry, EFMC-ISMC 2014, Lisbon, PT, September 2014
- DSM Kaiseraugst, CH, November 2014

Gebauer, K.

- Day of Chemistry, TU Dortmund, DE, February 2014
- ORCHEM 2014, 19. Lecture Conference, Weimar, DE, September 2014

Heyden, M.

- TSRC Meeting: Protein Dynamics, Les Houches, FR, May 2014
- Institute de Biologie Structurale (IBS), Grenoble, FR, May 2014
- Heinrich Heine University Düsseldorf, DE, May 2014
- Helmholtz-Zentrum Berlin, DE, June 2014
- Gordon Research Conference (GRC) on Water and Aqueous Solutions, Holderness, NH, US, July 2014
- Heidelberg Institute for Theoretical Studies (HITS), Heidelberg, DE, July 2014
- University of Freiburg, DE, July 2014

Klußmann, M.

- Paderborn University, DE, February 2014
- Chemiedozententagung, Paderborn University, DE, March 2014
- EUCHEM Conference on Organic Free Radicals, Prague, CZ, June/July 2014

Lehmann, C. W.

- Nano 2014, Moscow, RU, July 2014

Leitner, W.

- Royal Society International Seminar, Chicheley Hall, UK, February 2014
- 4th International Congress on Green Process Engineering (GPE 2014) Seville, ES, April 2014
- BMBF Statuskonferenz und Workshop Petersberg, Bonn, DE, April 2014
- DGMK Fachtagung „Konversion von Biomasse“, Rotenburg an der Fulda, DE, May 2014
- Fachgespräch Biomasse NRW MiWF, Düsseldorf, DE, May 2014
- 17. Steinheimer Gespräche des Fonds der Chemischen Industrie, Bad Homburg, DE, June 2014
- TMFB-Konferenz, Aachen, DE, June 2014
- SYNFLOW Final Public Event, Aachen, DE, July 2014
- GDCh Lecture, University of Stuttgart, DE, July 2014
- Chemistry Seminar, Universitat Rovira i Virgili, Tarragona, ES, July 2014
- Chemistry and Global Stewardship - Plenary Session 248th Annual Meeting of the American Chemical Society, San Francisco, US, August 2014
- 5th EuCheMSChemistry Congress, Istanbul, TR, September 2014
- The CO2 Forum, 3rd Edition Lyon, FR, September 2014
- GDCh Lecture, Leipzig, DE, October 2014
- Chemisty Seminar, University of York, UK, November 2014
- Scientific Advisory Board of L’Oréal, Paris, FR, November 2014

List, B.

- 8th Singapore Intern. Chem. Conference, SG, December 2014
- University of Shenzhen, Shenzhen, CN, December 2014
- University of Hong Kong, CN, December 2014
- Germany-Japan Bilateral Meeting 2014, Berlin, DE, September 2014
- Instituto di Química, Universidade de Sao Paulo, BR, February 2014

Marlow, F.

- RESOLV Workshop, Ruhr University Bochum, DE, December 2014

Morandi, B.

- University of Illinois, US, January 2014
- University of Chicago, US, January 2014
- Max-Planck Research Group Selection Symposium, Munich, DE, January 2014
- Institute of Science and Technology Austria, AT, January 2014
- Max-Planck-Institut für Kohlenforschung, Mülheim, DE, January 2014
- The Ohio State University, US, February 2014
- Ruhr University Bochum, DE, July 2014

Pörschke, K.-R.

- Materials Valley e.V. Workshop “Homogene Katalyse”, BASF, Ludwigshafen, DE, January 2014

Prieto, G.

- Institute of Chemistry Research of Catalonia (ICIQ),Tarragona, ES, March 2014
  Rockwood-Lithium, Frankfurt, DE, May 2014

Reetz, M. T.

- GDCh Lecture, University of Münster, DE, January 2014
- University of Hamburg, OC-Kolloquium, DE, January 2014
- Rauischholzhausen, Symposium on Aspect of Time in Drug Design, DE, March 2014
- University of Florida, Paul Tarrant Lectureship I-IV, Gainesville, US, May 2014
- École Polytechnique Féderale de Lausanne, CH, May 2014
- Karls-University, Chirality Medal Lecture, Prague, CZ, July 2014
- Heinrich Heine University Düsseldorf, CLIB/GRASP-Symposium, DE, September 2014
- J. J. Barluenga Lectureship, Oviedo, ES, November 2014

Sánchez-García, E.

- RESOLV Symposium, Ruhr University Bochum, DE, January 2014
- Autumn Workshop of the Graduate School of Solvation Science, Bochum, DE, October 2014
- ISRIUM 2014 Symposium, Hiroshima, JP, April 2014

Schmidt. W.

- ProcessNet Jahrestreffen der Fachgruppe Adsorption, Fulda, DE, March 2014
- Workshop on Targeted Characterization of Porous Solids, Seeheim, DE, April 2014
- Fifth Max-Planck LeadNet Meeting, Mainz, DE, May 2014

Schrader, W.

- Workshop ASMS Interestgroup Energy, Petroleum and Biofuels, Baltimore, US, June 2014
- Colloquium Analytical Chemistry, Univ. Mainz, DE, July 2014

Schüth, F

- Meet the Female Faculty, Ruhr University Bochum, DE, January 2014
- University of Oldenburg, DE, January 2014
- GDCh Lecture, Heinrich Heine University Düsseldorf, DE, January 2014
- Symposium of Leopoldina, Halle, DE, February 2014
- University of Oldenburg, DE, January 2014
- Leopoldina, Potsdam, DE, April 2014
- Deutsche Physikalische Gesellschaft, Bad Honnef, DE, April 2014
- Anniversary Lecture, Max-Planck-Institut für Kohlenforschung, Mülheim, DE, April 2014
- GDCh Lecture, University of Regensburg, DE, April 2014
- University of Marburg, DE, May2014
- BASF, Ludwigshafen, DE, June 2014
- MSE-Congress, Darmstadt, DE, September 2014

Theyssen, N.

- International Green Catalysis Symposium, Rennes, FR, April 2014

Thiel, W.

- GDCh Lecture, University of Würzburg, DE, January 2014
- Physical Chemistry Seminar, University of Würzburg, DE, January 2014
- CECP-2014 Meeting on Photochemistry, Bad Hofgastein, AT, February 2014
- CarLa Winterschool, Heidelberg University, DE, February 2014
- SFB 749 Symposium,Venedig, IT, March 2014
- Southern Methodist University, Department of Chemistry, Dallas, US, April 2014

- Theoretical Chemistry Seminar, University of North Texas, Denton, US, April 2014
- Davidson Lecture, University of North Texas, Denton, US, April 2014
- UC Berkeley, Department of Chemistry, Berkeley, US, April 2014
- Heraeus-Symposium: Biokatalyse, Ludwigshafen, DE, April 2014
- Marian-Symposium, Heinrich Heine University Düsseldorf, DE, June 2014
- Bunsen-Lecture, University of Marburg, DE, June 2014
- 18th International Flavin Symposium, Phechaburi, Thailand, TH, June 2014
- ACS National Meeting, Symposium on Proton Transfer, San Francisco, US, August 2014
- ACS National Meeting, Handy Symposium, San Francisco, US, August 2014
- 50th Symposium for Theoretical Chemistry, Wien, AT, September 2014
- WATOC-2014 Congress, Santiago de Chile, CL, October 2014
- WATOC-2014 Satellite, Concepcion, CL, October 2014
- Theoretical Chemistry Seminar, Université de Lorraine, Nancy, FR, December 2014
- International Symposium on Molecular Machines, Schloss Ringberg, DE, December 2014

Tüysüz, H.

- Nano and Giga Challenges in Electronics, Photonics and Renewable Energy, Tempe AZ, US, March 2014
- Bayer Material Science, Leverkusen, DE, May 2014
- Max-Planck Institut für Eisenforschung, Düsseldorf, DE, June 2014

Weidenthaler, C.

- LeadNet Meeting of the MPG, Mainz, DE, May 2014
- Metal Hydride Conference, Manchester, UK, July 2014

Zheng, Yiying

- 7th GCCCD-NRW Annual Workshop, Ruhr University Bochum, DE, May 2014
- University of Marburg, DE, December 2014

2015

Alcarazo, M.

- TU Braunschweig, DE, January 2015
- LIKAT, Rostock, DE, March 2015
- Ludwig Maximilians University Munich, DE, May 2015
- University of Sevilla, ES, June 2015
- 1st Sino-German Meeting in Catalysis, Wuhang, CN, October 2015
- Gordon Conference, Salve Regina University, US, July 2015

Barbatti, M.

- Université Josef Fourrier, Grenoble, FR, January 2015
- Thai-German Workshop on Photovoltaics, Nakhon Ratchasima, TH, February 2015
- École Normale Supérieure, Paris, FR, April 2015
- MPG LeadNet Meeting 2015, Berlin, DE, April 2015
- German-Thai Workshop on Photovoltaics, Max-Planck-Institut für Kohlenforschung, Mülheim, DE, April 2015

Dral, P.

- 29th Molecular Modeling Workshop 2015, Erlangen, DE, March 2015

Fazzi, D.

- German-Thai Workshop on Photovoltaics, Max-Planck-Institut für Kohlenforschung, Mülheim, DE, April 2015
- MQM Conference: Modeling Photoactive Molecules, Nantes, FR, April 2015
- EPFL, Lausanne, CH, July 2015
- psi-k Conference 2015, Donostia-San Sebastian, ES, September 2015
- ICT-HPCC15 Conference, Qingdao, CN, September 2015
- Zernike Institute, University of Groningen, NL, September 2015
- Workshop: Theoretical Challenges in Organic Electronics, Heidelberg University, DE, October 2015

Felderhoff, M.

- International Hydrogen Energy Development Forum 2015, Kyushu University, Fukuoka, JP, February 2015
- Pacifichem 2015, Honolulu, HI, US, December 2015

Fürstner, A.

- GDCh Lecture, Johannes Gutenberg University Mainz, DE, February 2015
- Heathcock-Lecture, Berkeley, US, April 2015
- Irvine Organic Synthesis Lecture, Irvine, US, April 2015
- Irvine Organic Synthesis Lecture, Irvine, US, April 2015
- Gilead, San Francisco, US, April 2015
- BASF, Basel, CH, May 2015
- Sandin-Lecture, University of Alberta, Edmonton, CA, May 2915
- Sandin-Lecture, University of Alberta, Edmonton, CA, May 2915
- Adolf-Windaus Commemoration Lecture 2015, Georg August University of Göttingen, DE, June 2015
- 21st Conference on Organometallic Chemistry (EuCOMC XXI), Bratislava, SK, July 2015
- 21st International Symposium on Olefin Metathesis and Related Chemistry (ISOM XXI), Graz, AT, July 2015
- Summerschool University of Zurich, Villars-sur-Ollon, CH, August 2015
- Summerschool University of Zurich, Villars-sur-Ollon, CH, September 2015
- AstraZeneca, Mölndal, SE, September 2015
- University of Copenhagen, DK, September 2015
- University of Kyoto, JP, November 2015
- University of Osaka, JP, 5 November 2015
- 15. Tateshina Conference, Hino/Nagano, JP, November 2015
- 13th International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-13), Kyoto, JP, November 2015
- 8th International Forum on Chemistry of Functional Organic Chemicals (IFOC-8), Kyoto, JP, November 2015

Haenel, M. W.

- Conference on the Coking Technology of the VDKF Association of the German Coking Professional, German Mining Museum, Bochum, DE, May 2015
- 83rd Session of the Working Group “Coal and Biomass Processing” of the DGMK German Society for Petroleum and Coal Science and Technology, Mining Academy University of Technology Freiberg, DE, November 2015.

Heyden, M.

- CECAM-Jülich School: Computational Trends in Solvation and Transport in Liquids, Jülich Supercomputing Centre, Jülich, DE, March 2015

- FU Berlin, DE, July 2015
- Sookmyung Women's University, Seoul, KR, September 2015
- 15th KIAS Conference: Protein Structure and Function, Korea Institute for Advanced Study (KIAS), Seoul, KR, September 2015
- Workshop: Water at the Interface between Biology, Chemistry, Physics and Materials Science, Abdus Salam International Center for Theoretical Physics (ICTP), Trieste, IT, October 2015
- University of Halle-Wittenberg, Halle, DE, November 2015
- MGMS Meeting: Exploring Mechanisms in Biology – Theory and Experiment, A*STAR Bioinformatics Institute, Singapore, SG, November 2015
- Pacifichem 2015, Honolulu, HI, US, December 2015

Klußmann, M.

- Max-Planck-Institut für Kohlenforschung, Mülheim, DE, April 2015
- Symposium of the Activation of Dioxygen and Homogeneous Catalytic Oxidation (ADHOC 2015), Madison, WI, US, June 2015
- European Symposium on Organic Reactivity (ESOR 2015), Kiel, DE, August 2015
- University of Münster, DE, October 2015

Lehmann, C. W.

- Diffraktions-Workshop, Dresden, DE, March 2015
- Newcastle upon Tyne, UK, March 2015
- Georg August University of Göttingen, DE, July 2015
- Kristallographie-Workshop, Frankfurt am Main, DE, October 2015

Leitner, W.

- Inaugural UK Catalysis Conference, Plenary Lecture, Loughborough, UK, January 2015
- Karlsruhe Institute of Technology (KIT) Karlsruhe, DE, January 2015
- KAUST Research Conference: Catalytic Carbon and Hydrogen Management, King Abdullah University of Science and Technology, Thuwal, SA, February 2015
- Bio-raffiniert VIII, Fraunhofer Umsicht, Oberhausen, DE, February 2015
- Integrating CO2 in the Value Chain: The role of chemistry, European Parliament & EuCheMS Workshop, Brussels, BE, March 2015

- Molecular Forum Lecture, Institute of Chemistry of the Chinese Academy of Sciences, Beijing, CN, March 2015
- Nankai Lectureship in Organic Chemistry, Nankai University, State Key Laboratory and Institute of Elemento-organic Chemistry, Tianjin, CN, March 2015
- Royal Society Discussion Meeting Supercritical Fluids - Green Solvents for Green Chemistry, London, UK, March 2015
- ThyssenKrupp Innovation R & D Conference 2015, ThyssenKrupp Industrial Solutions, Dortmund, DE, March 2015
- SynGas Convention 2, Autumn School, Zevenwacht, Capetown, ZA, March 2015
- SYNGAS Convention 2, Plenary Lecture, Capetown, ZA, March 2015
- Technologies for Sustainability and Climate Protection–Chemical Processes and Use of CO2, 5th BMBF Status Conference, Berlin, DE, April 2015
- Agenda Workshop “Impact of the SPIRE cPPP”, Brussels, BE, April 15
- ICB Seminar, ETH Zurich, CH, May 2015
- GDCh Lecture, University of Würzburg, Würzburg, DE, May 2015
- Royal Society Discussion Meeting „Catalysis Improving Society“, London, UK, June 2015
- ACHEMA 2015, Frankfurt am Main, DE, June 2015
- Facultat Quìmica, Universitat Rovira i Virgili, Tarragona, ES, June 2015
- Instituto de Síntesis Química y Catálysis Homogénea (ISQCH), Universidad de Zaragoza, ES, July 2015
- Institut Català d‘Investigaciò Química / Insitute of Chemical Research of Catalonia (ICIQ), Tarragona, ES, July 2015
- 7th International Conference on Green and Sustainable Chemistry (GSC-7) and joint 4th JACI/GSC Symposium,Tokyo, JP, July 2015
- EUROPACAT XII, Kazan, RU, September 2015
- Astra-Zeneca, Macclesfield, UK, September 2015
- 2nd EuCheMS Congress on Green and Sustainable Chemistry, Lisboa, PT, October 2015
- GDCh Festkolloquium on the occasion of the 80th birthday of Prof. Dr. Henri Brunner, Regensburg, DE, October 2015
- Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, Budapest, HU, October 2015
- Frontiers in Organic Synthesis Technology FROST-5, Budapest, HU, October 2015

- Universität Koblenz-Landau, Koblenz, DE, November 2015
- Ernst-Haage-Kolloquium, MPI for Chemical Energy Conversion, Mülheim, DE, December 2015
- TRENDS 2015, Aachen, DE, December 2015

Leutzsch, M.

- GDCh FGMR 37th Annual Meeting, Darmstadt, DE, September 2015

List, B.

- UCSD, San Diego, US, February 2015
- Pfizer-MIT Lectureship, Massachusetts Institute of Technology, US, March 2015
- ACS Symposium, Roche, Basel, CH, April 2015
- GDCh Lecture, Georg August University of Göttingen, DE, May 2015
- University of Potsdam, DE, May 2015
- University of Osaka, JP, June 2015
- University of Kyoto, JP, June 2015
- Process Chemistry Conference, Kyoto, JP, June 2015
- 39th Naito Conference, Hokkaido, JP, June 2015
- IUPAC 2015 World Chemistry Congress, Busan, KR, August 2015
- Pacifichem, Hawaii, HI, US, December 2015
- Carl Shipp Marvel Lecture, University of Illinois at Urbana-Champaign, US, December 2015

Marlow, F.

- IWATEC Winter School, El Gouna, EG, February 2015
- IRTG 1524 Colloquium, TU Berlin, DE, July 2015

Morandi, B.

- Technical University of Munich, DE, October 2015

Prieto, G.

- University of the Basque Country (UPV-EHU), Bilbao, ES, May 2015
- Abengoa Inc, Sevilla, ES, May 2015
- University of Oviedo, ES, December 2015

Reetz, M. T.

- GDCh Lecture, Ruhr University Bochum, DE, January 2015
- FineCat 2015 Symposium, Palermo, IT, April 2015
- Evonik, Marl, DE, April 2015
- GDCh Lecture, University of Gießen, DE, June 2015
- Jean-Marie Lehn Symposium, Strasbourg, FR, July 2015
- ICIQ-UniCat Summer School (1), Berlin, DE, July 2015
- ICIQ-UniCat Summer School (2), Berlin, DE, July 2015
- 8th European Biotechnology Congress, Frankfurt, DE, August 2015
- Enzyme Engineering Conference XXIII, St. Petersburg, Florida, US, September 2015
- Swiss Chemical Society-Syngenta Symposium, Stein, CH, October 2015
- Inter-Academy Symposium Chemistry, Jerusalem, IL, November 2015
- Seymour Schulich Lecture, Haifa, IL, November 2015
- EFMC-ASMC International Symposium, Rehovot, IL, November 2015

Ritter, T.

- Erdtman Lecture 2015, Stockholm, SE, October 2015
- 5th Annual Symposium of Organic Chemistry, Universidad Autónoma de Madrid “UAM”, Madrid, ES, October 2015
- GDCh Lecture, Ruhr University Bochum, DE, November 2015
- IKCOC-13, Kyoto, JP, November 2015
- The Autumn 2015 meeting of the French Chemical Society-Organic Chemistry division, Paris, FR, December2015
- Pacifichem 2015, Honolulu, HI, US, December 2015

Roemelt, M.

- Bunsen-Tagung, Bochum, DE, May 2015
- ORCA User’s Meeting, Gelsenkirchen, DE September 2015

Sánchez-García, E.

- Seminars of Advanced Studies of Molecular Design and Bioinformatics, Varadero, CU, June 2015
- CRC 1093 International Symposium: Supramolecular Chemistry on Proteins, University of Duisburg-Essen, DE, September 2015
- Pacifichem 2015, Honolulu, HI, US, December 2015

Schaubach, S.

- Meeting of the Scholarship Holder of the Verband der Chemischen Industrie (VCI), Munster, DE, December 2015

Schmidt. W.

- University of Marburg, DE, January 2015

Schrader, W.

- Mebe Company Workshop, April 2015
- Euroanalysis, Keynote Lecture, Bordeaux, FR, September 2015
- BP Company Virtual Colloquium, November 2015

Schüth, F.

- GDCh Lecture, University of Siegen, Siegen, DE, January 2015
- Humboldt-Lecture, Humboldt University Berlin, DE, June 2015
- Ruhr University Bochum, DE, June 2015
- ZMPC, Sapporo, JP, July 2015
- International Symposium on Mechanochemistry, Montpellier, FR, July 2015.
- Faculty Club, RWTH Aachen, DE, July 2015
- MPG-Forum, Munich, DE, August 2015
- ACS Symposium, Boston, US, August 2015
- GDCh-Wissenschaftsforum, Dresden, DE, September 2015
- Cenide, University of Duisburg-Essen, Duisburg, DE, October 2015
- MaterielScience Symposium, Bayer AG, Leverkusen, DE, October 2015
- Otto-Warburg-Lecture, University of Bayreuth, DE, October 2015

Theyssen, N.

- 22. Umwelttagung der Max-Planck-Gesellschaft, Hohenroda, DE, November 2015

Thiel, W.

- Annual Indian Science Congress, ACES Symposium, Mumbai, IN, January 2015
- GDCh Lecture, Universität of Frankfurt, DE, January 2015
- Indo-German MCBR4 Meeting, Heidelberg, DE, February 2015
- MQM Conference: Modeling Photoactive Molecules, Nantes, FR, April 2015
- Technion, Department of Chemistry, Haifa, IL, April 2015

- Lise-Meitner Symposium, Tel Aviv, IL, May 2015
- ICQC Satellite Meeting: Modeling and Simulation, Chanchun, CN, June 2015
- 10th European Conference on Computational Chemistry, Fulda, DE, September 2015

Tuna, D.

- Heinrich Heine University Düsseldorf, DE, January 2015
- MQM Conference: Modeling Photoactive Molecules, Nantes, FR, April 2015
- 51st Symposium for Theoretical Chemistry, Potsdam, DE, September 2015

Tüysüz, H.

- 249th ACS National Meeting, Denver, CO, US, March 2015
- University of Gießen, DE, February 2015
- KAUST, Thuwal, SA, February 2015
- UC Davis, US, April 2015
- University of Twente, NL, October 2015

Ungeheuer, F.

- Day of Chemistry, TU Dortmund, DE, February 2015

Weidenthaler, C.

- Gordon Research Conference: Hydrogen-Metal Systems, Stonehill College, Easton MA, US, July 2015
- ChemKrist. Workshop, Frankfurt, DE, October 2015

2016

Dral, P.

- Workshop on Excited States Simulations: Bridging Scales, Marseille, FR, November 2016
- 2016 AIChE Annual Meeting, San Francisco, US, November 2016

Fazzi, D.

- Heidelberg University, DE, June 2016
- MRS 2016 Fall Meeting, Boston, US, November 2016

Felderhoff, M.

- HydEM Conference 2016, Aarhus University, DK, June 2016

Fürstner, A.

- Technical University Munich, DE, February 2016
- Blechert Symposium, TU Berlin, DE, March 2016
- 251st ACS National Meeting, Herbert C. Brown Award for Creative Research in Synthetic Methods, San Diego, US, March 2016
- Abbvie Lecture, University of Chicago, US, April 2016
- Abbvie, North Chicago, IL, US, April 2016
- Amgen, Boston, MA, US, April 2016
- Gilbert Stork Lecture, Columbia University, New York, NY, US, April 2016
- Novasep, Bothwynn, PA, US, May 2016
- Sigma-Aldrich Lecture, Bologna, IT, July 2016
- XXXIV Congress of the Organometallic Chemistry Specialized Group of the Spanish Royal Society of Chemistry (XXXIV GEQO meeting), Girona, ES, September 2016
- 5th Lilly Chemistry Symposium, Madrid, ES, October 2016
- Adolf Lieben Lectureship, University of Innsbruck, AT, November 2016
- Adolf Lieben Lectureship, University of Linz, AT, November 2016
- Adolf Lieben Lectureship, TU Wien, AT, November 2016
- Adolf Lieben Lectureship, University of Graz, AT, November 2016
- UCB, Slough, Berkshire, UK, December 2016

Haenel, M. W.

- 84rd Session of the Working Group “Coal and Biomass Processing” of the DGMK German Society for Petroleum and Coal Science and Technology, Rotenburg an der Fulda, DE, May 2016.

Heyden, M.

- University of California, Irvine, CA, US, January 2016
- University of California, San Diego, CA, US, January 2016
- Ohio State University, Columbus, OH, US, January 2016
- Purdue University, West Lafayette, IN, US, January 2016
- American Physical Society March Meeting, Baltimore, MD, US, March 2016
- École Normale Supérieure, Paris, FR, March 2016
- TSRC Meeting: Protein Dynamics, Les Houches, FR, April 2016
- University of Duisburg-Essen, Essen, DE, April 2016
- 115th General Assembly of the German Bunsen Society for Physical Chemistry (Bunsentagung), University of Rostock, DE, May 2016
- TU Darmstadt, DE, June 2016
- TSRC Meeting: Interfacial molecular and electronic structure and dynamics, Telluride, CO, US, July 2016
- Mini-Symposium on Solutions and Solvation: A Computational Viewpoint, Katholieke Universiteit Leuven, BE, August 2016
- 52nd Symposium on Theoretical Chemistry: Chemistry in Solution - STC2016, Ruhr University, DE, September 2016
- University of Chemistry and Technology, Prague, CZ, November 2016

Klußmann, M.

- University of Oldenburg, DE, February 2016
- Chemiedozententagung, Heidelberg University, DE, March 2016
- University of Rostock, DE, May 2016
- Georg August University of Göttingen, DE, June 2016

König, G.

- SFB 716 Status Seminar, Bad Herrenalb, DE, September 2016
- 52nd Symposium on Theoretical Chemistry: Chemistry in Solution - STC2016, Ruhr University Bochum, DE, September 2016

Lehmann, C. W.

- Bruker SC-XRD User's Meeting, MPI für Biochemie, Martinsried, DE, October 2016
- 1st Panafrican Crystallography Congress, University of Dschang, CM, October 2016
- 13th Conference of the Asian Crystallographic Association 2015, Science City, Kolkata, IN, December 2015
- Hochschule Niederrhein, Krefeld, DE, November 2015

Leitner, W.

- Science for a Sustainable Society, McGill University, Montreal, CA, January 2016
- Nottingham Green Chemistry Workshop, Breadsall Priory, Derbyshire, UK, February 2016
- IIIrd SinChem Winter School, Università di Bologna, IT, February 2016
- Schweizerische Chemische Gesellschaft / Société Suisse de Chimie / Swiss Chemical Society - Spring Meeting 2016, University of Zurich, CH, April 2016
- 15th European Meeting on Supercritical Fluids, Essen, DE, May 2016
- Tunable Solvents for Green Processing, SFB/Transregion InPROMPT, Berlin, DE, June 2016
- 2nd International Conference on Biomass, IConBM2016, Giardini Naxos-Taormina, Sicily, IT, June 2016
- CO2 Utilization: Catalyst for the European Industrial Renessaince, SCOT Status Conference, Brussels, BE, June 2016
- 16th International Congress on Catalysis ICC-16, Bejing, CN, July 2016
- 20th International Symposium on Homogeneous Catalysis, ISHC-XX, Kyoto, JP, July 2016
- Seminar of the Faculty of Chemistry, Universidad Rovira i Virgili Tarragona, ES, July 2016
- Gordon Research Summer School on Green Chemistry, Stowe, Vermont, US, July 2016
- Gordon Research Conference on Green Chemistry, Stowe, Vermont, US, August 2016
- 9th Asian-European Symposium on Metal-Mediated Efficient Organic Synthesis (AES-9) Stockholm, SE, September 2016
- 14th International Conference on Carbon Dioxide Utilization (ICCDU XIV) Sheffield, UK, September 2016

- Institute of Nanotechnology (INT), Karlsruhe Institute of Technology, Karlsruhe, DE, October 2016

Leutzsch, M.

- NMR-Diskussionstagung: Praktische Probleme der Kernresonanzspektroskopie Annual Meeting, Erlangen, DE, January 2016

List, B.

- XVIIth Netherlands' Catalysis & Chemistry Conference (NCCC), conference at Leeuwenhorst, Noordwijkerhout, NL, March 2016
- Astra Zeneca Lectureship, University of Cambridge, UK, May 2016
- Dr. Reddy's Laboratories Ltd, Cambridge, UK, May 2016
- Gordon Research Conference on Stereochemistry at Salve Regina University in Newport, Rhode Island, US, July 2016
- JCO 2016 – Journées de Chimie Organique, FR, September 2016
- Solvay Conference on Chemistry "Catalysis in Chemistry and Biology", Brussels, BE, October 2016
- The 3rd International Symposium on Natural Product Synthesis and Process Methods for Drug Manufacture" (NPSPM), Peking University, Beijing, CN, October 2016

Marlow, F.

- SPIE conference Photonic Crystal Materials and Devices XII, Brussels, BE, April 2016

Mittal, S.

- Joint CRC765 and CRC1093 Student Symposium 2016, Hannover, DE, August 2016

Morandi, B.

- Chemiedozententagung, Heidelberg University, DE, March 2016
- Münster Symposium on Cooperative Effects in Chemistry, DE, April 2016
- University of Siegen, DE, May 2016
- Göttinger-Chemie-Forum, DE, June 2016
- Chemical & Engineering News' Talented 12 symposium, ACS Meeting Philadelphia, US, August 2016
- EuCheMS Conference, Sevilla, ES, September 2016

- EPFL, Lausanne, CH, November 2016
- University of Marburg, DE, November 2016
- ETH Zurich, CH, November 2016
- Ludwig Maximilian University of Munich, DE, December 2016

Pörschke, K.-R.

- 6st Int. Conf. on Metals in Genetics, Chemical Biology and Therapeutics, Indian Institute of Science, Bangalore, IN, February 2016.
- 251st ACS National Meeting, San Diego, US, March 2016
- University of Hawaii at Hilo, Big Island, HI, US, March 2016
- University of Hawaii at Manoa, Oahu, HI, US, March 2016
- University of Hawaii at Manoa, Oahu, HI, US, March 2016

Prieto, G.

- HLN-Chemistry Symposium, Ruhr University Bochum, DE, April 2016
- EMN conference on Mesoporous Materials, Prague, CZ, June 2016
- University of Chemistry and Technology, Prague, CZ, June 2016
- Technical University Denmark DTU, Copenhagen, DK, August 2016
- IRCELyon, CNRS research institute, Lyon, FR, September 2016

Reetz, M. T.

- GDCh Lecture, University of Bonn, DE, February 2016
- Chemikum, Marburg, DE, February 2016
- GDCh Lecture, Humboldt University Berlin, DE, May 2016
- Technion, Haifa, IL, June 2016
- GDCh Lecture, University of Darmstadt, DE, June 2016
- Biomillenia (company), Paris, FR, August 2016
- International Conference on Biocatalysis (BIOCAT 2016), Hamburg, DE, August 2016
- 5th Conference on Novel Enzymes, Groningen, NL, October 2016

Ritter, T.

- Heterocyclic and Synthesis Group of the Royal Society of Chemistry at the Institute of Cancer Research, Chelsea 2016, London, UK, January 2016
- 9th CaRLa Winter School 2016 Lecture, Heidelberg, DE, February 2016
- PAC Symposium, Leiden, NL, March 2016
- Max-Planck-Institut for Chemical Energy Conversion, Mülheim, DE, April 2016

- MPI Dortmund, DE, April 2016
- UCB Super Network Conference 2016 London, UK, April 2016
- GDCh Lecture, University of Duisburg-Essen, DE, May 2016
- Boehringer-Ingelheim, Ingelheim am Rhein, DE, May 2016
- Colloquium Summer Semester, GDCh Ortsverband Köln-Leverkusen, DE, May 2016
- Organic Chemistry Colloquium 2016 Kaiserslautern, DE, June 2016
- 19. Steinheimer Gespräche des Fonds für den Hochschullehrernachwuchs, Bad Homburg, DE, June 2016
- Actelion Chemistry Lectures, Basel, CH, June 2016
- ECHC 2016 - XXVII European Colloquium on Heterocyclic Chemistry, Amsterdam, NL, July 2016
- Institute of Organic Chemistry RWTH Aachen, DE; July 2016
- 57th GECO Conference Basque, FR, August 2016
- EFMC-ISMC 2016 XXIV EFMC, International Symposium on Medicinal Chemistry, Manchester, UK, August 2016
- GSK External Lecture, GlaxoSmithKline Medicines Research Centre, Stevenage, UK, August 2016
- Sanofi-Aventis Deutschland GmbH R&D LGCR / Chemistry Frankfurt am Main, DE, September 2016
- Boehringer Ingelheim Pharma GmbH & Co. KG, Biberach an der Riss, DE, September 2016
- David Geffen School of Medicine at UCLA, US, October 2016
- University of Oslo, NO, November 2016
- Technical University of Denmark, Lyngby, DK, November 2016
- University of Lund, SE, November 2016
- Ludwig-Maximilian-University, Munich, DE, November 2016
- Karl-Franzens- Universität, Graz, AT, November 2016
- University of Vienna, AT, November 2016
- 25th International Isotope Society, (UK Group) Symposium University of Cambridge, UK, November, 2016
- MedChem 2016, Annual One-Day Meeting on Medical Chemistry, Mont-Saint-Guilbert, BE, November 2016
- Ernst Haage Symposium 2015, Max-Planck-Institute for Chemical Energy Conversion, Mülheim an der Ruhr, DE, November 2016
- 1st ISOTOPICS Meeting, Paris, FR, November 2016
- Pierre and Marie Curie University, Paris, FR 2016

- One-Day Symposium on Late Stage Functionalization for Synthesis and Medicines, Mathematical Institute, Oxford, UK, December 2016
- Vertex Pharmaceuticals Europe Limited, Oxfordshire, UK, November 2016
- Eli Lilly Company Limited, Windlesham, UK, November 2016

Roemelt, M.

- Theoretical Chemistry Seminar, Georg August University of Göttingen, DE, February 2016
- Theoretical Chemistry Seminar, Paderborn University, DE, July 2016

Rumpel, S.

- GDCh FGMR 38th Annual Meeting, Düsseldorf, DE, September 2015

Sánchez-García, E.

- Mini-Workshop: Supramolecular Chemistry and Protein Aggregation, University of Duisburg-Essen, DE, January 2016
- RESOLV Klausurtagung 2016, Velen, DE, February 2016
- International Symposium of Chemistry, Santa Maria Key, CU, June 2016
- 2016 Meeting of the International Society of Quantum Biology and Pharmacology (ISQBP), Bergen, NO, June 2016
- 23rd IUPAC Conference on Physical Organic Chemistry, Sydney, AU, July 2016
- Heron Island Conference on Reactive Intermediates and Unusual Molecules, Heron Island, AU, July 2016
- Conference: Radical in the Rockies, Telluride, US, August 2016
- 52nd Symposium on Theoretical Chemistry: Chemistry in Solution - STC2016, Ruhr University Bochum, DE, September 2016

Schmidt, W.

- 3rd Indo-German Workshop on Advances in Materials, Reaction & Separation Processes, Guwahati, IN, February 2016
- School of Chemistry and Chemical Engineering, Shandong University, Jinan, CN, April 2016
- Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, CN, April 2016
- Guest Professorship, Shandong University, Jinan, CN, April 2016

- Institut für Chemische Verfahrenstechnik, University of Stuttgart, Stuttgart, DE, June 2016

Schrader, W.

- Colloquium MSW Workshop, Institute of Pure and Applied Mass Spectrometry, University of Wuppertal, DE, March 2016
- Antrittsvorlesung University of Duisburg-Essen, DE, May 2016
- Analytica Conference - Energy & Fuel Session, DE, May 2016
- BP High Resolution Mass Spectrometry Symposium, London, UK, July 2016
- Colloquium SFB 1109 Summer School, Humboldt University Berlin, DE, August 2016

Schüth, F.

- Cardiff Catalysis Institute Conference, Cardiff, UK, January 2016
- GDCh Lecture, University of Augsburg, DE, January 2016
- Mutterthies Lectures, University of Berkeley, US, February 2016
- Kongress Material Innovativ, Würzburg, DE, February 2016
- Scientific Symposium, TUM, Munich, DE, May 2016
- UOP Honeywell invitational lecture, UOP, Chicago, US, June 2016
- NorthWestern, Chicago, US, June 2016
- Brdička Lecture, J. Heyrovský Institute of Physical Chemistry, Prague, CZ, June 2016
- MSE Kolloquium, TUM, Munich, DE, July 2016
- EuCheMS, Seville, ES, September 2016
- HEIKA Symposium, Heidelberg University, DE, October 2016
- Conference ISIS, Strasburg, FR, November 2016
- Körber-Stiftung, Hamburg, DE, November 2016
- Total, Seneffe, B, December 2016

Thiel, W.

- MPI Workshop on Theoretical Challenges: Simulating Materials out of Equilibrium, Hamburg, DE, June 2016
- IQTCUB Symposium, Barcelona, ES, June 2016
- 8th Molecular Quantum Mechanics Conference, Uppsala, SE, June 2016
- Harvard University, Department of Chemistry, Cambridge, US, August 2016
- ACS National Meeting, Symposium on QM/MM Methods, Philadelphia, US, August 2016

- Summerschool: Modern Wavefunction Methods in Electronic Structure Theory, Gelsenkirchen, DE, October 2016
- GDCh Lecture, Karlsruher Institut für Technologie, DE, November 2016

Tüysüz, H.

- Ruhr University Bochum, DE, January 2016
- Carl von Ossietzky University of Oldenburg, DE, February 2016
- 48. Jahrestreffen Deutscher Katalytiker, Weimar, DE, March 2016
- Georg August University of Göttingen, DE, April 2016
- AMOLF, NL, October 2016

Weidenthaler, C.

- School of Chemistry and Chemical Engineering, Shandong University, CN, April 2016
- Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, CN, April 2016
- Metal Hydride Conference, Interlaken, CH, August 2016
- University Vienna, AT, October 2016
- GDCh Lecture, University of Essen-Duisburg, Essen, DE, December 2016

Zheng, Y.

- 28th CGCA Annual Conference, Heinrich Heine University Düsseldorf, DE, June 2016

7.3 Scientific Honors, Name Lectureships, Awards

Fürstner, A.

- Hans Herloff Inhoffen Medal, 2014
- Gay-Lussac-Humboldt Prize, FR, 2014
- Thomson Reuters Highly Cited Researcher, 2014 and 2015
- Clayton-Heathcock Lectureship, Berkeley, US, 2015
- Organic Synthesis Lectureship, Irvine, US, 2015
- Sandin Lectureship, Edmonton, CA, 2015
- JSPS Fellowship, Kyoto/Tokyo, 2015
- Adolf Windaus Medal, DE, 2015
- Gilbert-Stork Lectureship, Columbia University, New York, US, 2016
- Inaugural Lieben-Lectureship, AT, 2016
- Herbert C. Brown Award for Creative Research in Synthetic Methods, US, 2016.

Galeano Nuñez, D.

- Forschungspreis Wasserstoff.NRW 2015

Heinrich, M.

- Steinhofer-Preis, 2016

Klußmann, M.

- Award by Angewandte Chemie for frequent and competent reviews in 2013, 2014
- Substitute professor for Prof. Frank Glorius, Universität Münster, DE, 2015
- Extension of the Heisenbergstipendium by the DFG, 2015
- Award by Angewandte Chemie for frequent and competent reviews in 2014, 2015

Leitner, W.

- European Sustainable Chemistry Award of the European Science Association of Chemical and Molecular Sciences (EuCheMS), jointly with Prof. Jürgen Klankermayer (RWTH), 2014
- Nankai University Lectureship in Organic Chemistry, Nankai University, CN, 2015

- Molecular Science Forum Lecture of Chinese Academy of Sciences and Chinese Chemical Society, 2015

Leutzsch, M.

- Turck Prize, Mülheim, DE, 2015

List, B.

- ERC Advanced Grant 2011-2016, European Research Council
- Arthur C. Cope Scholar Award, US, 2014
- Thomson Reuters Highly Cited Researcher, 2014
- Carl Shipp Marvel Lectures, University of Illinois at Urbana-Champaign, US, 2015
- Gottfried Wilhelm Leibniz-Prize, 2015
- ERC Advanced Grant 2016, European Research Council

Morandi, B.

- Thieme Journal Award, 2015
- Ružička prize and medal, 2016
- Bayer Early Excellence in Science Award, 2016
- Chemical & Engineering News' Talented 12, 2016
- MS_CEC Young Researcher Award, 2016
- European Young Chemist Award Special Mention, 2016
- JSP Fellowship, 2016

Prieto, G.

- Best poster award at the Young Chemists Symposium, Bochum, DE, 2014.
- Best poster award 18th Workshop on Stereology and Stochastic Image Analysis, Osnabruck, DE, 2015

Reetz, M. T.

- Chirality Medal, 2014
- Paul Tarrant Lectureship (University of Florida/US), 2014
- Schulich Distinguished Lectureship (Technion/Israel), 2015
- Honorary Member of the Israeli Chemical Society, 2015

Schrader, W.

- Appointment as apl. Professor, University of Duisburg-Essen, December 2014

Schüth, F.

- Carl Friedrich von Weizsäcker-Preis, 2014
- Humboldt-Lecture, Humboldt University Berlin, DE, June 2015
- Otto-Warburg-Lecture, University of Bayreuth, DE, October 2015
- Mutterthies Lectures, University of Berkeley, US, February 2016
- Brdička Lecture, J. Heyrovský Institute of Physical Chemistry, Prague, CZ, June 2016
- UOP Honeywell invitational lecture, UOP, Chicago, US, June 2016
- Ehrendoktor TUM Munich, DE, 2016

Thiel, W.

- ERC Advanced Grant 2014-2018, European Research Council
- Davidson Lecture, University of North Texas, Denton, US, April 2014
- Robert Bunsen Lecture 2014, Deutsche Bunsengesellschaft

Tüysüz, H.

- Chemistry of Materials Reviewer Award, 2015
- Jochen-Block-Prize of the DECHEMA, awarded by the German Catalysis Society, 2016

Wang, Guang-Hui

- Turck Prize, Mülheim, DE, 2016

Willwacher, J.

- Runner-Up Award Syngenta Workshop for talented PhD students, 2014
- Reaxys PhD Prize Finalist, 2015

7.4 Contacts with Universities

All research group leaders are associated with a university at which the doctoral students receive their degrees. The group leaders as well as a few other members of the Institute hold classes and/or workshops at universities. Official cooperations are held with the Ruhr University Bochum and the Louis Pasteur Université de Strasbourg. During the period of 2014-2016 the following lectures/workshops were held:

Alcarazo, M.

- Organometallic Chemistry (II), TU Dortmund, WS 2013/2014
- Modern Topics in Inorganic Chemistry, TU Dortmund, WS 2013/2014

Barbatti, M.

- Short school on excited-state methods aimed at graduate Students, Abdulaiz University, SA, 2014
- Short schools on excited-state methods aimed at graduate Students, Ching Mai University, TH, 2015

Felderhoff, M.

- seit 2015 Lehrbeauftragter an der Westfälischen Hochschule, Lehrgebiete: Wasserstoffenergietechnik, Werkstoffanalytik

Fürstner, A.

- Modern Synthetic Methods, TU Graz, AT, 2014

Heyden, M.

- Concepts of Spectroscopy, Ruhr University Bochum, WS 2016/17

Klußmann, M.

- Fortgeschrittene Organische Chemie, Universität zu Köln, WS 2013/2014 (shared equally with Dr. Jan Deska, Universität zu Köln)
- Fortgeschrittene Organische Chemie, Universität zu Köln, SS 2014 (shared equally with Dr. Jan Deska, Universität zu Köln)
- Klussmann, M., Fortgeschrittene Organische Chemie, Universität zu Köln, WS 2014/2015 (shared equally with Dr. Jan Deska, Universität zu Köln)
- Organische Chemie II, Universität Münster, WS 2015/2016
- Calorimetry and Kinetics, Universität zu Köln, SS 2016

- Kinetics in Catalysis, Georg August University of Göttingen, SS 2016

Lehmann, C. W.

- Seminar zum Praktikum Synthesechemie, Bergische Universität Wuppertal, WS 2014/15, WS 2015/16, WS 2016/17
- Praktikum Anorganische Materialien, Bergische Universität Wuppertal, SS 2014, SS 2015, SS 2016
- Seminar zum Praktikum Anorganische Materialien, Bergische Universität Wuppertal, SS 2014, SS 2015, SS 2016
- Vorlesung Charakterisierung von Materialien und Oberflächen, Bergische Universität Wuppertal, WS 2014/15, WS 2015/16, WS 2016/17

Leitner, W.

all Rheinisch-Westfälische Technische Hochschule Aachen

- Vorlesung „Technische Chemie A“, SS 2014
- Vorlesung „Katalysator Immobilisierung und Mehrphasenkatalyse“, SS 2014
- Vorlesung „Technische Chemie F“, WS 2014/15
- Vorlesung „Angewandte Molekulare Katalyse“, WS 2014/15
- Ringvorlesung „Faszination Technik“ (alle Fakultäten), WS 2014/15
- Vorlesung „Technische Chemie A“, SS 2015
- Vorlesung „Katalysator Immobilisierung und Mehrphasenkatalyse“, SS 2015
- Vorlesung „Technische Chemie F“, WS 2015/16
- Vorlesung „Angewandte Molekulare Katalyse“, WS 2015/16
- Ringvorlesung „Faszination Technik“ (alle Fakultäten), WS 2015/16
- Vorlesung „Technische Chemie F“, WS 2016/17
- Vorlesung „Angewandte Molekulare Katalyse“, WS 2016/17
- Ringvorlesung „Faszination Technik“ (alle Fakultäten), WS 2016/17

List, B.

- IMPRS Recharge – Day of Catalysis, 2016

Marlow, F.

- Aktuelle Probleme der Nanostrukturphysik. Vorlesung für Masterstudenten, University of Duisburg-Essen, WS 2013/14
- Projektpraktikum Aktuelle Probleme der Nanostrukturphysik. University of Duisburg-Essen, WS 2013/14

- Optical Properties of Solids. Lecture and Lab Course for students in the training program of the IMPRS SurMat (Ruhr University Bochum, MPI Mülheim, and MPI Düsseldorf), 2014
- Photonic Crystals. Lecture for students in the training program of the IMPRS SurMat (Ruhr University, MPI Mülheim und MPI Düsseldorf), 2014, 2016
- Photonik. Vorlesung für Masterstudenten, University of Duisburg-Essen, WS 2014/15, 2015/16, 2016/17
- Projektpraktikum Photonik. University of Duisburg-Essen WS 2014/15, WS 2015/16, WS 2016/17
- Optical Properties of Solids and Optical Analysis of Solids. Lecture for students in the training program of the IMPRS SurMat (Ruhr University Bochum, University of Duisburg-Essen, MPI Mülheim, and MPI Düsseldorf), 2016

Morandi, B.

- Introduction to Organocatalysis, Ruhr University Bochum, SS 2015 (graduate school)

Pörschke, K.-R.

- Metallorganische Komplexchemie, Heinrich Heine University Düsseldorf, SS 2014, WS 2014/15, SS 2015, WS 2015/16, SS 2016, WS 2016/15

Prieto, G.

- Invited lecturer, "Advanced Reactor Design", bilingual MSc course, Department of Chemical Engineering, University of Oviedo, ES, WS 2015/16, 2016/17
- Grundzüge der Chemie für Studierende des Maschinenbaus, Umwelttechnik und Ressourcenmanagement und Sales Engineering and Product Management, Ruhr University Bochum, WS 2016/17

Roemelt, M.

- Advanced Electronic Structure Theory, together with Prof. Dr. C. Hättig, WS 2016/17, Ruhr University Bochum
- Modern Wavefunction Methods in Electronic Structure Theory, Tutorium Workshop, 2016, Prof. Dr. J. Gauss and Prof. Dr. F. Neese
- Theorie der Chemischen Bindung, Dr. Joerg Behler, WS 2015/16 Ruhr University Bochum
- Theoretische Chemie I, Tutorium of Prof. Dr. D. Marx, WS 2014/15, Ruhr University Bochum

Schmidt, W.

- The structure of solids. Lectures for students in the training program of the IMPRS SurMat (Ruhr University Bochum, MPI KOFO Mülheim, and MPI Düsseldorf), WS 2014
- Porous solids and Analysis of porosity. Lectures for students in the training program of the IMPRS SurMat (Ruhr University Bochum, MPI KOFO Mülheim, and MPI Düsseldorf), WS 2014
- Basics of porosity determination and related methods. Lectures for students at the MPI für Kohlenforschung. WS 2015
- Characterization of Solid Catalysts. Guest Professorship, Shandong University, Jinan, CN, April 2016
- Diffraction, Sorption, and Small Angle X-ray Scattering. Lectures for students in the training program of the IMPRS RECHARGE (Ruhr University Bochum, MPI CEC Mülheim, MPI KOFO Mülheim, MPI Düsseldorf, University of Bonn, University of Duisburg-Essen), SS 2016
- Analysis of porosity. Lectures for students in the training program of the IMPRS SurMat (Ruhr University Bochum, MPI KOFO Mülheim, and MPI Düsseldorf), WS 2016

Schrader, W.

- Lecture “Advanced Mass Spectrometry”, University of Duisburg-Essen, SS 2014
- Lecture “Advanced Mass Spectrometry”, University of Duisburg-Essen, SS 2015
- Lecture “Advanced Mass Spectrometry”, University of Duisburg-Essen, SS 2016

Schüth, F.

- Member of the Board of Trustees of the University of Duisburg-Essen, since 2007
- Member of the Board of Trustees of the University Oldenburg, 2010 – 2016
- Grundzüge der Chemie für Studierende des Maschinenbaus, Ruhr University Bochum (WS 2013/2014, WS 2014/2015, WS 2015/2016)
- "Introduction to MaterialsChemistry", Ruhr University Bochum (WSM 2013/2014, WS 2014/2015, WS 2015/2016)

Theyssen, N.

- Lecture „Katalyse in überkritischen Fluiden“ und „Ionische Flüssigkeiten“, Ruhr University Bochum, Ruhr-Lehrverbund Katalyse, December 2014
- Lecture „Katalyse in überkritischen Fluiden“ und „Ionische Flüssigkeiten“, TU Dortmund, Ruhr-Lehrverbund Katalyse, December 2016

Thiel, W.

- Molecular Modeling (QM/MM Module), Heinrich Heine University Düsseldorf, WS 2013/14
- CarLa Winterschool, Heidelberg University, February 2014
- Molecular Modeling (QM/MM Module), Heinrich Heine University Düsseldorf, WS 2014/15
- IMPRS ReCharge, Day of Catalysis, Lecture: Theoretical Methods in Catalysis, Mülheim/Ruhr, April 2016
- Molecular Modeling (QM/MM Module), Heinrich Heine University Düsseldorf, SS 2016
- Summerschool: Modern Wavefunction Methods in Electronic Structure Theory, Gelsenkirchen, October 2016

Tüysüz, H.

- Justus Liebig University of Giessen, DE, February 2015
- UC Davis US, April 2015
- University of Twente, NL, October 2015
- Ruhr University Bochum, DE, January 2016
- Carl von Ossietzky University of Oldenburg, DE, February 2016
- Georg August University of Göttingen, DE, April 2016
- AMOLF, NL, October 2016
- Gen. Chemistry for Engineering Departments, Ruhr University Bochum, WS 2013/14, WS 2014/15, WS 2015/16
- Inorganic Chemistry III, Ruhr University Bochum, WS 2016/17
- Habilitation Ruhr University Bochum, Inorganic Chemistry, November 2016

Weidenthaler, C.

- Introduction to Crystallography and Diffraction Techniques, IMPR SurMat, September 2014
- Organization of summer School „Theory and Practice of Modern Powder Diffraction“, Ellwangen, October 2014

- Habilitation University of Duisburg-Essen, Inorganic Chemistry, December 2015
- Introduction to Modern Diffraction Techniques, Shandong University, Jinan, CN, April 2016
- Inorganic Chemistry IV, University of Duisburg-Essen: SS 2016
- Introduction to Crystallography and Diffraction Techniques, IMPR SurMat, September 2016
- Modern Diffraction Methods, University of Duisburg-Essen, WS 2016/2017
- Introduction to Modern Diffraction Techniques, Shandong University, Jinan, CN, April 2016

7.5 Special Events and Activities

Kohlenforschung Centennial Lectureship Series

The Centennial Lectureship Series in 2014 was meant to introduce and explain different research milestones of the Institute to the general public.

9 April	Prof. Dr. Krijn de Jong (Universität Utrecht, NL) *Fischer-Tropsch-Catalysis – from nanometer to kilometer*
24 April	Prof. Dr. Ferdi Schüth (Max-Planck-Institut für Kohlenforschung) *Wenn das Öl zur Neige geht – Was treibt die Autos von morgen an?*
7 May	Dipl.-Ing. Volker Weuthen (HPP Architects, Düsseldorf) *Eine Zeitreise durch die Architektur des Max-Planck-Instituts für Kohlenforschung*
21 May	Prof. Dr. Klaus Müllen (MPI für Polymerforschung, Mainz) *Plastikwelt*
11 June	Prof. Dr. Manfred Reetz (Philipps-Universität, Marburg) *Evolution im Reagenzglas*

Karl Ziegler Lectureships

In 1978 the wife and daughter of Karl Ziegler, Nobel Prize winner and Director of the Max-Planck-Institut für Kohlenforschung, initiated this lectureship in honor of Prof. Karl Ziegler. Since that time, this Foundation allowed us to invite more than 25 world-renowned scientists as Karl Ziegler Guest Professors to the Institute for lectures and workshops.

Karl-Ziegler-Lectureship 2015: **Prof. Dr. Stefan Grimme** (University Bonn, DE)

19 May	Workshop I: *Quantum Chemistry for Non-Covalent Interactions and Supramolecular Systems*
20 May	Main Lecture: *Accurate Quantum Chemistry for Complex Chemical Systems*
21 May	Workshop II: *Automatic Generation of Inter- and Intramolecular Force-Fields for Molecules and Condensed Phase Simulations*

Karl Ziegler Lectureship 2016: Prof. Dr. Erick M. Carreira (ETH Zurich, CH)

7 June	Workshop I: *Surprises and Discoveries with Natural Products*
8 June	Main Lecture: *Surprises and Discoveries with Small Molecules*
9 June	Workshop II: *Total Synthesis in the 21st Century. Why bother?*

Summer School „Theory and Practice of Modern Powder Diffraction“
October 2014, Ellwangen, DE, Organization: Dr. Claudia Weidenthaler

German-Thai Workshop on Photovoltaics
April 2015, Mülheim, DE, Involved: M. Barbatti together with O. Weingart

Advanced Materials Analysis by Latest STEM Technologies, Inauguration of the newly purchased HD-2700, electron microscope
February 2015, Organizer: Professor C. Lehmann

Symposium Program

- Prof. C. W. Lehmann (Max-Planck-Institut für Kohlenforschung)
  Electron microscopy at our Institute
- Prof. G. Dehm (Max-Planck-Institut für Eisenforschung, Düsseldorf)
  New insights into materials phenomena by advanced TEM
- Dr. R. Wepf (ETH Zurich)
  Dedicated UHR-STEM applications at the ETH Zurich: From light to heavy elements – from phase contrast to analytical imaging
- Dr. M. Willinger (Fritz-Haber-Institut of MPG, Berlin)
  Direct imaging of octahedral distortion in a complex molybdenum vanadium mixed oxide
- Dr. Inz. T. Plocinski (Warsaw University of Technology)
  Cs-corrected dedicated STEM in material science: examples and case studies
- Mr. M. Konno (Hitachi-High-Technologies, Japan)
  Latest application of HD2700A + FIB system
- Dr. R. Schmidt (Hitachi-High-Technologies, Europe)
  The bridge from TEM to SEM: low voltage STEM Hitachi SU9000
- Dr. M. Schleifer (Ametek Deutschland)
  Newest SDD developments for Hitachi HD2700

MBLA Lectureships

October 2014 Prof. Daisuke Uraguchi (Nagoya University, JP)
Molecular design and applications of chiral organic ion pair catalysts featuring anion-controlling ability

October 2016 Prof. Satoshi Maeda (Hokkaido University, JP)
Development of automated reaction path search methods toward systematic understanding and design of organic reactions

Day of Catalysis

Lectures on aspects of catalysis for IMPRS Recharge, April 2016, Mülheim, DE
Conference Organizer: Professor Benjamin List

- Prof. Benjamin List (Max-Planck-Institut für Kohlenforschung)
  Organocatalysis
- Dr. Gonzalo Prieto (Max-Planck-Institut für Kohlenforschung)
  Multilevel solid catalyst design: from atomic to macroscopic lengthscales
- Prof. Tobias Ritter (Max-Planck-Institut für Kohlenforschung)
  From fundamental chemistry to medical applications
- Prof. Walter Thiel (Max-Planck-Institut für Kohlenforschung)
  Theoretical studies of transition metal catalysis and biocatalysis

Public Information Evening on Radiochemistry

Presentation of new Radioisotope Laboratory and the Research Area "*Fluorination*" by Prof. Tobias Ritter to Mulheim residents, October 2016

Liebig Lecture

November 2016 Dr. Geraldine Masson (Institut de Chimie des Substances Naturelles)
Visibile light photoredox catalysis as a tool for organic synthesis

Roadshow: Initiative zur Verbesserung der NMR-Datenqualität, November 2016, Organizer: Dr. Christophe Farès

Program

- Dr. Johannes Liermann (Leiter der NMR-Abteilung, Johannes-Gutenberg Universität Mainz)
  Das IDNMR-Projekt: Qualitätskontrolle von NMR-Daten
- Dr. Nils Schlörer (Leiter der NMR-Abteilung, Universität zu Köln)
  NMR-Daten in akademischen Labors: LIMS, ELN, Datenbank & Co.
- Stefan Kuhn, (nmrshiftDB2, Universität zu Köln)
  Software für die Qualitätskontrolle: Quickcheck und nmrshiftdb2
- *Practical testing of the software*

Institute Seminars

The Institute Seminar is a platform for communication and exchange between the researchers of the different laboratories. It is an opportunity to get into touch with the other departments, listen to oral presentations and participate at a poster session. In 2015 and 2016 the Institute Seminar was linked with the awarding of the Turck Prize that went to a young scientist with an outstanding publication.

4 December 2015

- Markus Leutzsch (Turck Prize Winner, Department of Homogeneous Catalysis)
  Unexpected formation of ruthenium carbenes discovered by hyperpolarized NMR
- Dr. Bill Morandi (Leader of the group of Homogeneous Catalysis and Reaction Design)
  Design and development of novel catalytic reactions for organic synthesis

13 June 2016

- Gregory Boursalian (Department of Organic Synthesis)
  Beyond C–H metallation: new approaches for C–H functionalization
- Prof. Wolfgang Schrader (Leader of the Group of Mass Spectrometry)
  Energy research and analytical chemistry: Studying chemical changes in very complex systems

16 December 2016

- Dr. Daniele Fazzi (Department of Theory)
  Photovoltaics: make it light, in theory *it is possible*
- Dr. Guang-hui Wang (Turck Prize Winner, Department of Heterogeneous Catalysis)
  Carbon-supported catalysts for biomass conversion

Visiting Scientists

Humboldt Research Laureates
Prof. Dr. Rodney J. Bartlett, University of Florida, US
Prof. Dr. Akiyama Takahiko, Gakushuin University, JP
Prof. Dr. Shu Kobayashi, University of Tokyo, JP
Prof. Dr. Maruoka Keiji, Kyoto University, JP

Humboldt Fellow
Dr. Candance Chan, Arizona State University, Tempe, US

7.6 List of Talks Given by Guests (2014-2016)

2014

9 January — Prof. Olaf G. Wiest (University of Notre Dame, US)
Computational studies of stereoselectivity

9 January — **GDCh-Lecture**: Prof. Michael R. Buchmeiser (University of Stuttgart)
CO_2- and metal ion-protected n-heterocyclic carbenes as latent catalysts in polymerization (organo-) catalysis

13 January — Prof. Richard Blair (University of Orlando, US)
Novel reaction pathways and scalability in mechanically-driven syntheses

20 January — Prof. Dr. O. A. von Lilienfeld (University of Basel, CH**)**
Quantum machine: supervised learning of Schroedinger's equation in chemical compound space

23 January — Prof. Martin Suhm (Georg August University of Göttingen)
GDCh-Lecture: *Physical energy conversion materials from a fundamental perspective: Hydrocarbon folding and stretching on the nanometer scale*

30 January — Prof. Karl J. J. Mayrhofer (MPI für Eisenforschung, Düsseldorf)
GDCh-Lecture: *Stability of catalyst materials - the key for the deployment of electrochemical energy conversion*

3 February — Prof. Dan P. Geerke, (VU University Amsterdam, NL)
Plasticity and free energy models to predict and understand selectivity in Cytochrome P450 metabolite formation

4 February — Prof. Jans Alzate-Morales (Universidad de Talca, CL)
Predicting the Protein-Ligand Affinity by Means of QM/MM, MD and MM-GBSA Computational Methods: Some Protein Kinases as Validation Systems

5 March	Deniz Tuna (TU Munich) *Quantum-Chemical Investigations into the Photophysics and Photochemistry of Bioorganic Molecules*
14 March	L. Therese Bergendahl (Heriot Watt University Edinburgh, UK) *Modelling the Photochemical Steps involved in Photodynamic Therapy*
8 April	Magdalena Joblonska (University of Krakow, PL) *Selective catalytic ammonia oxidation into nitrFlooren and water vapour in the presence of multicomponent oxide systems doped with noble metals*
9 April	Prof. Krijn de Jong (University Utrecht, NL) *Fischer-Tropsch Catalysis – from nanometer to kilometer*
9 April	Prof. Björn Hauback (University Oslo, NO) *Structural studies of complex hydrides for hydrFlooren storage*
10 April	Dr. Matthew Thomas Clough (Imperial College London, UK) *Understanding the Thermal Stability of Ionic Liquids: A Combined Experimental and Theoretical Approach*
10 April	Prof. Masahiro Murakami (Universität Kyoto, JP) *Collaboration of Light and Metals for C-C Bond Activation*
11 April	Friedrich Kreyenschmidt (Heidelberg University) *Nanostrukturierung von Oberflächen*
23 April	Dr. Victor Muñoz (Universität Barcelona, ES) *Towards the in silico design of Artificial Metalloenzymes*
25 April	Hannah Schreyer (University of Munich) *Oxidative DehydrFloorenation of Ethane*
7 May	Dipl.-Ing. Volker Weuthen (HPP Architects, Düsseldorf) *Centennial-Lecture: Eine Zeitreise durch die Architektur des Max-Planck-Instituts für Kohlenforschung*

8 May	Wolfgang Groh (Hy-Lok GmbH) *All around fittings: Tubes, clamp ring connections, (re)assembly (and mistakes), leakage (and evaluation)*
9 May	Dr. Michael Boots (Technische Universiteit Eindhoven, NL) *Octane Boosters and Marine Fuels from Lignin*
16 May	Prof. Dr. Carsten Sievers (Georgia Institute of TechnolFloory, US) *Stability of Solid Catalysts in Hot Liquid Water and Biomass Solutions*
21 May	Prof. Dr. Klaus Müllen (MPI für Polymerforschung, Mainz) *Centennial-Lecture: „Plastikwelt“*
26 May	Prof. Rodney J. Bartlett (University of Florida, US) *Making Kohn-Sham density functional theory gives the right answer for the right reason*
2 June	Prof. Shu Kobayashi (University of Tokyo, JP) *Metal Nanoparticles as Novel HeterFlooreneous Catalysts for Green Sustainable Chemistry.*
4 June	Dr. Artur Mardyukov (Justus-Liebig-Universität, Giessen) *Synthesis and Functionalization of Polymeric Materials - Polymer Brushes Exhibiting Versatile Supramolecular Interaction Structured via Microcontact Chemistry*
10 June	Frau Lavinia Utiu (Radboud University Nijmegen, NL) *Linking chemically specific structure information to physical properties of polypropylene*
11 June	Prof. Dr. Manfred T. Reetz (Philipps-Universität Marburg) *Centennial-Lecture: Evolution im Reagenzglas*
11 June	Dr. Javier Peña (Universität Salamanca, ES) *Green Chemistry with Sulfones*

11 June	Herr Anusree Viswanath K. (University of Leipzig) *Multinuclear Solid-State NMR Spectroscopy of Metal-Organic Frameworks*
12 June	Prof. Rodney J. Bartlett (University of Florida, US) *GCCh-Lecture: The Evolution of the Gold Standard in Quantum Chemistry: Coupled-Cluster Theory and its Applications*
17 June	Stefan Schünemann (Ruhr University Bochum) *UV and visible-light photochemistry in nanostructured 3D Au-TiO2 aerFloorels and ambigels*
17 June	Kun Chen (University Siegen) *Multianalyte Chemosensors in Solution and at Surface*
17 June	Prof. Robert K. Boeckman, Jr. (University of Rochester, NY, US) *New Organocatalytic Asymmetric Synthesis MethodolFloory with Application to the Total Synthesis of the Novel Apoptosis Modulator (-)-Rasfonin*
26 June	Dr. Michael Roemelt (Princeton University, US) *N-Electron Valence Perturbation Theory for Matrix Product States*
1 July	Thomas Bernert (Johann Wolfgang Goethe University Frankfurt/Main) *Hexaphenyldisilane: Crystal Structure and Thermodynamic Properties from Powder Data and DFT Calculations*
1 July	Ping Wang (Ruhr University Bochum) *Niobate and tantalate semiconductor-based photocatalysts for solar energy conversion and environmental remediation*
7 July	Prof. Chris Vanderwal (University of California, Irvine, US) *Synthesis of Unusual Natural Products*
8 July	Elisabeth Maurer (RWTH Aachen) *Transition metal catalysts for the electrochemical nitrFlooren reduction - Characterization using cyclic voltammetry and chronoamperometry*

9 July	Peter Schröder (MPI für molekulare Physiologie, Dortmund) *Synthesis and biolFloorical evaluation of neurotrophic compound collections*
10 July	Jenagathan Akilavasan (University Peradeniya, Sri Lanka) *Dye Sensitized Solar Cells based on Hydro thermally synthesized TiO_2 nanotubes*
10 July	Puneet Gupta (Johann Wolfgang Goethe-Universität, Frankfurt a. Main) *Hydroxylation Reactions in Bioinorganic Models for Copper Enzymes: A DFT Assessment*
11 July	Prof. Dr. Philipp Kurz (Albert-Ludwigs-Universität, Freiburg) *Calcium manganese oxides as bio-inspired anode materials for water-electrolysis*
15 July	Maximilian Domaschke (hte, Ludwigshafen) *Synthesis of functional nanostructured materials via flame spray pyrolysis*
17 July	Prof. Dr. Klaus Roth (FU Berlin) Lecture zum Summer BBQ des Jung Chemiker Forums *Vom ersten Bier zum Kater*
22 July	Prof. Thomas Junkers (Universiteit Hasselt, BE) *Sequence control in radical polymerization: From batch to flow synthesis*
23 July	Sonja Hanebaum (University of Bielefeld) *Polymer based Floor polishes*
25 July	Aurélie Blond (Université Paris Descartes, FR) *Diversity-oriented synthesis of cis-1,3-diamines as RNA binders*
30 July	Giulio Cassano (University of Pisa, IT) *New Copper-Catalyzed Nucleophilic Addition to the Pyridines and Vinylaziridines*

20 August	Dr. Erhan Ozkal (Institute of Chemical Research of Catalonia, ES) *Triazole-Based Ligands for Click Chemistry and Asymmetric Catalysis*
26 August	Morton Brix Ley (Universität Aarhus, DK) *Complex metal hydrides-Synthesis and multifunctionality*
27 August	Michele Queirolo (University of Parma, IT) *Palladium-catalyzed synthesis in ordered sequence focused on the introduction of carbon monoxide into organic substrates*
1 September	Gabriele Prina Cerai (Universita degli Studi di Torino, IT) *Gold Catalysis in Organic Chemistry: Synthesis of VinylFloorous Amides*
02 September	Dr. Yang Lou (East China University of Sc. and Technol. Shanghai, CN) *CO oxidation over Co_3O_4-based catalysts and low temperature*
8 September	Luca Legnani (Universita degli Studi di Milano, IT) *Photocatalytic decarboxylation studies of modified amino acids*
8 September	Dr. Maria Khrenova (Lomonosov Moscow State University, RU) *Modeling Mechanism of Proteolysis and Inhibition of Matrix Metalloproteinase-2*
16 September	Mrs. Lucia Pagliari (Universtität Mailand, IT) *Grain size effect on solid state reactivity*
16 September	Dr. Naoya Kumagai (Institute of Microbial Chemistry, Tokyo, JP) *Exploration of Cooperative Asymmetric Catalysis Toward the Efficient Synthesis of Therapeutics*
17 September	Marie Picher (Bayer Healthcare, Berlin) *Synthesis of isotope-labelled Dihydroartemisinin*
24 September	Prof. Suzanne A. Blum (University of California, Irvine) *Alkoxyboration & Microscopy for Organic Chemists*

24 September	Dr. Roberta Properzi (University of Camerino, IT) *Synthesis of pharmaceutically active heterocycles and lipid targets: novel rearrangements and methods for carbon-heteroatom bond formation*
26 September	Nicolas Lenner (LMU München) *An extended Hamiltonian approach for continuous tempering in molecular dynamics simulations*
2 October	Prof. Christoph Janiak (Heinrich Heine University Düsseldorf) **GDCh-Lecture:** *Chemistry in the World of Dwarfs - from Nanopores to Nanoparticles*
15 October	Prof. Daisuke Uraguchi (Nagoya University, JP) *MBLA Lectureship: Molecular design and applications of chiral organic ion pair catalysts featuring anion-controlling ability*
22 October	Giuseppe Zuccarello (ETH Zürich, CH) *Stereodivergent Total Synthesis of Δ9-tetrahydrocannabinols*
28 October	Dr. Olga Petrova (RUB Bochum) *Preparation and X-ray absorption-based characterisation of nano-phased carbon supported Pt-alloy electrocatalysts for proton exchange membrane fuel cells*
4 November	Dr. Pieter C. A. Bruijnincx (Universität Utrecht, NL) *Valorization of the carbohydrate and lignin fractions of biomass: catalyst development for new and drop-in biobased chemicals production*
5 November	Dr. Kola Sattaiah Naidu (Universität Bangaloa, IN) *Chemistry of Ru(II) complexes bearing sigma bonded H−X (X = H, Si, C) species/fragments*
10 November	Dr. Christina Taouss (TU Braunschweig) *PhosphanchalkFloorenide und ihre Goldkomplexe*

12 November	Mathias Mamboury (EPFL, CH) *Towards the Total Synthesis of Lophirone H & Titanium-mediated Synthesis of Indoles*
19 November	Prof. Marco Antonio Chaer Nascimento (Universität Rio de Janeiro, BR) *Permutation Symmetry and Non-Dynamic Correlation Energy*
25 November	Marta Gubitosi (Universität Rom, IT) *Sugar-bile acid-based bolaamphiphiles: building blocks for supramolecular architectures*
26 November	Irene Felker (Givaudan Schweiz AG, CH) *Design and Enantioselective Synthesis of Novel Cashmeran Odorants Enabled by Enol Catalysis*
27 November	Prof. Ning Jiao (Universität Peking, CN) *Highly Efficient MethodolFloories via C-H/C-C Bond NitrFloorenation*
3 December	Mathies Evers (RUB, Bochum) *Synthesis of Bimetallic Nanocrystals of Group 10 and 11*
8 December	Dr. Ning Yan (University Singapore, SG) *Value Added Chemicals and Materials from Chitin, Lignin and Cellulose*

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13 January	Chris-Julian Fruhner (TU Clausthal) *Scintillation properties of doped cesium iodide*
14 January	Dr. Gregg Beckham (National Renewable Energy Laboratory, US) *Towards integrated processes for lignin valorization*
16 January	Dr. Jason P. Hallett (Imperial College London, UK) *Low cost ionic liquids for biorefining*
21 January	Patricia E. Podsiadly (Novartis Basel, CH) *Isomerising metathesis: A key technology for the chemical utilisation of Cashew NutShell Liquid*
28 January	Dr. A.-F. Pecharman (Universität Toulouse, FR) *From Uranium Chemistry to Nickel Chemistry*
30 January	Robin Frauenlob (LIKAT Rostock) *New methodologies for catalysis and combinatorial chemistry*
5 February	Prof. Albrecht Berkessel (Universität Köln) **GDCh-Lecture:** *Carbene Catalysis and the Breslow Intermediate*
10 February	Dr. Thibaud Etienne (Université de Lorraine & Université de Namur, FR) *Topological Investigation of Molecular Excited States*
12 February	Prof. Massimo Bietti (Universität Rom, IT) *Reactivity and selectivity patterns in hydrogen atom transfer from aliphatic C-H bonds to alkoxyl radicals. The role of structural and medium effects*
25 February	Bernd Waldecker (Georg August University of Göttingen) *Synthese von zweifach helicalen Molekularen Schaltern*

25 February	Prof. Dr. Robert Morris (Universität Toronto, CA) *Bifunctional hydrogenation - moving from ruthenium- to iron-based catalysts*
25 February	Dr. Garima Jindal (Indian Institute of Technology Bombay. IN) *Mechanistic Insights on Stereoinduction in Asymmetric Organocatalysis and Palladium Catalysis*
26 February	Torben R. Jensen (University in Aarhus, DK) *Hydrogen Containing Solids – New Perspectives*
3 March	Prof. Jochem Marotzke (MPI für Meteorologie, Hamburg) *Klimawandel*
4 March	Dr. Ali Hassanali (International Center for Theoretical Physics (ICTP), Triest, IT) *Probing complexity in aqueous systems*
4 March	Dr. Matthew Tredwell (Universität Oxford, UK) *New Strategies for [18F]Radiolabeling*
4 March	Kai Averesch (TU Dortmund) *Ruthenium-catalyzed Tandem-reactions for the Synthesis of branched, primary Alcohols from 1-Alkenes*
6 March	Dr. Kun Xu (Universität Freiburg) *Rhodium Catalyzed Hydrofunctionalization of Allenes and Alkynes*
25 March	Georgios Gerogiokas (University of Edinburgh, UK) *Prediction of hydration thermodynamics in protein-ligand binding with Grid Cell Theory*
25 March	Marion Daniel (University of Marseille, FR) *Photooxidation of dicarbonyl compounds and guanidines. Cyclization using hypervalent iodine reagents*

26 March	Prof. Andreas Seidel-Morgenstern (MPI für Dynamik komplexer technischer Systeme, Magdeburg) **GDCh-Lecture:** *Processes to separate enantiomers*
1 April	Prof. Brian Crane (Cornell University, US) *Mechanisms of Redox and Photo Sensing by Flavoproteins*
15 April	Prof. Dr. Christel M. Marian (Heinrich Heine University Düsseldorf) *Spin-forbidden molecular excited-state processes*
20 April	Prof. Kazuhiro Takanabe (King Abdullah University of Science and Technology, SA) *Photocatalytic overall water splitting: Towards photocatalysis by design*
21 April	Adam Zielinski (University of Warsaw, PL) *Synthesis and properties of Hoveyda-Grubbs catalysts modified at the etheric fragment*
27-29 April	German-Thai Workshop on Photovoltaics
29 April	Prof. Yaroslav Filinchuk (UCL Université, Louvain, BE) *Exploring new directions in chemistry of hydrides*
8 May	Dr. Thomas Lunkenbein (Fritz-Haber-Institut, Berlin) *Beam Sensitive Mixed Metal Oxides in the Electron Microscope - A Chemical Analysis*
8 May	Prof. Yundong Wu, (University of Peking, CN) *Bridging Theory and Experiment in Establishing the Mechanisms of Catalytical Reactions*
8 May	Dr. Thomas Lunkenbein (Fritz-Haber-Institut, Berlin) *Beam Sensitive Mixed Metal Oxides in the Electron Microscope - A Chemical Analysis*

13 May	Dr. Julien Michel (University of Edinburg, UK) *Exploring biomolecular hydration thermodynamics with grid cell theory*
19-21 May	Prof. Dr. Stefan Grimme (University Bonn) Karl-Ziegler-Lecture Series:
19 May	*Quantum Chemistry for non-covalent interactions and supramolecular systems*
20 May	*Accurate Quantum Chemistry for Complex Chemical Systems*
21 May	*Automatic generation of inter- and intramolecular force-fields for molecules and condensed phase simulations*
22 May	Dr. Junwang Tang (University College, London, UK) *Efficient visible driven photocatalysts for water reduction and oxidation: novel materials and fundamental understanding*
25 May	Dr. Vahid Khakyzadeh (University of Freiburg) *Moving Toward Green Chemistry and Clean Production*
3 June	Dr. Yin Zhang (University of Toulouse, FR) *Backbone-decoration of imidazol-2-ylidenes by amino groups as a rational strategy towards improved NHC-catalysts*
8 June	Dr. Benjamin Bhawal (Cambridge University, UK) *Synthesis of 2-substituted indoles via Sonogashira coupling and Design of a chemically robust variant of the Hayashi-Jørgensen catalyst*
11 June	Dr. Ulrich Hintermair (University of Bath, UK) *Molecular Oxidation Catalysis with Iridium - Water Splitting and CH-oxygenation*
18 June	Prof. Tiow-Gan Ong (Academia Sinica, Taipei, TW) *All Manifestations of Carbodicarbene and Amino-NHC in Catalysis and Main Group Elements*

22 June	Prof. Candace Chan (Arizona State University, US) *Tutorial Lecture: Electrochemical Techniques for Characterization of Energy Materials*
24 June	Prof. Tehshik P. Yoon (University of Wisconsin-Madison, US) *Photocatalysis with Visible Light*
25 June	Prof. Oliver Trapp (Heidelberg University) **GDCh-Lecture:** *From Novel Stereodynamic Self-Amplifying Catalytic Systems to the Coulomb Explosion Imaging of Chiral Molecules*
26 June	Prof. Dr. Pierre Karam (American University of Beirut, LB) *Conjugated Nanohybrid Particles as Imaging and Nanothermometer Probes*
30 June	Mr. Marco Rehosek (University of Bochum) *Photoelectrochemical hydrogen peroxide sensing*
2 July	Prof. Filipp Furche (UC Irvine, CA, US) **GDCh-Lecture:** *Transition Metal-Like Lanthanide and Actinide Ions*
3 June	Marius Bilke (Universität München) *Characterization of supported, bimetallic Pd/Au-catalysts for VAM synthesis in gas-phase - a FTIR study*
9 July	Prof. Dr. Metin Tolan (TU Dortmund) *JCF-Lecture: Shaken not Stirred! James Bond in the Focus of Physics*
19 July	Matthias Trunk (Universität München) *Synthesis and Characterization of New Metal-Organic Frameworks*
28 August	Anna Grünert (Ruhr University Bochum) *Synthesis of Metal@MOF and Metal Oxide@MOF Composites by Chemical Vapour Infiltration*
28 August	Maren Könemann (Hochschule Niederrhein, Krefeld) *Lecture*

3 September	Prof. Sensuke Ogoshi (Osaka University Suita, JP) *Nickel-catalyzed Transformation of Carbonyl Compounds via Hetero-Nickelacycle Intermediates*
7 September	Ilija Coric (Yale University, US) *Molecular Design in Organocatalysis and Coordination Chemistry: Confined Acids & Nitrogenase Mimics*
17 September	Prof. Pavel Kocovsky (Charles University, Prague, CZ) *Organocatalyzed Multiple Allylation and Metal-Catalyzed Functionalizaton: Symbiosis and Diversity*
18 September	Adriano Bauer (Imperial College London, UK) *Kinetic resolution of amines using DMAP-N-Oxide derived catalysts*
22 September	Prof. Dr. Peter Fulde (MPI für Physik komplexer Systeme) **GDCh-Lecture:** *Korrelierte Elektronen in Molekülen und Festkörpern*
23 September	Dr. Céline Taglang (Paris-Sud University, FR) *Enantiospecific C(sp3)-H activation catalyzed by ruthenium nanoparticles: application to isotopic labeling of molecules of biological interest*
25 September	Dr. Desislava Petkova (University of Wien, AT) *Towards the total synthesis of Quinine*
6 October	Sabine Josten (Martin-Luther University of Halle-Wittenberg) *PdCu core-shell-electrocatalysts for the oxygen reduction reaction and formic acid oxidation*
6 October	Beatriz Roldán (Ruhr University Bochum) **GDCh-Lecture:** *In Situ and Operando Characterization of Model Nanocatalysts: Size, Shape, and Chemical State Effects*
7 October	Francesca Mandrelli (Novartis Pharma AG, Basel, CH) *Development of thiourea organocatalysts as enabling tools for asymmetric Michael Addition*

13 October	Prof. Kurt Wüthrich (ETH Zurich, CH) *NMR, a Physics Phenomenon for Use in Structural Biology and Medical Diagnosis*
14 October	Dr. Jun Takaya (Tokyo Institute of Technology, JP) *MBLA Lectureship: Development of New Synthetic Reactions Catalyzed by a Transition Metal Complex Featuring Fluxional Behavior of a Silyl-Ligand*
27 October	Dr. Martin Oschatz (University of Utrecht, NL) *Nanoporous Carbon Materials for Gas Adsorption, Electrochemical Energy Storage and as Catalyst Supports for the Direct Production of Lower Olefins from Synthesis Gas*
29 October	Dr. Pilar Franco (Chiral Technologies Europe, FR) *Ingredients for a robust and scalable chromatographic chiral method*
4 November	Nils Flodén (Imperial College London, UK) *Old Methods with New Technologies - Towards a Scalable Peptide Synthesis in Flow and the Total Synthesis of Segetalin A & B*
5 November	Prof. Franziska Schönebeck (RWTH Aachen) **GDCh-Lecture:** *Adventures in Organometallic Catalysis – Computation and Experiment*
18 November	Oleg Grossmann (LMU München) *Enantioselective Synthesis of Chromanones via Peptidic Phosphane Catalyzed Rauhut−Currier Reaction*
24 November	Prof. Rubén Martín (Institute of Chemical Research of Catalonia, Tarragona, ES) *Ni-catalyzed reductive carboxylation technologies and C-O bond-functionalization*
24 November	Dr. Sascha Ott (University Uppsala, SE) *A journey through synthetic (FeFe) hydrogenases – from bioinorganic models to their incorporation into metal-organic frameworks*

25 November	Dr. V. S. Thirunavukkarasu (University of Basel, CH) *Transition-Metal Catalyzed C-H Bond Functionalization Reaction*
26 November	Prof. Dr. J. Neugebauer (Universität Münster) **GDCh-Lecture:** *QM/QM Embedding Methods for Chemistry in Complex Environments*
30 November	Prof. Dr. Bernd Engels (University of Würzburg) *New approaches for photo-induced processes in organic dyes and the development of covalent ligands*
1 December	Rowshanak Irani (University of Teheran, IR) *Lead-free perovskite solar cells*
1 December	Farshad Riyahi (Friedrich-Alexander Universität Erlangen) *Controlling Pore Sizes and Microstructures of Porous Carbon Shells on Carbide Cores by Using High Temperature Vacuum Annealing*
2 December	Weiping Liu (Georg August University of Göttingen) *Selectivity in Ruthenium and Manganese Catalyzed C-H Functionalization*
2 December	Dr. Oliver Weingart (Heinrich Heine University Düsseldorf) *Ultraschnelle Singulett-Photoreaktionen - von kleinen Modellsystemen zur Protein-Photodynamik*
16 December	Mr. Edward Nürenberg (TU Dortmund) *Derivatization of cyclo- and dicyclopentadiene to amides and amines by homogenous transition metal catalysis*
18 December	Prof. Dr. Osamu Terasaki (University of Floorholm, SE) *Formation of excess adsorbate-superlattice in porous MOF crystals challenges prevailing view*
21 December	Professor Shridhar R. Gadre (I.I.T. Kanpur, IN) *Electrostatics of atoms and molecules*

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12 January	Bidyut Bikash Sarma (Weizmann Institute of Science, Rehovot, IL) *Oxidation of biomass and methyl arenes by polyoxometalate*
17 February	Dr. Shunxi Dong (RWTH Aachen) *Chiral guanidine derivatives and N-heterocyclic carbenes (NHC) catalyzed asymmetric transformations*
19 February	Prof. Sukbok Chang (KAIST, Daejeon, KR) *Development of Catalytic Direct C-H Amination Reactions*
19 February	Dr. Jeremy Godemert (Université de Rouen, FR) *New applications of chiral cooperative ions pair in organocatalysis: 1,2 additions reactions catalysed by in situ generated Brønsted base*
2 March	Dr. Igor Lyskov (Heinrich Heine University Düsseldorf) *Redesign of the DFT/MRCI Hamiltonian*
3 March	Prof. John M. Herbert (Ohio State University, US) *Beyond TDDFT Using Only Single Excitations: Methods for Computational Studies of Excited States in Complex Systems*
9 March	Prof. Takahiko Akiyama (Gakushuin University, Japan) *Recent Progress in the Chiral Phosphoric Acid Catalysis*
11 March	Dr. Ivo Leito (University of Tartu, Estonia) *Acidic and superacidic molecules: acidity in different media*
17 March	Prof. Masahiro Terada (Tohoku University, Japan) *Enantioselective Catalysis by Chiral Brønsted Acids and Bases*
23 March	Prof. Thomas D. Kühne (Paderborn University) *The name is bond - Hydrogen bond*

4 April	Prof. Kristina Tschulik (Ruhr University Bochum) *New Electrochemical Methods to Study Reactions of and at Nanomaterials*
4 April	Prof. Zhongfang Chen (University of Puerto Rico, San Juan, US) *Extending Professor Schleyer's Legacy to Nanomaterials Science*
6 April	Mr. Mingquan Yu (University of Shanghai, CN) *Developing transition metal based electrocatalysts for water oxidation*
20 April	Prof. Mu-Hyun Baik Korea (Korea Adv. Inst. of Science and Technology, KR) *Predictive Computational Molecular Modeling? - Using Computers to Design New Catalytic Reactions*
21 April	Dr. Norbert Hoffmann (CNRS, Université de Reims, FR) *Photochemical electron and hydrogen transfer in stoichiometric and catalytic organic reactions*
27 April	Dr. Somnath Das (University of Cologne) *Organocatalysis by electron-deficient pyridinium salts: from halide-binding to glycosylation*
29 April	Andreas Zech (Heidelberg University) *Industrial synthesis of (S)-a-Damascon*
17 May	Prof. Dr. Tewodros Asefa (Rutgers, The State University of New Jersey, US) *Multifunctional Nanostructured Materials: From Rational Design and Synthesis to Potential Applications in Catalysis and Electrocatalysis*
18 May	Prof. Felix R. Fischer (University of California Berkeley, US) *Teaching Polymers the Meaning of Life & Nanographene Quantum Confinement*

7-9 June	Prof. Erick M. Carreira (ETH Zurich, CH) Karl-Ziegler-Lecture Series:
7 June	*Surprises and discoveries with natural products*
8 June	*Surprises and Discoveries with Small Molecules*
9 June	*Total synthesis in the 21st Century: Why bother?*
13 June	Dr. Akira Taguchi (University of Toyama, JP) *Porous polymer as catalyst support in tritium process*
13 June	Prof. Hai Lin (University of Colorado Denver, US) *Adaptive-QM/MM Schemes for Simulations of Ion Solvation and Transport*
22 June	Prof. Dr. Yuriy Roman (Massachusetts Institute of Technology, US) *Architecture at the nanoscale: engineering next-generation catalysts for energy applications*
28 June	Dr. Michael Fischer (University of Bremen) *Computational studies of adsorption in crystalline microporous materials - Insights into structure-property relationships*
29 June	Prof. Bron (Martin-Luther-Universität, Halle) *Nanostructured materials for electrochemical energy conversion: synthesis, properties, challenges*
5 July	PD. Dr. Ulrich Sternberg (Karlsruhe, Institute of Technology (KIT) *Configurations and Conformers of Molecules Studied by Molecular Dynamics with Orientational Constraints*
6 July	Prof. Dr. Ulrich Tallarek (Philipps-Universität Marburg) *Ultrahigh Performance Solid–Liquid Catalysis with Silica-Based Monoliths*
8 July	Prof. Mehtap Özaslan (Carl von Ossietzky University of Oldenburg) *Advanced electrocatalysts for energy systems*

8 July	Dr. Carsten Dosche (Carl von Ossietzky University of Oldenburg) *Functional dyes for in-situ analysis*
25 July	Prof. Motomu Kanai (University of Tokyo, JP) *Catalysis Development Targeting Small Molecules to Proteins*
26 July	Emine Kayahan (Middle East Technical University, Ankara, Turkey) *Design and Operation of a Tubular Photobioreactor for Bio-hydrogen Production*
2 August	Mr. Ilker Satlimis (Leibnitz University Hannover) *Synthesen in miniaturisierten Durchflusssystemen mit induktiv geheizten Kupferkatalysatoren und Studien zur Synthese eines Thiol basierten Linkers für den Einsatz in einem Wirkstoff-Goldnanopartikel Konjugat*
8 August	Prof. Kizashi Yamaguchi (Osaka University, JP) *Large-scale quantum mechanics(QM)/molecular mechanics(MM) studies on oxygen evolving complex (OEC) of photosystem II (PSII) in combination with XRD, XFEL, EXAFS and EPR experimental results*
12 August	Prof. Rajib Kumar Mitra (S.N. Bose National Centre for Basic Sciences, IN) *Application of Terahertz Spectroscopy in Chemistry and Biology*
12 August	Julia Tseglakova (TU München) *MoVTeNb Mixed Oxides: Structure and Reactivity*
16 August	Prof. Jeffrey Bode (ETH Zürich, CH) *Cross Coupling Approaches to Chiral, Saturated N-Heterocycles*
31 August	Dr. Raja Mitra (University of Duisburg-Essen) *Synthesis of a Bifunctional Chiral [2]Catenane as Artificial Receptors and Catalyst*

31 August	Hrishikesh Ravindra Joshi (BITS-PIlani, Goa, IN) *Development of Nano-based Hetero-systems;* *A Perspective in Heterogeneous Reaction Catalysis*
14 September	Dr. Peter Spannring *Fe-catalyzed oxidative cleavage and SABRE in water with Ir-catalysts*
20 September	Prof. Larry Overman (University of California, Irvine, US) *Fragment Coupling Using Carbon Radicals*
21 September	Prof. Lili Zhao (Nanjing University of Technology, CN) *Applications of computational chemistry in catalyst design, understanding reaction mechanisms, and designing new electronic structures*
21 September	Sebastian Schwengers (Heinrich Heine University Düsseldorf) *Contributions to the chemistry of electronpoor N-heterocyclic carbenes*
30 September	Dr. Josep Cornella (Scripps Research Institute, La Jolla, CA, US) *Redox-Active Esters in Cross-Coupling Reactions*
4 October	Sra Erika de la Rosa Reyna (VUAnCH, UniCRE, CZ) *Synthesis and evaluation of catalysts in the Production of Biofuels by Hydroprocessing*
12 October	Prof. Satoshi Maeda (Hokkaido University, JP) *MBLA-Lecture: Development of Automated Reaction Path Search Methods toward Systematic Understanding and Design of Organic Reactions*
25 October	Prof. Dr. Karsten Reuter (TU München) **GDCh-Lecture:** *Mobile and Bound Electrons in Computational Energy Research*
26 October	Prof. Dr. Tobias Ritter (Max-Planck-Institut für Kohlenforschung) *Radiochemische Grundlagenforschung*

11 November	Prof. Matthew Sigman (University of Utah, US) *Bringing Modern Data Analysis Tools to Prediction and Understanding in Organic Chemistry*
15 November	Prof. Dr. Hans-Joachim Freund (FHI Berlin) **GDCh-Lecture:** *Model Studies on Heterogeneous Catalysts at the Atomic Scale: From Supported Metal Particles to Two-dimensional Zeolites*
17 November	Dr. Geraldine Masson (Institut de Chimie des Substances Naturelles, FR) **Liebig-Lecture:** *Visible light photoredox catalysis as a tool for organic synthesis*
18 November	Prof. Dr. Hanwei Gao (University of Florida, US) *Perovskite Optoelectronics—Cheaper for Better?*
15 December	Prof. Fernando Coelho (University of Campinas, BR) *The Morita Bylis-Hillman reaction in Organic Synthesis: Recent Advances*

7.7 Local Activities of the Young Chemists Forum (JCF) of the German Chemical Society (GDCh)

List of Talks Given by Guests 2014-2016

30 July 2014	Prof. Dr. Klaus Roth (FU Berlin, DE) *Vom ersten Bier bis zum Kater*
11 December 2014	Prof. Hans-Dieter Barke (Universität Münster, DE) *Misconceptions in Chemistry*
9 July 2015	Prof. Dr. Metin Tolan (TU Dortmund, DE) *The Physics of James Bond*
23 July 2015	Dr. Niklas Meine (Bayer MaterialScience, DE) *"MPI – What's Next?"* *Innovative Solutions for Renewable Polymers*
14 December 2015	Dr. Tobias Gruber (University of Lincoln, UK) *Chemistry of X-Mas*
15 June 2016	Dr. Shanshan Wang (Nexant, UK) *"MPI – What's Next?" From Kohle to Coal – From Germany to UK*
23 June 2016	Dr. Elke Maase (Wiley-VCH, DE) *"MPI – What's Next?" Book Publishing at Wiley-VCH*
21 July 2016	Dr. Jean Pascal Schulte (Covestro AG, DE) *"MPI – What's Next?" Curious, Courageous, Colorful – Careers@Covestro*

Other Activities Organized by the JCF Mülheim

6 February 2014	JCF Kegeln, Hotel Thiesmann, Mülheim, DE Possibility for new members of the Institute to get to know each other
24 May 2014	Tag der offenen Tür, MPI für Kohlenforschung, Mülheim, DE Molecular kitchen
28 June 2014	Excursion to Zeche Zollverein, Essen, DE
17 July 2014	8th Annual Summer Barbecue, MPI für Kohlenforschung, Mülheim, DE
23 October 2014	JCF Kegeln, Hotel Thiesmann, Mülheim, DE Possibility for new members of the Institute to get to know each other
9 December 2014	5th Junges Chemie Symposium, Ruhr-Universität Bochum, DE Chemistry students of the Ruhr area presented and discussed research results of their Bachelor-, Master- and PhD-theses. The symposium was organized by the JCFs of Bochum, Dortmund, Essen, and Mülheim.
5 February 2015	JCF Kegeln, Hotel Thiesmann, Mülheim, DE Possibility for new members of the Institute to get to know each other
9 July 2015	9th Annual Summer Barbecue MPI für Kohlenforschung, Mülheim, DE

17 September 2015	6th Junges Chemie Symposium, University of Duisburg-Essen, DE Chemistry students of the Ruhr area presented and discussed research results of their Bachelor-, Master- and PhD-theses. The symposium was organized by the JCFs of Bochum, Dortmund, Essen and Mülheim
8 October 2015	JCF Kegeln, Hotel Thiesmann, Mülheim, DE Possibility for new members of the Institute to get to know each other
11 October 2015	Excursion to Deutsches Bergbau-Museum, Bochum DE
13 October 2016	7th Junges Chemie Symposium, TU Dortmund, DE
6 December 2016	JCF Kegeln, Hotel Thiesmann, Mülheim, DE Possibility for new members of the Institute to get to know each other
16 December 2016	Mulled wine and cookies after the Institute Seminar Possibility for members of the Institute to get in touch with JCF members and learn about their activities

7.8 Public Relations (I. Schiffhorst)

In 2014, the Max-Planck-Institut für Kohlenforschung celebrated its 100th birthday with a number of special activities and events for the general public, the Institute's employees, and partners from industry and universities. Collectively, these activities were meant to increase the public awareness of the many research accomplishments made at the Institute during the last century.

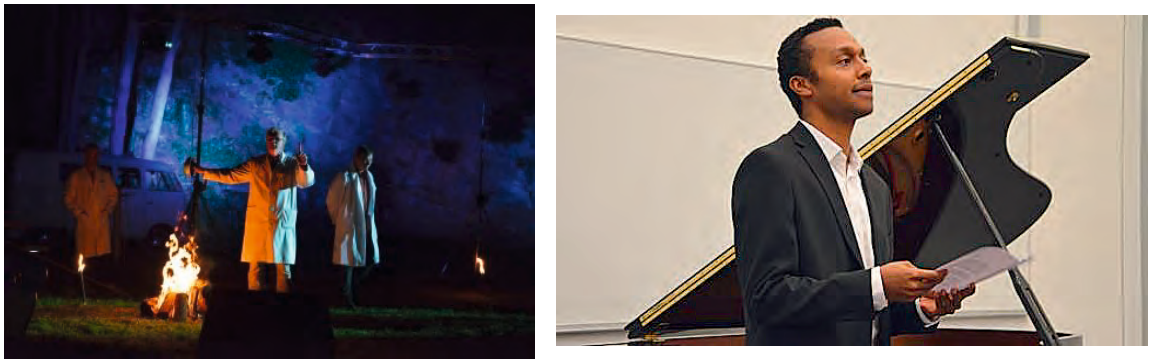
A ceremony and a scientific symposium were held at the Mülheim Town Hall on August 24, 2014 to celebrate the event. In her address, the Mayor of Mülheim, Dagmar Mühlenfeld, congratulated the Kohlenforschung Institute on its outstanding scientific research that had even brought a Nobel Prize winner to the city. Federal Prime-Minister Hannelore Kraft emphasized the fact that the Institue attracts scientists from all over the world to Mülheim. Klaus Engel, CEO of Evonik Industries, elaborated on the impact of the fundamental research carried out at the Institut on chemical industry at large, and how these inventions have arguably changed the world. Finally, the then newly elected President of the Max-Planck-Society, Prof. Martin Stratmann, outlined that the Institute's success has to do with its ability to balance continuity and change. A scientific symposium held in the afternoon featured different timely aspects of catalysis research. The lectures were given by world-renowned scientists and attracted much interest of the specialist audience.

Official ceremony at the Mülheim townhall with Federal Prime-Minister Kraft, Mayor Mühlenfeld, the MPG President Statmann, the Evonik CEO Engel, and the former and current Directors of the Institute

A highlight for the Mülheim citizens was the Open House Day, when 1500 people visited the Institute. The laboratories and workshops opened their doors; the employees demonstrated their work in more than 30 experimental stations and presentations that they had designed for this special occasion.

Experimental stations at Open House Day 2014.

Throughout the year, the Institute organized an additional "*Centennial Lectureship Series*" entitled "Kohle, Kunststoff, Katalyse" which was meant to introduce and explain different research milestones of the Institute to the general public. This series included an entertaining experimental lecture by Ferdi Schüth and his colleagues on the Mülheim Open Air Theatre which attracted thousands of visitors. A charity concert for UNICEF given by ex-Group Leader Nuno Maulide added a final touch to the centennial celebrations in 2014. He demonstrated his qualities as a piano player in a concert entitled "Chemistry meets Chopin" and, at the same time, managed to raise money for the children's help organization.



Experimental lecture and charity concert by Nuno Maulide – 2014 was a year full of memorable events.

Apart from the special centennial activities, the Institute participated at the "WissensNacht Ruhr" in 2014 and again in 2016, when this event was held at the Mülheim Art Museum. In a cooperation with a science centre in Gelsenkirchen, coworkers of the Institute presented experimental stations for children and families.

Publications and Press Review

A special issue of "*Angewandte Chemie*", a flagship journal in the chemical sciences, was published in 2014. In addition to several articles highlighting the development of the Kohlenforschung during the last century, this edition comprised a series of current research highlights from coworkers of the Institute as well as from friends and peers from other leading institutions worldwide.

A comprehensive summary of the history and the scientific achievements of the Max-Planck-Institut für Kohlenforschung is provided by a special publication entitled "*Katalyse auf dem Kahlenberg – 100 Jahre Max-Planck-Institut für Kohlenforschung*". This book was distributed to partnering institutes, stakeholders and employees, as well as to people with special interest in the Institute's history.

Moreover, several articles for a broader audience were published in local, regional and national newspapers and magazines. Likewise, the electronic media reported on several occasions on the Institute.

Due to the increasing importance of online communication, the Institute's website was refreshed and a new Intranet was set up. An information system was installed in the entrance hall of the Institute to inform visitors and employees about upcoming events and the latest news. The ties to the neighboring institute MPI for Chemical Energy Conversion (CEC) were invigorated with the first joint Summer party in 2016.

Activities for Schools and Families & Girls' Day

The Institute entertains several school contact programs and welcomes pupils in its laboratories to foster young people's interest in science. Dr. Claudia Weidenthaler is in charge of most of these activities; together with PhD students from the different departments, she visits classes and prepares practical courses in cooperation with the responsible school teacher. The Institute welcomes interested young people for training days, interviews and public tours, which are carried out in cooperation with the public relations officer.

Along the same lines, we continue to participate in the nationwide "Girls' Day" meant to encourage girls to consider job perspectives in science and engineering. Together with more than 20 staff members, Dr. Weidenthaler organizes this event which is very popular and always booked out.

The MPI für Kohlenforschung offers many different practical training possibilities for pupils and cooperates closely with schools and teachers.

Public Activities in Chronological Order

28 March 2014	Girls' Day
9 April 2014	Centennial Lectureship, Prof. Dr. Krijn de Jong
23 April 2014	Centennial Lectureship, Prof. Dr. Ferdi Schüth
25 April 2014	Open House Day at the Institute
7 May 2014	Centennial Lectureship, Dipl. Ing. Volker Weuthen
21 May 2014	Centennial Lectureship, Prof. Dr. Klaus Müllen
11 June 2014	Centennial Lectureship, Prof. Dr. Manfred Reetz
24 August 2014	Official Birthday Ceremony in the Town Hall
13 September 2014	Experimental Lecture with Ferdi Schüth
02 October 2014	WissensNacht Ruhr, Gelsenkirchen
19 November 2014	Charity Concert with Nuno Maulide

26 February 2015	90th Birthday of Günther Wilke with Guest Lecture
23 April 2015	Girls' Day
19 - 21 May 2015	Ziegler Lecture by Prof. Stefan Grimme
28 April 2016	Girls' Day
7 - 9 June 2016	Ziegler Lecture by Prof. Erick M. Carreira
10 September 2016	Experimental Lecture at Open Air Theatre, Mülheim
30 September 2016	WissensNacht Ruhr, Art Museum, Mülheim
26 October 2016	Public Information Evening on Radiochemistry presenting the Department of Organic Synthesis of Prof. Ritter

7.9 How to Reach the Institute

Travel Directions

By Road:

If approaching from the south on the A3 autobahn, exit at Breitscheid and join the A52 heading for Essen. After about 100 m turn off onto the B1 in the direction of Mülheim an der Ruhr. After about 8 km, follow the signs marked Max-Planck-Institute.

If travelling from the north (A3 autobahn) or west (A40 autobahn), exit at Duisburg-Kaiserberg in the direction of Mülheim an der Ruhr, continue to the town center (Friedrichstraße) and follow the signs marked Max-Planck-Institute.

If arriving from the east (A40 from Essen), join the B1 heading for Mülheim an der Ruhr. After about 5 km, follow the signs marked Max-Planck-Institute.

By Rail:

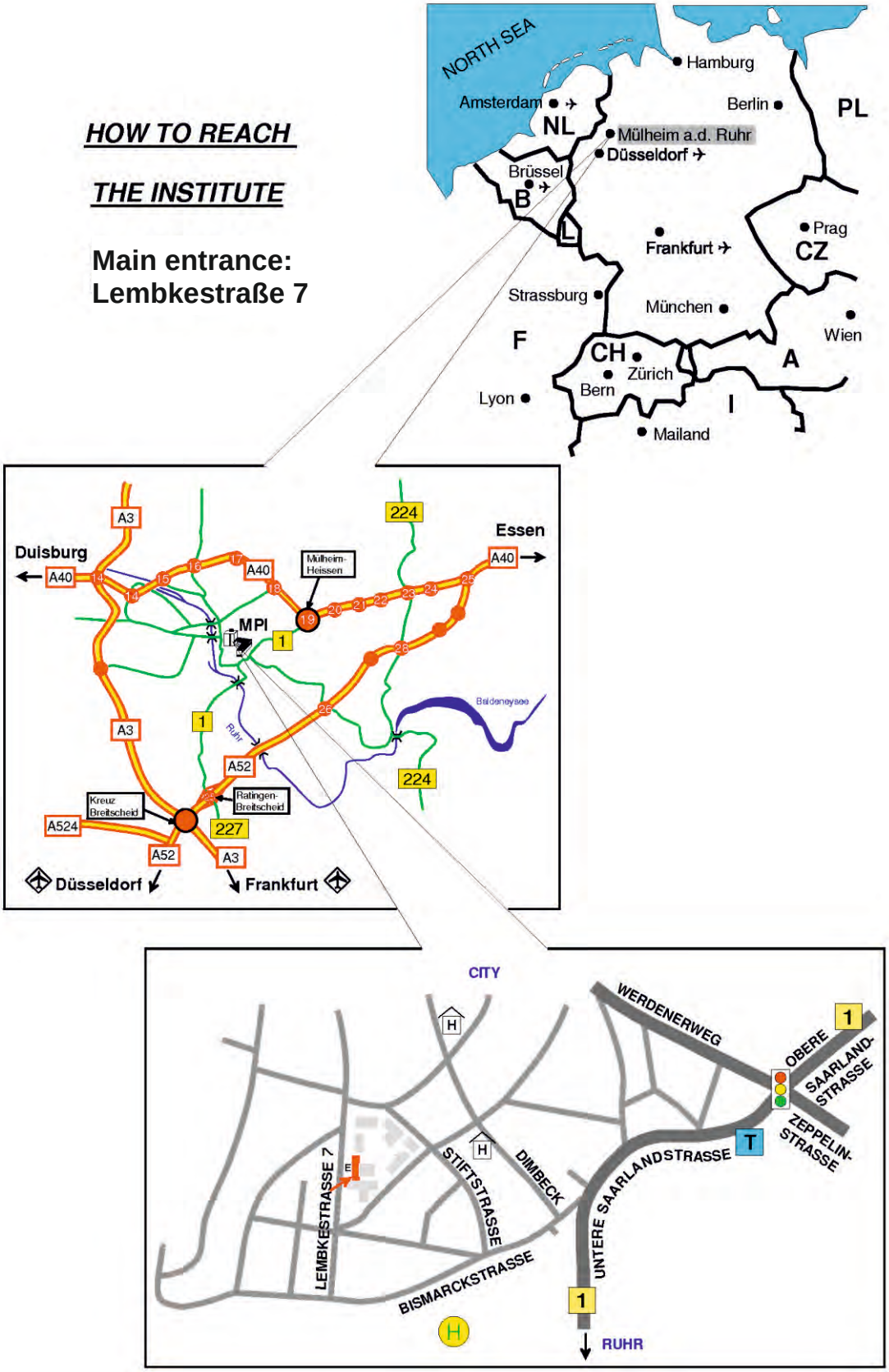
Take the train to Duisburg or Essen, and then the local railway (S-Bahn, Regionalexpress) to Mülheim an der Ruhr Hauptbahnhof. Then take a taxi or walk (20 minutes).

By Air:

From Düsseldorf Airport, either take a taxi directly to the Institute (about 22 km) or take the S-Bahn or Regionalexpress (RE 2) to Mülheim an der Ruhr Hauptbahnhof.

HOW TO REACH THE INSTITUTE

Main entrance:
Lembkestraße 7



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