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

Professor Dr. Günther Wilke
Professor Dr. Roland Köster (deceased, June 2009)

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Professor Dr. Alois Haas
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Members of the Scientific Council of the Max Planck Society,
Section of Chemistry, Physics and Technology

Dr. Wolfgang Schmidt (August 2003 – July 2009)
Dr. Claudia Weidenthaler (since July 2009)

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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 Landmarks of Chemistry) on the Institute in 2008. A bronze plaque on the historic building commemorates this event. On this occasion, a brochure was published, which reviews the Ziegler era in some detail. This information is also available via the Internet at http://www.mpi-muelheim.mpg.de/kofo/english/institut/geschichte_e.html.

Günther Wilke followed Karl Ziegler as Director in 1969. His research concentrated on the organometallic chemistry of the transition metals (especially nickel) and its application in homogeneous catalysis. The 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 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 was first described by Kurt Zosel in Mülheim/Ruhr 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.

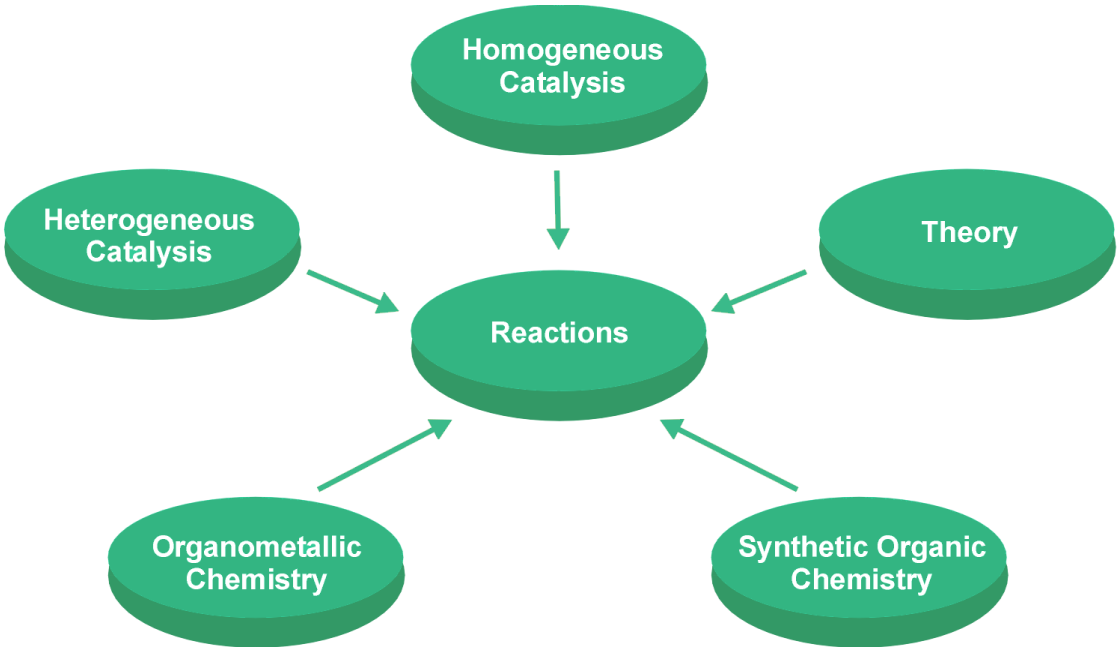
In 1993 Manfred T. Reetz was appointed Director of the Institute. As an organic chemist he initiated projects in his own group pertaining to catalysis, transition metal colloids and directed evolution of enzymes. He also re-defined the scientific activities of the Institute as a whole, a development 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 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.

The Directors of the Departments form a Board which is responsible for all decisions. The affairs of the Institute are taken care of by a Managing Director elected from this Board. As successor to Manfred Reetz, Ferdi Schüth served as Managing Director from 2003-2005, followed by Walter Thiel (2006-2008) and Alois Fürstner (2009-2011).

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.



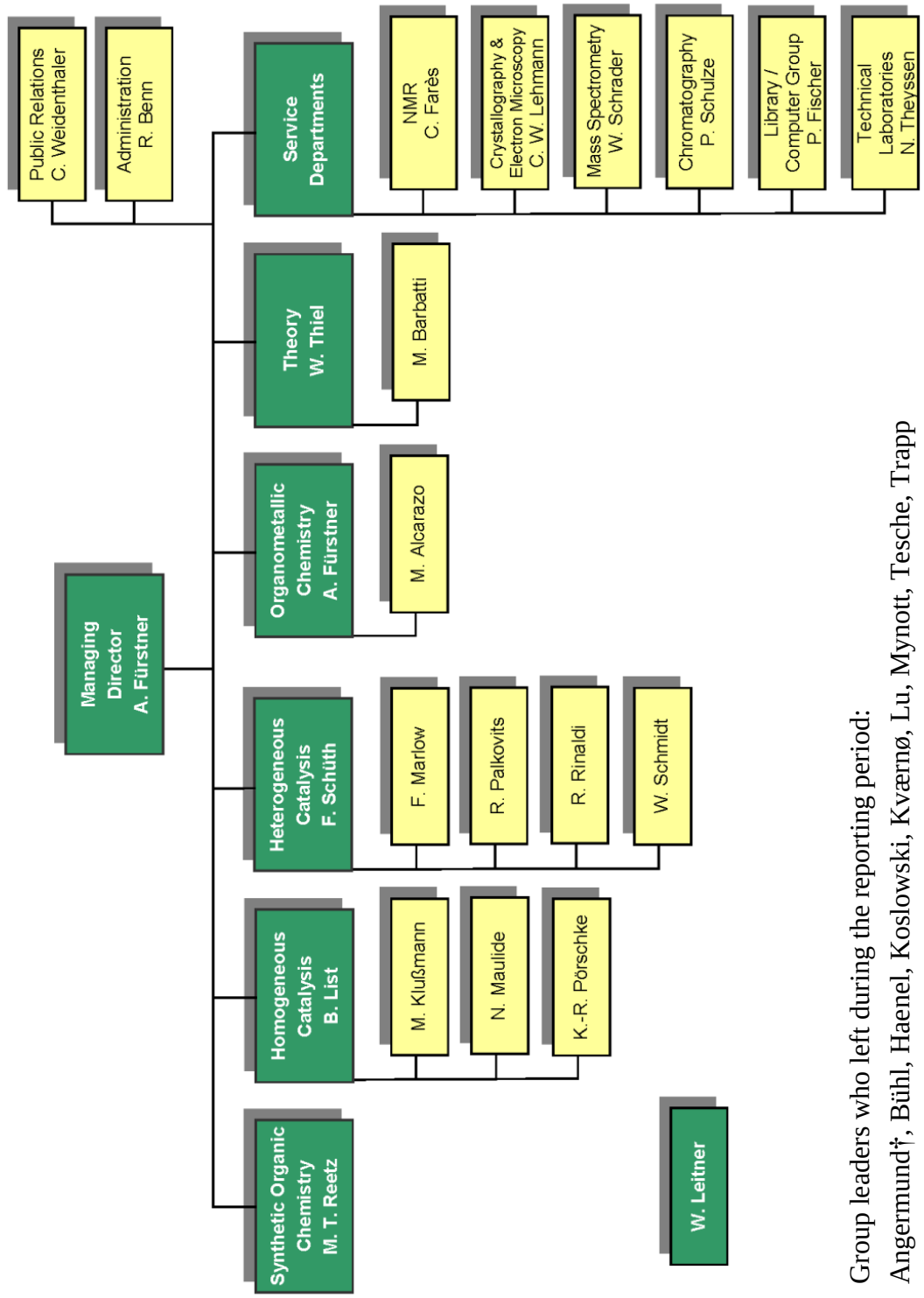
Catalysis is viewed world-wide as the key technology in the establishment of economically viable and ecologically benign chemical processes of the future. However, the efficiency of numerous catalytic systems is far from ideal and for many important chemical transformations appropriate catalysts have 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. Finally, a four-semester cycle of lectures, which covers homogeneous and heterogeneous catalysis, organocatalysis, biocatalysis, theory, and aspects of chemical engineering, provides special training for the doctoral students and post-docs of the Institute and contributes to the unique nature of the Institute.

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, 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 complex natural products and biologically interesting compounds, the implementation of environmentally benign one- and two-phase solvent systems for catalytic reactions, 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 2010



Group leaders who left during the reporting period:
Angermund†, Bühl, Haenel, Koslowski, Kværnø, Lu, Mynott, Tesche, Trapp

1.4 Members of the Scientific Advisory Board

(a) For the period until the end of 2005:

Professor Dr. Avelino Corma	Universidad Politécnica de Valencia Instituto de Tecnologia Quimica Avenida de los Naranjos s/n. 46022 Valencia, Spain
Professor Dr. Pierre Henri Dixneuf	Université de Rennes 1 UMR 6509 CNRS Campus de Beaulieu 35042 Rennes Cedex, France
Professor Dr. Dieter Enders	Institut für Organische Chemie der RWTH Aachen Professor-Pirlet-Straße 1 52074 Aachen, Germany
Professor Dr. Ben L. Feringa	University of Groningen Faculty of Mathematics and Natural Sciences Organic and Molecular Inorganic Chemistry Nijenborgh 4 9747 AG Groningen, The Netherlands
Professor Dr. John A. Gladysz	Institut für Organische Chemie der Universität Erlangen-Nürnberg Henkestraße 42 91054 Erlangen, Germany
Professor Dr. Henri Kagan	Université de Paris Sud Institut de Chimie Moléculaire d'Orsay CNRS Upresa 8075 91405 Orsay Cedex, France
Professor Dr. Joachim Sauer	Humboldt-Universität zu Berlin Institut für Chemie Unter den Linden 6 10099 Berlin, Germany
Professor Dr.-Ing. Jens Weitkamp	Universität Stuttgart Institut für Technische Chemie I Pfaffenwaldring 55 70569 Stuttgart, Germany

(b) For the period 2006-2011:

Professor Dr. Pierre Henri Dixneuf	Université de Rennes 1 UMR 6509 CNRS Campus de Beaulieu 35042 Rennes Cedex, France
Professor Dr. Dieter Enders	Institut für Organische Chemie der RWTH Aachen Professor-Pirlet-Straße 1 52074 Aachen, Germany
Professor Dr. Peter Hofmann	Organisch-Chemisches Institut der Universität Heidelberg Lehrstuhl für Organische Chemie III Im Neuenheimer Feld 270 69120 Heidelberg, Germany
Professor Dr. Eric N. Jacobsen	Harvard University Department of Chemistry 12 Oxford Street Cambridge, MA 02138, USA
Professor Dr. Joachim Sauer	Humboldt-Universität zu Berlin Institut für Chemie Unter den Linden 6 10099 Berlin, Germany
Professor Dr. Richard R. Schrock	Massachusetts Institute of Technology Department of Chemistry 77 Massachusetts Ave. Cambridge, MA 02139, USA
Professor Dr. Rutger A. van Santen	Eindhoven University of Technology Chemical Engineering and Chemistry PO Box 513, Helix STW 3.35 5600 MB Eindhoven, The Netherlands
Professor Dr.-Ing. Jens Weitkamp	Universität Stuttgart Institut für Technische Chemie I Pfaffenwaldring 55 70569 Stuttgart, Germany

1.5 Members of the Board of Governors ("Verwaltungsrat") 2007-2011

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

Ralf Blauth

Dr. Barbara Bludau, Secretary General of the Max Planck Society

Michael Dettmann

Professor Dr. Michael Dröscher

Professor Dr. Dieter Jahn

Dagmar Mühlenfeld, Mayor of the City of Mülheim an der Ruhr

Dr. Jörn Rüter

Professor Dr. Günther Wilke, Honorary Member

Dr. Werner Schwilling, Honorary Member

CHAPTER 2

Research Programs

2.1 Department of Synthetic Organic Chemistry

Director:

Manfred T. Reetz (born 1943)
Publications: 6, 47, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 101, 119, 161, 173, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 283, 305, 367, 377, 383, 384, 385, 386, 387, 388, 407, 419, 425, 426

Further group leaders:

Matthias W. Haenel (born 1944)
retired from the Institute in June 2009
Publications: 42, 43, 187, 188, 333

Walter Leitner (born 1963)
external scientific member of the Institute
Publications: 10, 16, 46, 54, 83, 114, 118, 145, 168, 191, 198, 202, 230, 299, 312, 317, 321, 322, 329, 334, 336, 340, 413

Other publications: 410

Curriculum Vitae: Manfred T. Reetz

1943	Born in Hirschberg, Germany
1965	BA Washington University, St. Louis, USA
1967	MS 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
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, USA
1991-	Director at the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr
1993-2002	Managing Director of the Max-Planck-Institut für Kohlenforschung
1992-	Honorary Professor at Ruhr-Universität Bochum
1993-	Chairman of the 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 Deutsche Akademie der Naturforscher 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)
1980-2010	> 150 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-	Member of Advisory Board, *Topics in Organometallic Chemistry*
1998-	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 (Denkmünze, GDCh)
1999-	Member of Selection Committee, Alfried Krupp-Prize
1999-	Member of Selection Committee, Otto Bayer-Prize (Bayer AG)
2000-	Member of Advisory Board, *Russian Journal of Organic Chemistry*
2000-	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-	Member of the Kuratorium der Alfried Krupp von Bohlen und Halbach-Stiftung

2003-	Member of the International Advisory Board, *QSAR & Combinatorial Science*
2005-	Member of the Editorial Advisory Board, *Bulletin of the Chemical Society of Japan*
2006-	Member of the Advisory Board, *Topics in Stereochemistry*
2006/2007	Member of the International Advisory Board of the Chemistry Department of Nagoya University (Japan)
2007-2011	Senator of the Chemistry Section, Deutsche Akademie der Naturforscher Leopoldina
2008-	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
Since 1980	Member of Advisory Committee of Numerous Scientific Conferences

Research in the Department of Synthetic Organic Chemistry

During the last three years the primary focus of research in the Reetz group was on methodology development in directed evolution of selective enzymes as catalysts in synthetic organic chemistry. The purpose was to make this Darwinian approach to asymmetric catalysis more efficient and therefore faster than in the past. Advanced gene mutagenesis methods and strategies were developed for the evolution of enhanced stereoselectivity, broader substrate scope (rate), higher thermostability and increased resistance to denaturing organic solvents. This involved the development of gene mutagenesis strategies characterized by high efficacy, improved molecular biological protocols, new approaches to high-throughput screening and selection as well as the design of bioinformatics-based and machine-learning techniques. Emphasis was also placed on 1) uncovering the reasons for increased efficacy, and 2) unveiling the source of enhanced stereoselectivity on a molecular level by means of mechanistic and theoretical studies.

Matthias Haenel, the only coal researcher in the Institute, retired in 2009. The External Member of the Institute, Walter Leitner (chair at TU Aachen), continued to run a small 2-3 person group here in Mülheim in the "Versuchsanlage", studying catalytic reactions in non-conventional solvents such as ionic liquids and supercritical CO_2. During the last three year evaluation period, research by the local Leitner group led to 24 publications.

The Director of the Department, Manfred T. Reetz, was originally scheduled to retire in 2008 at the age of 65, but received special permission from the President of the Max Planck Society to continue until 68 (extension of contract until 31 August 2011). Due to the Institute's plans regarding the successor and the concomitant extensive renovation of the respective floors in the high-rise laboratory building, the Reetz labs were closed in October 2010. Parallel to this development, Manfred Reetz accepted an offer from the University of Marburg to become the first Hans-Meerwein-Research-Professor starting 2011. The Marburg Chemistry Department will provide gene labs for about five coworkers as well as the general infrastructure, while the Max Planck Society has agreed to finance the research for five years following the formal termination of the Reetz-Directorship in August 2011. Thus, Manfred Reetz will head an external research group of the Max-Planck-Institut für Kohlenforschung, while also being a member of the Marburg faculty.

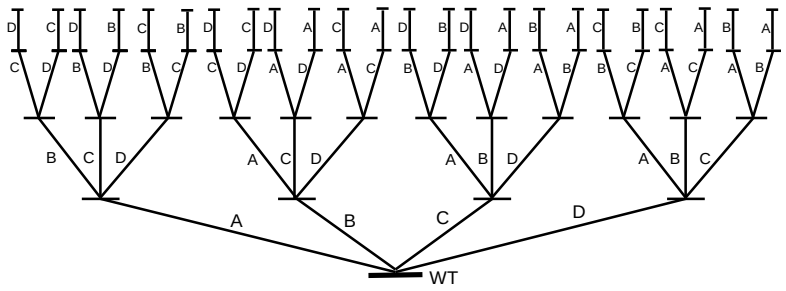
Due to the upcoming retirement of Manfred Reetz, new group leaders (assistant professors for Habilitation) were not recruited for the Department.

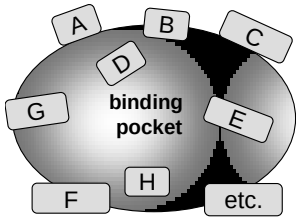
2.1.1 Research Area "Methodology Development in Directed Evolution" (M. T. Reetz)

Involved: J. P. Acevedo, M. Bocola, D. J. Bougioukou, J. D. Carballeira, J. Drone, L. Fernàndez, L. Gonzaga de Oliveira, Y. Gumulya, H. Höbenreich, F. Hollmann, N. Jiao, D. Kahakeaw, S. Kille, R. Lohmer, J. J.-P. Peyralans, J. Podtetenieff, S. Prasad, J. Sanchis, F. Schulz, M. Rusek, P. Soni, A. Taglieber, S. Wu, H. Zheng, F. E. Zilly

Objective: The goal was methodology development in the quest to make directed evolution more efficient and faster than the state of the art in 2007.

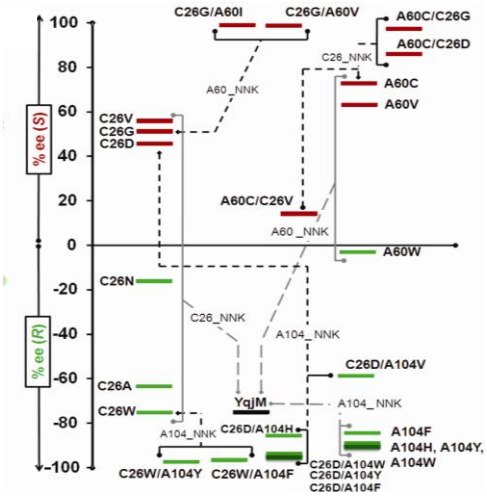
Some degree of catalyst improvement can always be expected from directed evolution, irrespective of the mutagenesis strategy or method, repeating rounds of error-prone PCR as a "shotgun method" being the most popular approach. However, especially in our group the focus of research has turned to methodology development in the quest to make directed evolution faster, more efficient and reliable. In the previous Report (2005-2007), we described initial results of what we termed Iterative Saturation Mutagenesis (ISM) as a means to generate high-quality mutant libraries, quality being defined in terms of the frequency of hits in a given mutant library and the degree of catalyst improvement, be it stereoselectivity, activity or thermostability. *ISM is a knowledge-driven approach to directed evolution which requires only small libraries and which has proven to be much more successful than originally anticipated.* Sites in an enzyme comprising one or more amino acid positions, labeled A, B, C, D, etc, are randomized by saturation mutagenesis, and the genes of the hits are then used as templates for randomization at the other sites. In the case of a 4-residue site, the scheme below pertains. It is not necessary to explore all pathways, but the appropriate choice of the sites is crucial. In the case of stereoselectivity and/or substrate acceptance, sites around the binding pocket are chosen (CASTing).

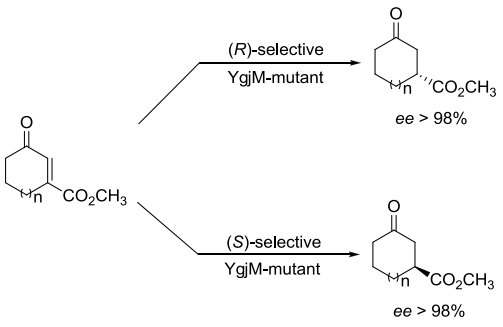




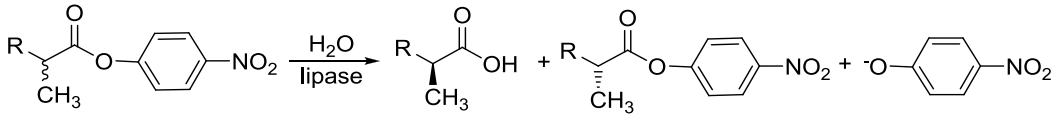
The first example of ISM in the embodiment of CASTing was described in the previous Report (2005-2007), in which the enantioselectivity of the epoxide hydrolase from *Aspergillus niger* (ANEH) as a catalyst in the hydrolytic kinetic resolution of a chiral epoxide was improved from E = 4.6 (WT) to E = 115, as compared to E = 11 using epPCR and screening the same number of transformants. This was the first indication that libraries resulting from ISM are "smart". During the last three years we have not only generalized this approach, the underlying reason for efficacy was also pinpointed: It is the absence of superfluous mutations coupled with the occurrence of cooperative epistatic effects operating between the point mutations within a site *and* between sets of mutations occurring at the sites A, B, C, D, etc. Cooperativity is the ideal form of epistasis in directed evolution because it means more than additive interactions. Moreover, we have shown in several studies that the utilization of reduced amino acid alphabets as ensured by the appropriate codon degeneracy reduces the amount of oversampling necessary for 95% library coverage drastically. For example, instead of using the normal NNK codon degeneracy encoding all 20 canonical amino acids, we have shown by statistical analysis (CASTER computer aid) that NDT codon degeneracy encoding only 12 amino acids (Phe, Leu, Ile, Val, Tyr, His, Asn, Asp, Cys, Arg, Ser and Gly) requires in the case of a 2-residue site the screening of only 430 transformants, while classically NNK calls for 3000! The quality of an NDT library matches or exceeds that of an NNK counterpart!

A recent application of ISM-based CASTing was the evolution of (*R*)- and (*S*)-selective mutants of the enoate reductase (YqjM) as catalysts in a model reaction involving the conjugate reduction of 3-methylcyclohexenone (scheme below, left), mutants that also catalyze the reduction of a wide variety of structurally different enones not at all accepted by WT YqjM, as for example illustrated on the right. *This shows once again that in directed evolution you can get more than what you evolved/screened for*.

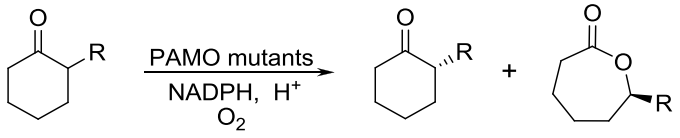




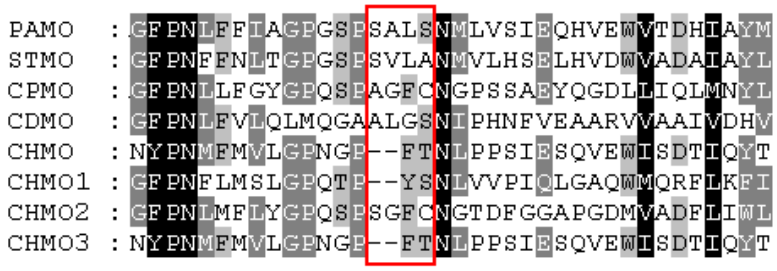
Perhaps the most impressive demonstration of the efficacy of ISM became apparent when we revisited our original system studied in 1995-2001 based on the lipase from *Pseudomonas aeruginosa* as a catalyst in the hydrolytic kinetic resolution of *rac*-2-methyldecanoic acid *p*-nitrophenyl ester. This is the most systematically studied enzyme in directed evolution. Among other attempts, epPCR at various mutation rates, DNA shuffling and non-systematic saturation mutagenesis, requiring the screening of 50,000 transformants, had resulted in a mutant with six point mutations, showing E = 51 compared to WT with E = 1.2. A theoretical analysis in cooperation with the Thiel group had predicted that only two of the six mutations are necessary, which was corroborated experimentally, a triumph of theory but also proving the inefficiency of such mutagenesis methods and strategies. With the new approach using a 3-site ISM scheme in which each site is composed of two residues and screening less than 10,000 mutants, a very active mutant showing E = 594 was rapidly evolved, characterized by only three point mutations. Here again, deconvolution studies uncovered dramatically strong cooperative effects. Superfluous mutations do not occur (in contrast to epPCR). The reason for enhanced activity and stereoselectivity was unveiled by extensive MD simulations.



In addition to the normal CASTing approach in which first sphere residues directly aligning the binding pocket are identified on the basis of the X-ray structure or homology model, second sphere residues can also be considered for saturation mutagenesis (extended CASTing), as shown in the evolution of active and stereoselective mutants of the Baeyer-Villiger-Monooxygenase PAMO. Oxidative kinetic resolution of the following substrates was found to occur with selectivity factors generally amounting to E > 100.



We also developed a *bioinformatics-based* approach to CASTing, by focusing on a loop region at the binding pocket of PAMO, but now aligning the respective sequences of eight different BV monooxygenases in order to identify conserved residues which were assigned as randomization sites. This information was utilized in designing greatly reduced amino alphabets which were subsequently used in saturation mutagenesis, leading to highly stereoselective oxidases.



***Further methodology development during the three year research period*:**

- ISM in the form of B-FIT was applied to an epoxide hydrolase by focusing on sites having high B-factors, resulting in a thermostabilization of 21°C.
- ISM was applied to an epoxide hydrolase as a catalyst for inducing *stereoconvergency* in the transformation of a racemic trans-1,2-disubstituted epoxide with formation of a single enantiomeric diol (99% *ee*).
- ISM was further generalized by evolving highly stereoselective mutants of the limonene epoxide hydrolase, showing broad substrate scope.
- The novel concept of saturation mutagenesis at a remote site which can be expected to induce *allosteric* effects with concomitant re-shaping of the binding pocket, therefore influencing substrate acceptance and stereoselectivity, was demonstrated for the first time using a Baeyer-Villiger Monooxygenase.
- A molecular biological method for saturation mutagenesis for difficult-to-amplify templates was developed based on the use of megaprimers.
- In collaboration with the Rabitz group (Princeton University), a *computational approach* was developed for identifying protein mutants with desired catalytic properties from minimal sampling of focused ISM libraries. The so-called Adaptive Substituent Reordering Algorithm (ASRA) was applied to the *Aspergillus niger* epoxide hydrolase, demonstrating notable predictive power regarding enantioselectivity. The algorithm reduces the screening effort, and therefore increases further the efficacy of ISM.
- A system for light-driven NADPH regeneration in monooxidases and reductases was developed.

Publications resulting from this research area: 85, 88, 90, 94, 101, 119, 161, 173, 232, 234, 238, 240, 241, 283, 305, 367, 384, 385, 386, 387, 388, 407, 419, 425, 426

External funding: Deutsche Forschungsgemeinschaft (Schwerpunkt 1170 “Gerichtete Evolution”); Fonds der Chemischen Industrie

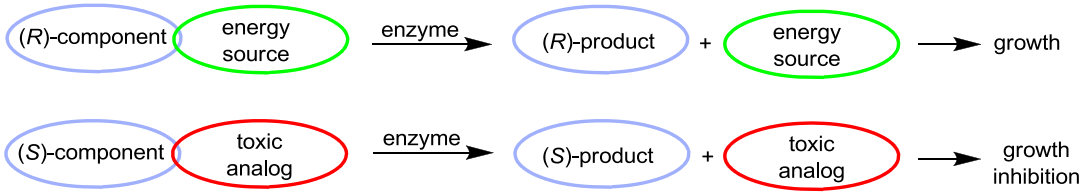
Cooperations: H. Rabitz (Princeton, USA)

2.1.2 Research Area "Methods for Enzyme Screening/Selection" (M. T. Reetz)

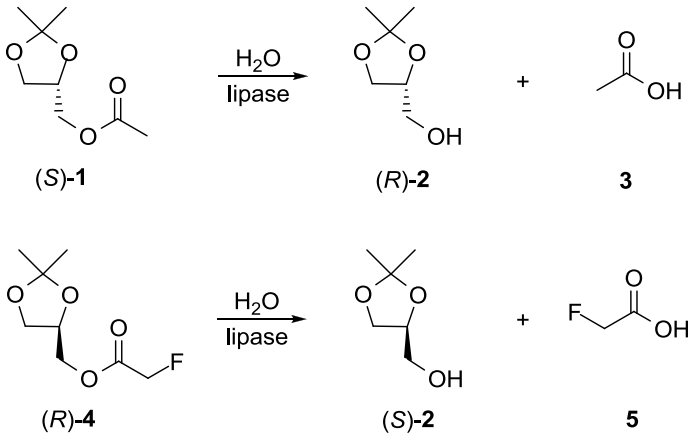
Involved: D. Bougioukou, L. Fernàndez, Y. Gumulya, H. Höbenreich, D. Kahakeaw, S. Kille, J. Sanchis, P. Soni, A. Taglieber, A. Vogel

Objective: The bottleneck of directed evolution is the screening/selection step, a problem that is particularly acute when evolving stereoselectivity. We therefore increased our efforts to develop high-throughput *ee*-screening assays. A conceptionally different goal was the development of the first selection system in which the host organism experiences a growth (survival) advantage because it harbors an enantioselective enzyme.

Results: The challenge of developing a selection system for the directed evolution of enantioselective enzymes was met by proposing the following concept:

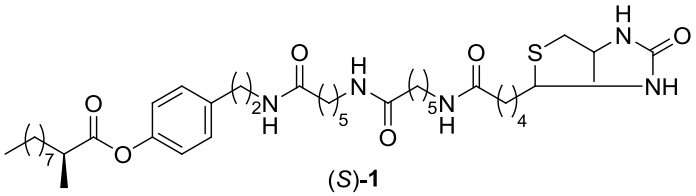


For proof-of-principle, the hydrolytic kinetic resolution of the pseudo-racemate (*S*)-**1**/(*R*)-**4** catalyzed by CALB lipase was chosen as the test reaction, generating either an energy source (**3**) for the chosen host organism (*Pichia pastoris*) or a poison (**5**). Following saturation mutagenesis, ideally only colonies harboring CALB mutants which favor substrate (*S*)-**1** should survive and therefore appear on the agar plates. Indeed, the anticipated effect was observed, > 80% expressing (*S*)-**1**-selective mutants.

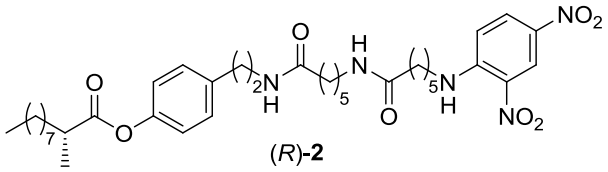


In another approach, the technique of fluorescence-activated cell sorting (FACS) was exploited for the first time in the quest to develop Super-High-Throughput *ee*-screening.

The basic idea was to label each of the two enantiomers conjugated to tyramide with a different fluorescent dye (green/red), FACS then allowing 10^8 cells and thus the number of enzyme clones to be evaluated on a single-cell basis!

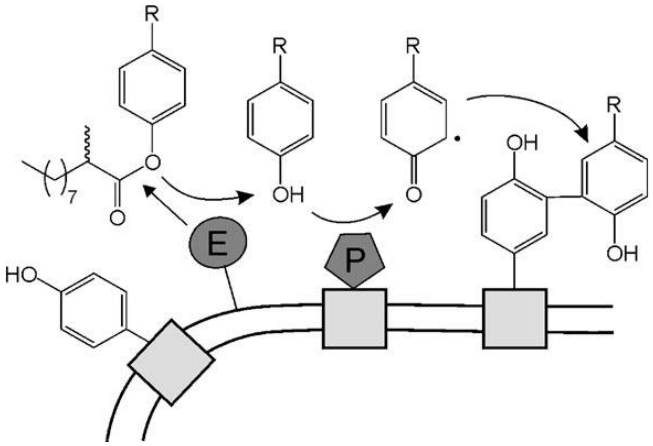


(*S*)-**1**

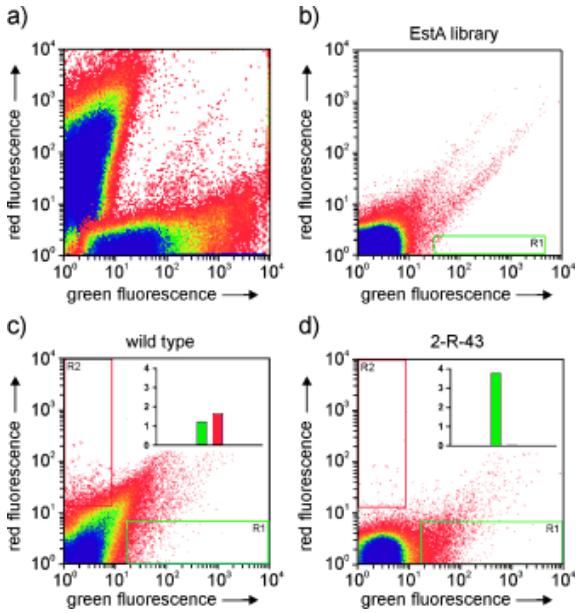


(*R*)-**2**

We chose the *Ps. aeruginosa* esterase-catalyzed hydrolytic kinetic resolution of a chiral ester, the challenge being the development of a method to trap the respective products on the surface of the bacterial cell. For this purpose, horse radish peroxidase-mediated radical formation was envisioned, which was designed to ensure the immediate covalent attachment of reaction products to the surface of the esterase-proficient bacterial cell:



In the case of the (*R*)-substrate, 2,4-dinitrophenolate labeling was detected by an Alexa Fluor 488-labeled antibody which mediates green fluorescence, whereas biotin deposition was detected using R-phycoerythrin conjugate (red fluorescence). The actual goal was to invert enantioselectivity (WT:E = 1.2 (*S*)). Indeed, this was achieved, the selectivity factor of the best mutant esterase amounting to E = 16 (*R*).



a) Overlay of flow-cytometry analyses of esterase-displaying cells that were incubated for 60 min with either *S* or *R* enantiomer of tyramide ester. **b**) EstA library sort. The green window indicates the sorting gate. **c**, **d**) FACS histogram of EstA wild-type; (**c**) and clone 2-R-43; (**d**) after 5 min incubation with a 1:1 mixture of both enantiomeric substrates and fluorescence staining. The inlet shows the percentage of cells within the respective green or red gate.

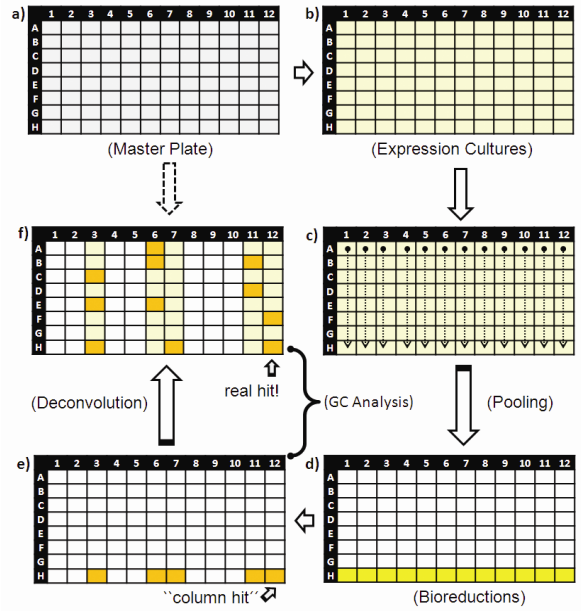
Further optimization was not strived for at this point, but it is obvious that the method could be used, for example, in simultaneous randomization at sites composed of 4-5 residues which would normally require the screening of 3 to 100 million transformants!

Rather than scanning larger portions of the (endless) protein sequence space by generating and screening by FACS or selecting large numbers of mutants (10^6-10^8) by appropriate systems, an alternative strategy is to strive for the opposite, namely to design strategies which generate small but highest-quality libraries (see previous Research Area), which can be screened by simple analytical assays. Most of our efforts are directed toward this goal, which in many cases has indeed been achieved, simply by generating small, but highest-quality libraries and then applying automated GC or HPLC. Nevertheless, we continued our efforts to design alternative medium- or high-throughput assays. One approach was the adaptation of multiplexing GC (or HPLC), an elegant technique which Oliver Trapp had first developed in the Institute in 2005. Before he left for the University of Heidelberg, a collaboration was initiated with the goal to assess within one day 3000 mutants of the epoxide hydrolase from *Aspergillus niger* as a catalyst in the hydrolytic kinetic resolution of a racemic epoxide. The envisioned system did in fact work because following optimization it was possible to rapidly separate all four compounds, (*R*)- and (*S*)-epoxide as well as (*R*)- and (*S*)-diol,

allowing for high-throughput determination of 3000 *ee*-values (mutants). Further optimization of the multiplexed system with respect to increasing the stability of the column material is in progress.

Two other strategies for increasing the throughput of enzyme evaluation were implemented. Whenever possible, it is desirable to develop on-plate assays as pre-tests for activity determination. We accomplished this in the case of epoxide hydrolases, specifically by adapting Reymond's assay (adrenaline color test) with the development of a cell-based color assay for automated high-throughput activity screening. A second more general strategy is to utilize pooling. In the case of manipulating the stereoselectivity of the enoate reductase YqjM in the asymmetric reduction of 3-methylcyclohexenone, a step-wise GC-based pooling protocol was devised, which led to the reduction of the overall screening effort by more than 50%!

Pooling protocol:



Publications resulting from this research area: 6, 47, 89, 161, 384

External funding: Deutsche Forschungsgemeinschaft (Schwerpunkt 1170/"Gerichtete Evolution"); Fonds der Chemischen Industrie

Cooperations: K.-E. Jaeger (Düsseldorf / Jülich, DE); H. Kolmar (Darmstadt, DE); O. Trapp (Mülheim/Ruhr / Heidelberg, DE)

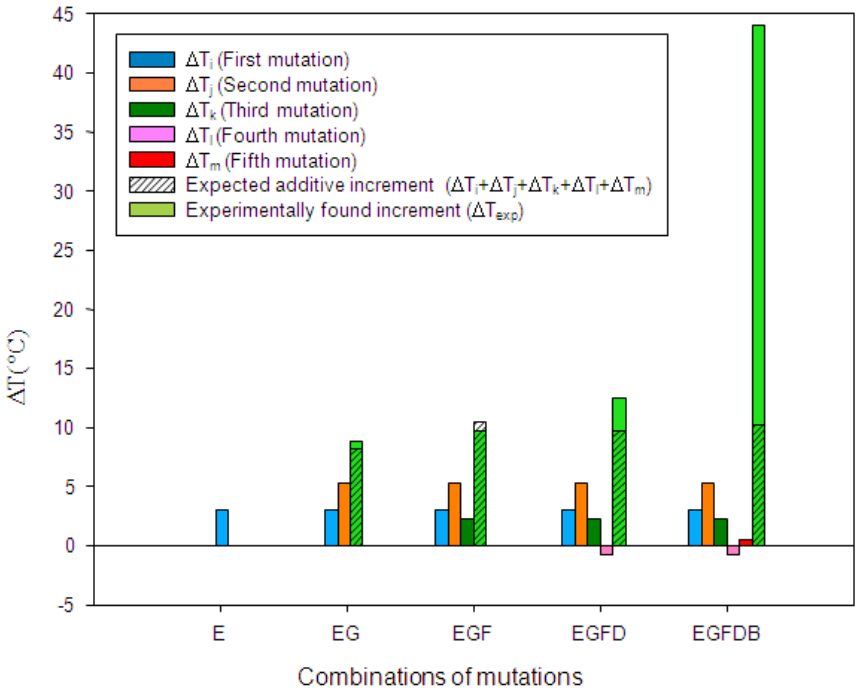
2.1.3 Research Area "Learning from Directed Evolution" (M. T. Reetz)

Involved: J. P. Acevedo, W. Augustyniak, D. J. Bougioukou, J. D. Carballeira, Y. Gumulya, D. Kahakeaw, S. Kille, R. Lohmer, S Prasad, J. Sanchis, P. Soni, A. Taglieber, L.-W. Wang, S. Wu, H. Zheng

Objective: 1) To uncover the reason for the observed efficacy of the ISM method; 2) to unveil the source of enhanced stereoselectivity or increased thermostability of evolved mutants on a molecular level.

Results: Considerable efforts were invested in the quest to understand why Iterative Saturation Mutagenesis (ISM) as a gene mutagenesis strategy in directed evolution provides superior results while requiring smaller libraries. It is more than an intellectual exercise, because such analyses point the way to achieving even greater efficacy. This research encompassed:

1) *Sequencing and characterizing as many improved enzymes in a given mutant library as possible, not just the very best hits*. This showed us that a) very different sequences lead to similarly improved functions, and that b) when attempting to improve two different properties such as activity and enantioselectivity, it is *not* optimal to select the very best hit for the subsequent cycle of ISM.
2) *Deconvoluting a given mutant characterized by x point mutations into all possible permutational combinations of single, double, triple, etc. mutants*. This allows epistatic interactions between point mutations and sets of mutations to be analyzed quantitatively in terms of $\Delta\Delta G^{\ddagger}$ values. We discovered that ISM is consistently accompanied by cooperative effects, i.e., the interactions are more than additive. In directed evolution this is the ideal form of epistasis. As an example, a *Bacillus* lipase mutant with five point mutations, evolved by ISM in five steps for increased thermostability (48°C → 93°C!), shows pronounced cooperativity, especially in the last evolutionary step of the ISM-sequence E → EG → EGF → EGFD → EGFDB (involving sites B, D, E, F and G):



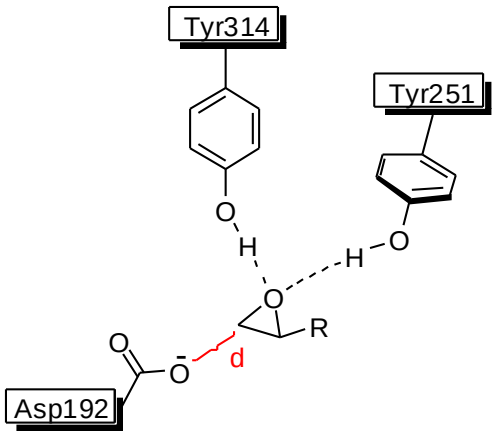
3) *Constructing fitness landscapes featuring all pathways leading from WT to a given evolved mutant, as in the case of the enantioselective Aspergillus niger epoxide hydrolase*. In the five-step process it means visualizing by experimental $\Delta\Delta G^{\ddagger}$ increments all 5! = 120 pathways. We found that not just the originally discovered pathway leads to the specific mutant, but about 50% of the others do as well showing no local minima (favored trajectories). In the case of disfavored trajectories characterized by local minima, backtracking provides a means to escape local minima. Such fitness landscapes allow for new mutants, but not for new mutations as in an actual ISM scheme. Construction of a corresponding fitness landscape of a complete ISM scheme is in progress, and preliminary results show that here too many pathways lead to improved enzymes.

The second type of lesson to be learned from directed evolution, namely uncovering the source of enhanced stereoselectivity, activity or thermostability, is important in its own right, and it also extends our knowledge of how enzymes function. One project concerned stereoselective Baeyer-Villiger-Monooxygenases, in collaboration with the Thiel group using a QM/MM approach (unpublished). In other cases our group utilized molecular dynamics (MD) simulations and induced docking experiments as well as algorithms allowing for the construction of covariance maps as indicators of correlated versus anti-correlated domain motions in enzymes.

An example concerns the mechanistic and structural study of a highly stereoselective mutant of the *Aspergillus niger* epoxide hydrolase, LW202, as a catalyst in the hydrolytic kinetic resolution of a chiral epoxide (E = 115 versus E = 4.6 of WT). The mutant LW202 had previously been obtained in five ISM steps. The mechanistic study for uncovering the source of enantioselectivity at each evolutionary stage included:

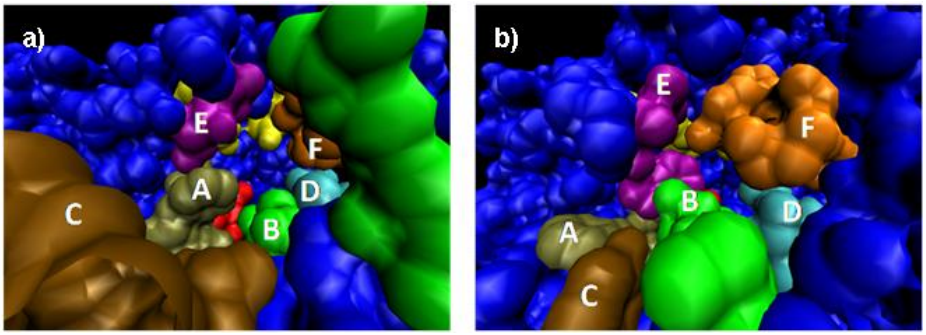
- Enzyme kinetics
- Inhibition experiments
- MD simulations and induced fit docking experiments
- X-ray structural analysis of the evolved enantioselective mutant (for the first time in directed evolution!)

The mechanism involves proper positioning of the epoxide and activation by Tyr314/Tyr251 in the binding pocket, followed by rate- and stereochemistry-determining nucleophilic attack of Asp192 with formation of a short-lived enzyme-ester intermediate which is rapidly hydrolyzed. The MD simulations showed that in the case of the best mutant the preferred (*S*)-substrate is perfectly aligned so that tyrosine activation is maintained and the distance, d, between the Asp-O-atom and the C-atom of the epoxide amounts to about 3.8 Å. In contrast, in the case of the disfavored (*R*)-enantiomer, d = 5.4 Å, too long for smooth nucleophilic attack to be possible. In the WT, the two respective d-values are similar (≈ 4 Å), but as the evolutionary process proceeds, the d_R value increases, until in the final mutant the reaction of this enantiomer is completely shut down, as in an ideal kinetic resolution. This prediction proved to be in line with the results of kinetics and inhibition experiments.



Mutant	d_R	d_S	Δd_{R-S}	*E* (expl.)
WT	4.3	3.5	0.8	4.6
LW081	4.8	4.0	0.8	14
LW086	4.9	4.0	0.9	21
LW123	5.1	4.0	1.1	24
LW44	5.1	3.9	1.3	35
LW202	5.4	3.8	1.6	115

The comparison of the crystal structures of WT and best mutant likewise proved to be eye-opening. Whereas the secondary and tertiary structures are essentially identical, the shape of the respective tunnel-like binding pockets are dramatically different as illustrated below (left: X-ray close-up of WT binding pocket; right: X-ray close-up of binding pocket of best mutant). Docking the (*R*)- and (*S*)-substrate into the respective binding pockets unambiguously shed light on the source of enhanced enantioselectivity, fully in line with the results of kinetics, inhibition experiments and MD simulations: In the best mutant it is impossible to position the disfavored (*R*)-substrate so that Tyr-activation and close distance d are both maintained.



Finally, in the directed evolution of the Baeyer-Villiger Monooxygenase PAMO, saturation mutagenesis at a remote site induced an allosteric effect leading to high activity and stereoselectivity. This was studied by MD simulations and covariance maps which revealed correlated and anti-correlated motions within the enzyme. This proved that the dynamics of the protein is essential for catalysis.

Publications resulting from this research area: 90, 93, 161, 235, 238, 239, 241, 386, 419, 425

External funding: Deutsche Forschungsgemeinschaft (Schwerpunkt 1170 “Gerichtete Evolution”); Fonds der Chemischen Industrie; EU Marie-Curie-Project

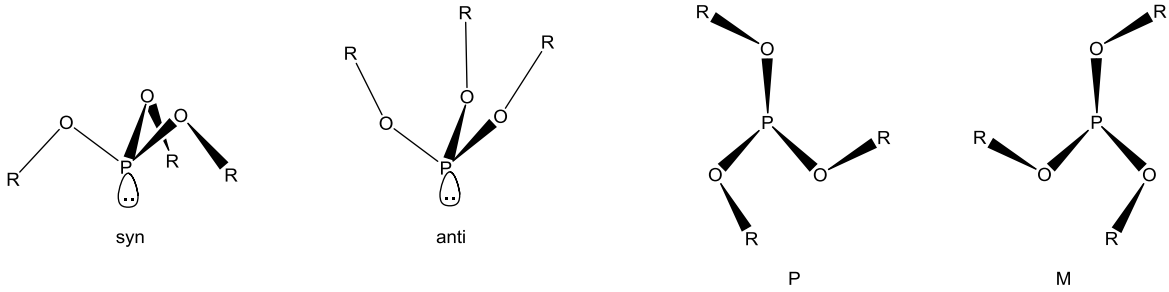
Cooperations: M. Arand (Zurich, CH); A. Archelas (Marseille, FR); M. Bocola (Regensburg, DE); S. L. Mowbray (Uppsala, SE); W. Thiel (Mülheim/Ruhr, DE)

2.1.4 Research Area "Transition Metal Catalysis" (M. T. Reetz)

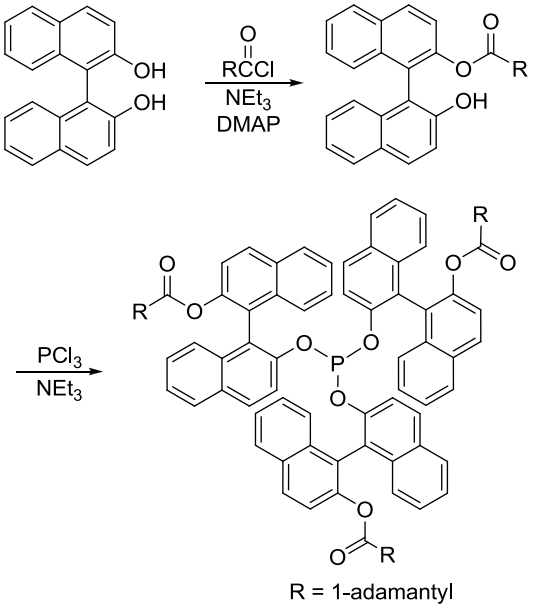
Involved: F. Berkermann, H. Guo, J.-A. Ma, G. Mehler, P. Wedemann, F. Hollmann, A. Taglieber, R. J. G. Mondière

Objectives: 1) Synthesis and application of the first helical phosphite; 2) Preparation of aqueous iridium oxide colloids/deposition on electrodes; 3) Design and preparation of a synthetic metalloenzyme.

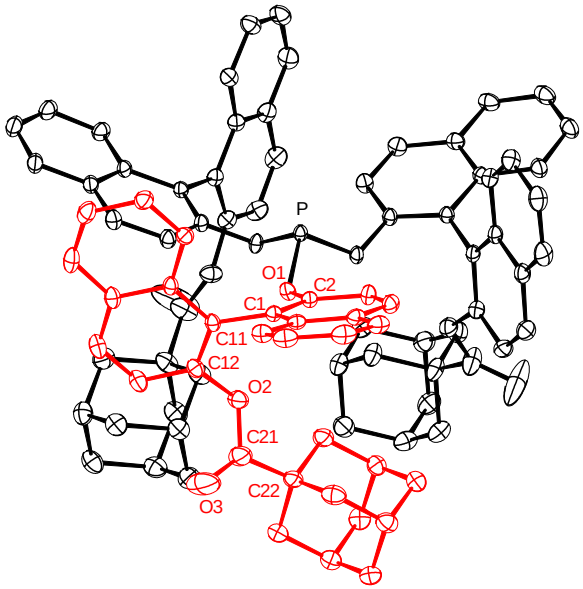
Results: Whereas a multitude of ligands for asymmetric transition metal catalysis based on central, axial and planar chirality have been described, very little is known regarding helical ligands. We have synthesized the first configurationally stable helical phosphite $P(OR)_3$. Such compounds can in principle exist as *syn* or *anti* conformers, and when helicity is involved either in the P or M forms:

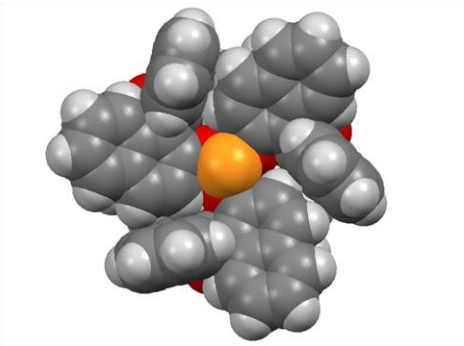


The challenge is to "lock in" a given conformer coding for a defined helicity, so that stereoisomerizing P ⇌ M interconversion cannot occur on energetic grounds. We devised a simple two-step sequence starting either from (*R*)- or (*S*)-BINOL:

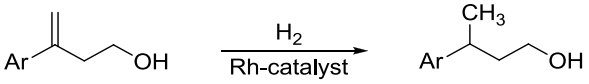


As X-ray analyses proved, (*R*)-BINOL leads to the (*R*,*R*,*R*)- compound with P-helicity, while (*S*)-BINOL provides the (*S*,*S*,*S*)-ligand characterized by M-helicity. The ligands are so sterically locked in that in each case the helicity does not interconvert, e.g., (*R*,*R*,*R*)/P $\rightleftharpoons$ (*R*,*R*,*R*)/M was not detected in the solid state (X-ray) nor in solution (NMR, CD). Only the *syn*-form was observed, as for example the crystal structure of the *syn*-(*S*,*S*,*S*)/M ligand shows:





The ligand was tested in Rh-catalyzed asymmetric hydrogenation of 14 different homo-allylic alcohols (which are known to be "difficult" substrates), leading to *ee* = 88-98%.



In a different project, we considered the 150 year old publication by Berzelius describing the NaOH-induced hydrolysis of iridium chloride with formation of blue solutions, presumably stable colloids even though no stabilizer had been added which are normally required today. We optimized the procedure, starting from either $IrCl_3$ or $IrCl_4$:

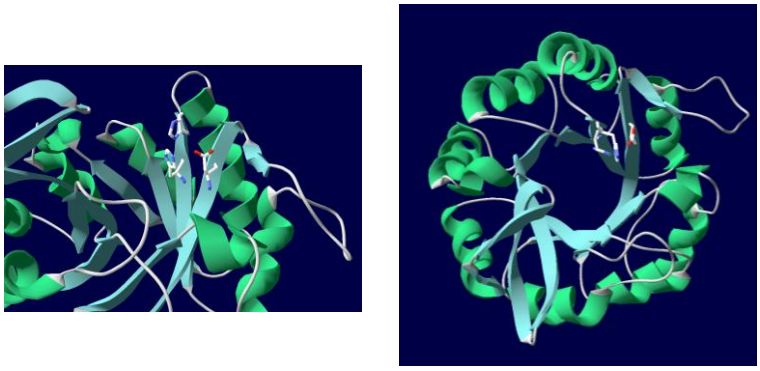
$$IrCl_x + NaOH \rightarrow Ir_yO_z \text{ (blue colloidal aqueous solution)}$$

The colloids were characterized by TEM (≈ 1 nm particles) and by other methods. Why such iridium-oxide nanoparticles in the absence of stabilizers are stable for months (electrostatic effects), and other transition metal oxides such as those of Pt, Pd, Os, are not, is not clear to us. We did, however, succeed in polymerizing other transition metals

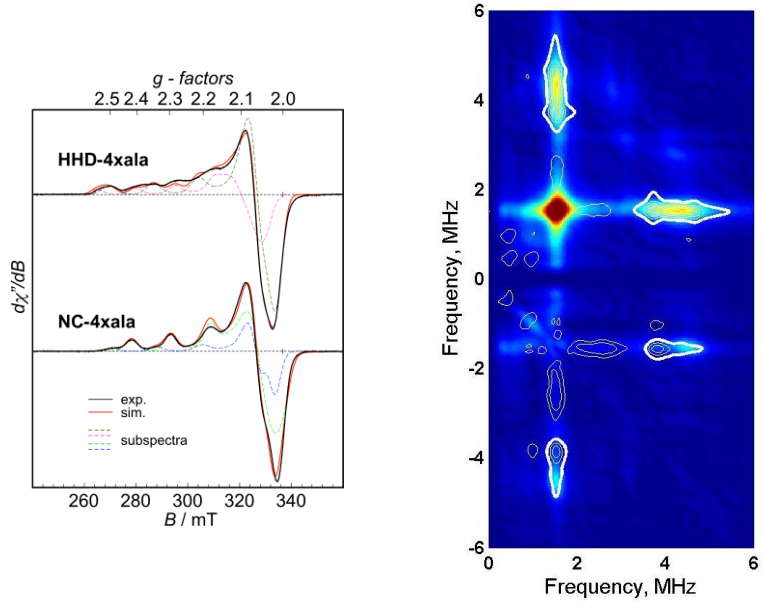
into the iridium oxide matrix with formation of mixed metal oxide colloids, which proved to be stable under the basic aqueous conditions.

We have used these materials in order to coat metal surfaces such as Pt-electrodes, which indeed show interesting electrocatalytic properties. They may be of interest in water splitting reactions or in classical electrochemical chlorine production. In the latter case, the state of the art describes Pt electrodes as being protected by a dip-coating process involving suspensions of bulk iridium oxide followed by heat treatment at high temperatures (750°C), a procedure that is repeated about 17 times for optimal effects in chlorine production. In sharp contrast, using the aqueous colloidal solutions, our dip-coating process needs to be performed only 3-4 times, and at much lower temperatures (≈ 275°C), leading to comparable stability/activity of the coated electrodes.

In a final project, transition metal catalysis was combined with protein science. In 2001/2002 we proposed the concept of directed evolution of hybrid catalysts, in which a synthetic ligand/transition metal entity is anchored covalently or non-covalently to a robust protein host, which as such delivers a single catalyst as previously sporadically described in the literature (e.g., Whitesides' system based on a biotinylated Rh-diphosphine complex in avidin as host). The novel part of our concept was the proposal that directed evolution can be performed on the protein host in general, *thereby providing a molecular biological tool for tuning a synthetic transition metal catalyst*. In the last Report (2005-2007), we described proof-of-principle of this Darwinian approach to asymmetric catalysis using the Whitesides' system, three ISM steps raising the *ee* of a Rh-catalyzed hydrogenation stepwise from 23% (WT) to 65% (final mutant). However, practical problems prevented us from exploring sufficiently large libraries. Recently we proposed an alternative approach, namely to utilize appropriate amino acids in a robust protein host for complexing transition metals directly (synthetic metalloenzyme). We chose a particularly stable enzyme, tHisF, as a robust host protein, which has a TIM-barrel eightfold α/β structure with a narrow "bottom" and a wide "top". At the top we applied site-specific mutagenesis with the creation of a potential transition metal binding site composed of His/His/Asp, the amino acids being "placed" geometrically in a correct (computed) manner for subsequent Cu(II)-complexation.



The design of this robust artificial metalloenzyme proved to be correct, because the mutant tHisF does indeed "soak up" Cu(II) specifically at the desired metal binding motif as proven by standard EPR measurements and sophisticated HYSCORE EPR experiments. The complex catalyzes the Diels-Alder reaction of a model compound (*ee* = 46%). This opens the door for directed evolution, for other Cu(II)-catalyzed reactions and for the complexation of other transition metals such as Fe, Mn or Co.



Publications resulting from this research area: 84, 86, 87, 91, 92, 233, 236, 237, 377

External funding: Fonds der Chemischen Industrie

Cooperations: E. Bill, R. Goddard, R. Mynott, E. J. Reijerse, W. Thiel (Mülheim/Ruhr, DE); R. Sterner (Regensburg, DE)

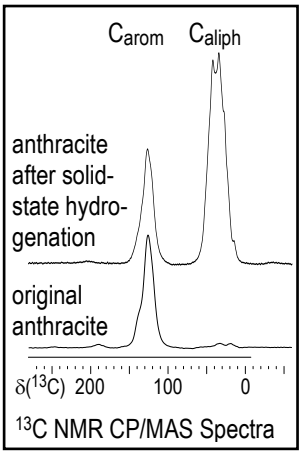
2.1.5 Research Area "Solid-State Hydrogenation / Hydrogenolysis of Coals with Gaseous Catalysts" (M. W. Haenel)

Involved: X. Li, U.-B. Richter, A. Rufińska

Objective: In view of depleting petroleum reserves, the importance of the more abundant coal as a source for fuels and chemicals will inevitably increase. Generally, two fundamental technologies to liquefy coal are available, the *Bergius* direct liquefaction with hydrogen and the indirect liquefaction via coal gasification and *Fischer-Tropsch*-Synthesis. The direct liquefaction is an extremely complex hydrocracking process to convert macromolecular solid insoluble coal with hydrogen under high pressures into liquids at 450°C in the presence of a solvent and a solid low-cost catalyst, commonly iron oxides and sulfides. Only low-rank coals (lignites, brown coals, subbituminous and high-volatile bituminous coals) can be liquefied, whereas high-rank coals (rank from medium-volatile to low-volatile bituminous coals and anthracites) are not reactive enough for such hydrocracking processes. For the bond breaking and hydrogen transfer to the carbon radicals the solvent containing polycyclic aromatic hydrocarbons and their partly hydrogenated counterparts plays major roles which includes solvent-mediated hydrogenolysis of strong C_{aryl}–C_{alkyl} bonds, hydrogen donation and hydrogen shuttling. On the other hand, the function of the catalyst is very limited. A solid (heterogeneous) catalyst cannot penetrate the macromolecular network structure of coal. Only after coal particles have been disintegrated and coal fragments begin to be solubilized can the catalyst develop activity to promote directly the further breakdown into liquids. Molecularly dissolved catalysts have the advantage that they can be imbibed by coal together with solvents, which is connected with the phenomenon of swelling. However, attempts to use molecularly dissolved (homogeneous) transition metal catalysts for coal liquefaction have failed, presumably because such catalysts are poisoned by sulfur and nitrogen constituents in coal and decomposed under the harsh reaction conditions.

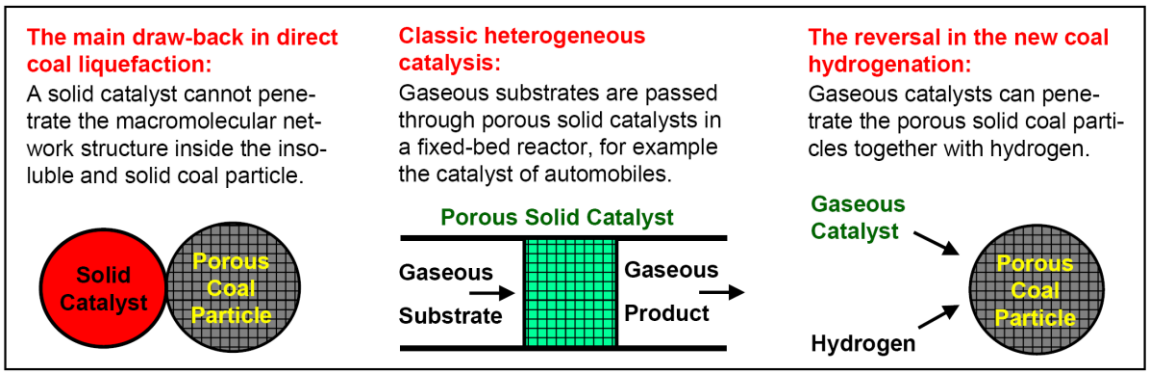
On the other hand, we previously have studied boranes and iodine as non-metallic homogeneous catalysts and have found a first case of an extensive hydrogenation/hydrogenolysis of high-rank coals. For instance, in the presence of the catalyst boron triiodide low-volatile bituminous (lvb) coals (Ess- and Magerkohle) and even anthracite as slurries in toluene reacted at 350°C under 25 MPa hydrogen to give solid products which were highly aliphatic (C_{aliph}**:**C_{arom} = 60**:**40, solid-state ^{13}C NMR spectra) as compared to the original coals (C_{aliph}**:**C_{arom} = <11**:**>89). Studies on model

compounds showed that the catalytic reaction cause the hydrogenation of polycyclic aromatic hydrocarbons into partly hydrogenated and perhydro-counterparts as well as hydrogenolysis (hydrogen-induced cleavage) of carbon-carbon single bonds. As a result of the increased aliphatic structure the hydrogenated products of high-rank coals could subsequently be liquefied by a conventional *Bergius* hydrocracking process in hydrogen donor solvents. Thus, in principle, direct liquefaction with hydrogen is applicable also to high-rank bituminous coals, which so far can be processed only by combustion or gasification.



^{13}C NMR CP/MAS Spectra

Since the iodoboranes and molecular iodine used as catalysts vaporize at the reaction temperature at 350°C, even the solvent-free solid-state hydrogenation of high-rank coals with gaseous catalysts became possible. When the powders (particles <0,08 mm) of the lvb coal (Magerkohle or anthracite) were agitated by a mechanical stirrer under 25 MPa hydrogen at 350°C in the presence of BI_3 (b.p. 210°C), an even higher extent of hydrogenation and hydrogenolysis was observed than in the reactions of the coals suspended in toluene. The ratio C_{aliph}**:**C_{arom} of the solid main products, which were formed in addition to some liquids and gas (C_1–C_4), increased up to 74**:**26 from 11**:**89 in the original Magerkohle or up to 70**:**30 from < 5**:**> 95 in the original anthracite, respectively (see the ^{13}C CP/MAS NMR solid state spectra). In the classic heterogeneous catalysis gaseous substrates are converted into products by being passed through porous solid catalysts in a fixed bed reactor, for instance the exhaust fumes in the catalyst of automobiles. The reversal is applied in our new coal hydrogenation, where a gaseous catalyst such as BI_3 penetrates, together with hydrogen, coal which is a porous solid substrate (see the Scheme). The iodoborane catalysts can be used also for hydrogenating and hydrocracking the heavy bottoms of crude petroleum, such as used for the asphalt on roads.



Results: In the period under review the solid-state hydrogenation/hydrogenolysis of lvb coal (Magerkohle) and anthracite was investigated mainly in dependence on the constitution of the gaseous catalyst. The catalyst activity of the boron trihalides, when measured by the ratio (C_{aliph}**:**C_{arom}) of the solid main product from the reaction of anthracite (<5**:**>95), varied as follows: BI_3 (65**:**35) > BBr_3 (40**:**60) > BCl_3 (21**:**79) ≈ BF_3 (23**:**77). Whereas in previous reactions, when toluene was used as the solvent, titanium tetrahalides were found to increase the activity of borane and iodine catalysts, the addition of $TiCl_4$ (b.p. 136°C) strongly decreased the activity of BI_3 for the solid-state hydrogenation of anthracite. As a possible explanation one can discuss the halogen exchange between BI_3 and $TiCl_4$ and the reduction of Ti(IV) into Ti(III) or Ti(II) halides (b.p. > 600°C) which cannot act as catalytic species in the gas phase anymore. This observation prompted us to focus on $AlCl_3$ (b.p. 183°C) which is volatile and resistant against reduction. In the case of the lvb coal (Magerkohle) the catalyst consisting of a 1**:**2 mixture of BI_3 and $AlCl_3$ resulted in a very similar extensive solid-state hydrogenation forming a bitumen-like product (C_{aliph}**:**C_{arom} = 69**:**31) as it was obtained with the equimolar amount of pure BI_3, i.e. two third of the BI_3 could be replaced by the readily available and much cheaper $AlCl_3$. Since we previously have found that iodoboranes remove oxygen containing functional groups in coals by stoichiometric reactions and as a result are consumed by forming borates and at the end presumably B_2O_3, the observed effect might mean that $AlCl_3$ preferably reacts with the oxygen bound in coal and consequently prevents BI_3 from being irreversibly consumed. This would be in line with the considerably higher heat of formation of Al_2O_3 than that of B_2O_3. On the other hand, in the solid-state hydrogenation of anthracite the mixture of BI_3 and $AlCl_3$ turned out to be catalytically much less active than pure BI_3, which in this case might go back to differences in the coal structure: the much larger polycyclic aromatics in the anthracite compared to those in the lvb coal (Magerkohle) might be more sensitive to $AlCl_3$-catalyzed condensations of aromatics under elimination of H_2 (Scholl reaction), which then would counteract the BI_3-catalyzed hydrogenation/hydrogenolysis. No matter how, the observed effects of $AlCl_3$ deserves further attention in the development of gaseous catalysts for the solid-state hydrogenation of coal.

Publications resulting from this research area: 42, 43, 187

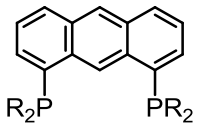
External funding: none

Cooperations: R. Mynott (Mülheim/Ruhr, DE)

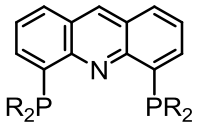
2.1.6 Research Area "Development of Thermostable Homogeneous Catalysts" (M. W. Haenel)

Involved: E. Wöstefeld

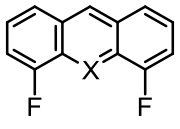
Objective: Thermally robust homogeneous catalysts have 3 major advantages: 1) catalytic conversion of less reactive substrates, for which the kinetics require high temperatures; 2) extension of homogeneous catalysis to endothermic processes, for which the thermodynamics require high temperatures; 3) facile catalyst separation by distillation of substrates and products. Our concept for designing such catalytically active metal complexes uses robust aromatic ligand frameworks and strong ligand-to-metal bonding by tridentate coordination. Previously we have introduced the ligands anthraphos **1** and acriphos **2** which are accessible in high yields from 1,8-difluoroanthracene **3** and 4,5-difluoroacridine **4** by nucleophilic substitution with alkali metal phosphides.



1: R = Ph, Cy, *t*Bu, *i*Pr

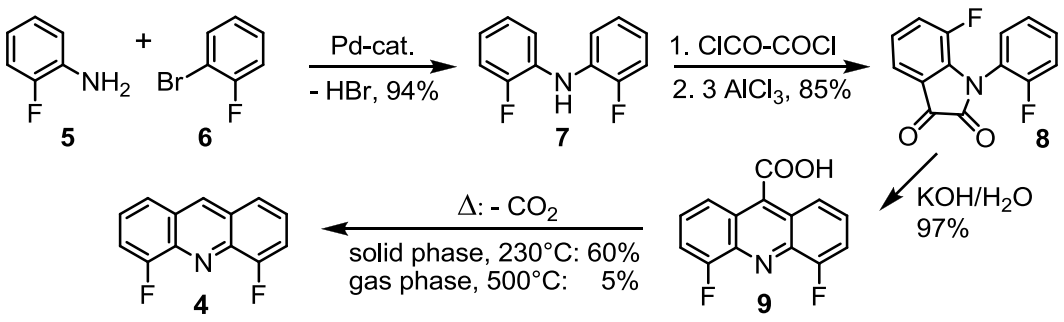


2: R = Ph

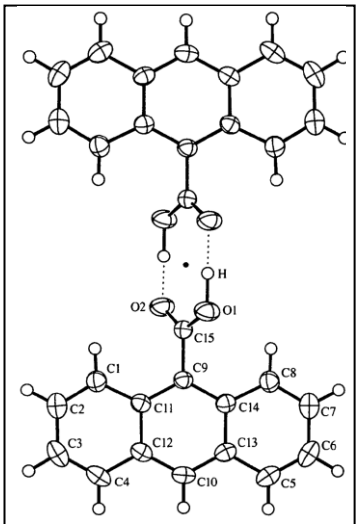


3: X = CH
4: X = N

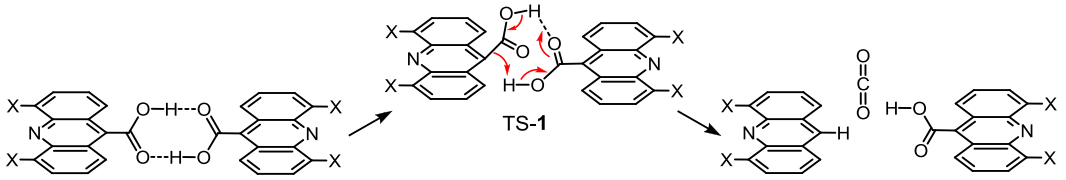
Whereas 1,8-difluoroanthracene **3** could be prepared by an efficient three-step synthesis from commercial 1,8-dichloro-9,10-anthraquinone, our previous seven-step synthesis of 4,5-difluoroacridine **4** was laborious and not very efficient in one step. By using modern Pd-catalyzed C–N coupling for an old synthetic route to acridines (M. S. Newman, 1961), we could elaborate a straightforward new synthesis of **4,** starting from cheap commercially available chemicals and having yields > 85% in the first three steps. However, the moderate yield in the decarboxylation of the aromatic carboxylic acid **9** to **4**, prompted us to look for improvement. This was found by an organocatalytic approach.



Results: The decarboxylation of 4,5-difluoroacridine-9-carboxylic acid **9** by heating the solid compound for 30 min to 230°C (in analogy to the procedure described in 1961 by M. S. Newman for the corresponding 4,5-dimethyl compound) yielded 4,5-difluoroacridine only in moderate yields of around 60%. We tried to improve the reaction by vacuum flash pyrolysis, but the carboxylic acid **9** turned out to be stable in the gas phase even at T > 500°C. We interpreted the result that apparently the pyrolysis proceeds preferably in the condensed phase from the hydrogen-bonded dimers **10**/**11** (compare e.g. the X-ray structure of anthracene-9-carboxylic acid) whereby an appropriate transition state might be formed enabling the elimination of CO_2 and the transfer of a hydrogen atom to the acridine C-9 carbon atom. The formation of a cyclic transition state TS-**1** can be envisaged when one of the two hydrogen bonds of the



X-ray structure of anthracene-9-carboxylic acid (L. J. Fitzgerald *et al*., *Acta Cryst*., **C53**, 71-73(1997)).

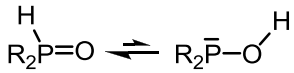


dimer **10**: X = H
dimer **11**: X = F

12: X = H
4: X = F

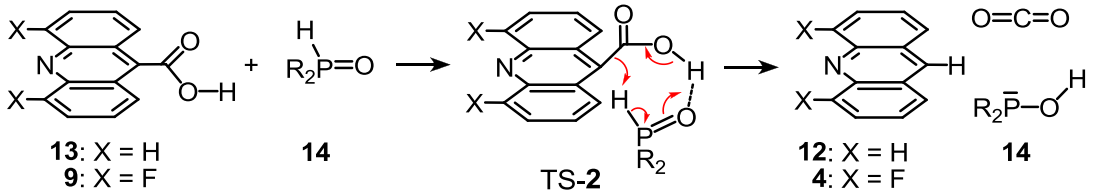
13: X = H
9: X = F

dimers **10**/**11** is opened and some minor geometrical deformations and translations are made. After the thermal decarboxylation has proceeded to 50% conversion, the preformed hydrogen bonded dimers in solid **10**/**11** are depleted which might explain the moderate yield obtained in the last step of our synthesis of **4**. Since also the catalysis with copper recommended in the literature did not work in the present case, we decided to look for organic molecules which can take the role of the second carboxylic acid in a hydrogen bonded structure and are suitable for the formation of a transition state in the decarboxylation. The compounds we considered to be especially promising were diorganyl phosphine oxides **14a**/**b** and phosphorous acid esters (diorganyl phosphites) **14c**/**d** which in their dominating tautomeric form all bear a neighboring hydrogen and double-bonded oxygen atom on the phosphorus centers. It was our hope that they would form hydrogen-bonded intermediates with the acridine-9-carboxylic acids **9** and **13** from which a transition state



14a: R = Ph
14b: R = *i*-Pr
14c: R = OEt
14d: R = OPh

like TS-**2** could lead to the decomposition into acridines, CO_2 and the phosphorus compounds **14** in the hydroxy-tautomeric form.

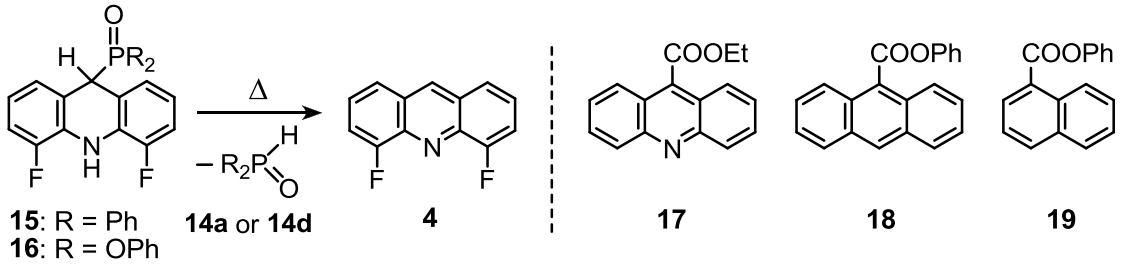


Indeed, when acridine-9-carboxlic acid **13** in mesitylene was heated for 12 h at 170°C in the presence of 22 mol% diphenylphosphine oxide **14a**, acridine **12** was formed and isolated by chromatography (for removing the solvent and **14a**) in 71% yield. In contrast, no acridine **12** was obtained in the absence of **14a**. From the corresponding reaction of 4,5-difluoroacridine-9-carboxylic acid **9** with **14a** (22 mol%) in mesitylene 4,5-difluoroacridine **4** was isolated in 37% yield, but in this case also the compound **15** was formed apparently by 1,4-addition of **14a** on **4** (previously we had already observed that diphenyl phosphine (Ph_2PH) undergoes 1,4-addtion to **4**). This addition reaction of **14a**, which consumes the organic catalyst, was one of the reasons to change to phosphorous acid esters which are high-boiling liquids and can be used in excess as solvent, but are also easy to remove by hydrolysis into phosphorous acid, alcohol or phenol and subsequent usual aqueous work-up implying extraction with an aqueous base.

Diethyl phosphite **14c** converted acridine-9-carboxlic acid **13** very fast into the ethyl ester **17**. On the other hand, the carboxylic acid **13** was nearly quantitatively decarboxylated into acridine **12** when it was heated (160°C, 6 h) with diphenyl phosphite **14d** in excess. Remarkably, the similar result was also obtained by using just 20 mol% of **14d** without any further solvent. The reaction of 4,5-difluoroacridine-9-carboxylic acid **9** with **14d** in excess yielded crystals of the decarboxylated adduct **16** in 84%. Since the adducts **15** and **16** can thermally be cleaved at $T > 200$°C, an improvement for the conversion of **9** into 4,5-difluoroacridine **4** compared to the direct thermal decarboxylation is available. However, anthracene-9-carboxylic acid and naphthalene-1-carboxylic acid did not decarboxylate on heating in **14d**, but formed the phenyl esters **18** and **19**.

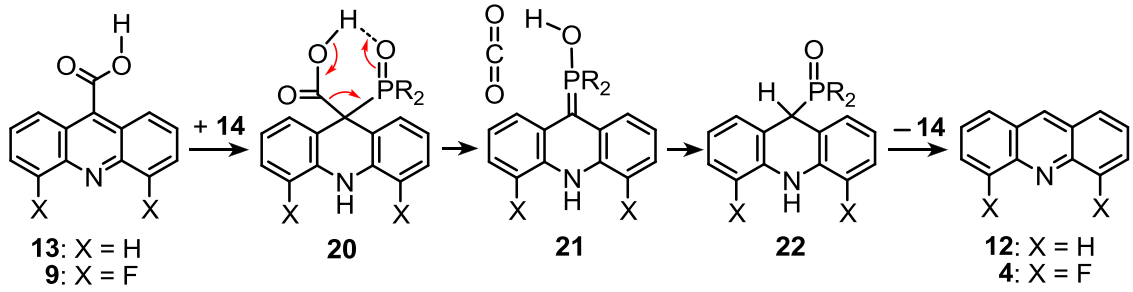
Preliminary experiments with diisopropylphosphine oxide **14b** showed that the decarboxylation of acridine-9-carboxlic acid **13** starts already around 130°C and in this

case also the formation of the adduct of the phosphorus compound to acridine **12** was observed. Hence it seems to be promising to investigate in more detail the influence which the electronic and steric properties of the substituents in diorganylphosphine oxides and diorganyl phosphites have on the catalytic reactivity.



15: R = Ph
16: R = OPh
14a or **14d**
4
17
18
19

Knowing the reversible formation of the adducts between the phosphorus reagents **14** and acridines, one can now in retrospect formulate a reasonable mechanism which replaces our original hypothesis of a transition state like TS-**2** and provides better explanations of all experimental facts. According to this proposal 1,4-addition of the phosphorus reagent on the acridine-9-carboxylic acids **13**/**9** leads to the adducts **20**, an electron rearrangement in the hydrogen-bonded six-membered ring of **20** generates CO_2 and the hydroxyl-phosphorus ylide **21** which immediately rearrange in a 1,3-shift of the hydroxyl proton to the higher basic ylidic carbon atom to form the observed decarboxylated adducts **22**. On basis of this mechanism one would not expect that anthracene-9- and naphthalene-1-carboxylic acids are decarboxylated, but only N-heteroaromatic carboxylic acids which are structurally related to **13** and **9**.



13: X = H
9: X = F
20
21
22
12: X = H
4: X = F

Obviously our admittedly rather speculative and optimistic hypothesis of a transition state like TS-**2** turned out to be wrong, but nevertheless led to an organocatalytic solution of our initial synthetic problem. Beyond that, the phosphine oxides and phosphites used in this special application seem to be not suitable to provide a general method for the catalytic decarboxylation of aromatic carboxylic acids.

Publications resulting from this research area: none

External funding: none

Cooperations: none

2.1.7 Research Area "Synthesis of Nanocatalysts by Chemical Fluid Deposition and their Application in the Transformation of Biomass" (W. Leitner / N. Theyssen)

Involved: F. Qin, R. Weiss, K. Yan

Objective: The transformation of lignocellulosic biomass into fuels, fuel components or platform chemicals is a task of prime importance. Our contributions in this area started in the beginning of 2008 and are currently dedicated to the development of powerful nano-catalysts for dehydration and reduction processes of oxygen-rich monomeric derivatives of cellulose.

Results: Up to now we have synthesized around 150 nano-catalysts in a bottom up procedure using Chemical Fluid Deposition (CFD) as universal and highly controllable production method. Such deposition of homo- or bimetallic ensembles includes several steps starting with the dissolution of CpPd(allyl) and/or (COD)$PtMe_2$ in supercritical carbon dioxide. Due to the very low surface tension of the obtained solution, a uniform impregnation of the chosen SBA-15 – a prototypic mesoporous support – with the metal complex(es) can be expected. In situ addition of molecular hydrogen then causes a reductive dissociation of the ligands which results in aggregation of "naked metal atoms" to nanoparticles under the chosen conditions (Figure 1).

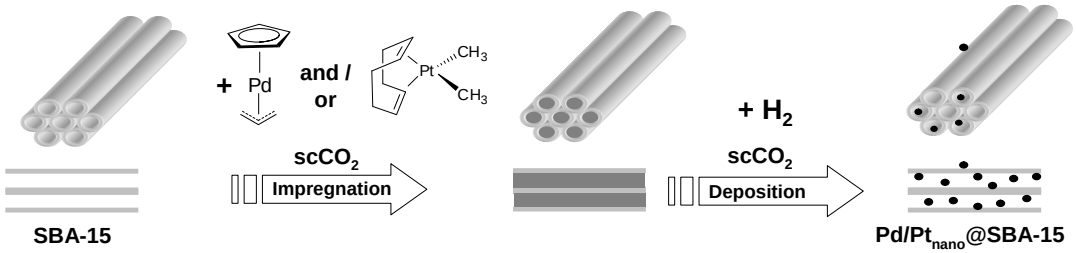
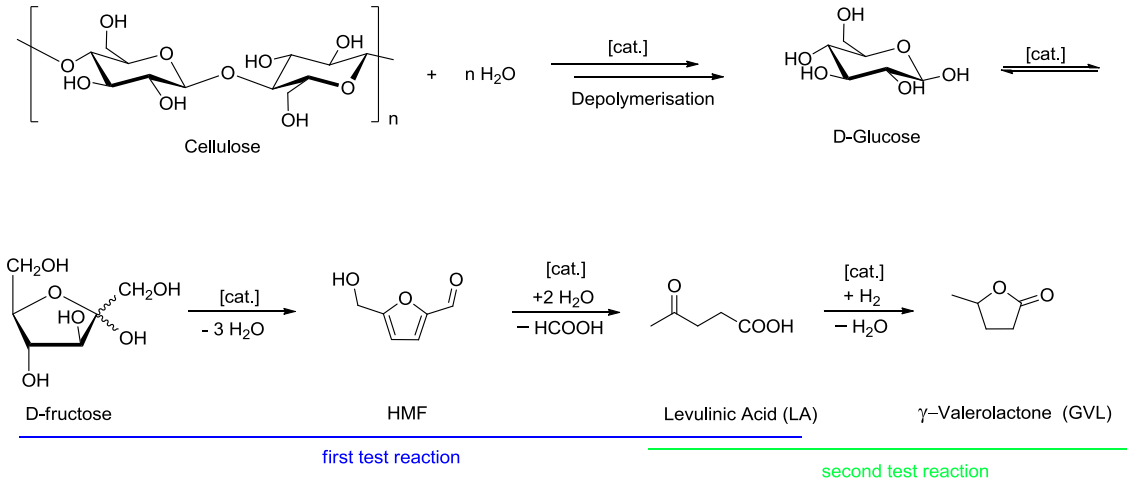


Fig. 1. Synthesis of homo- and bimetallic Pd and/or Pt nanoparticles by CFD.

The experimental planning and analysis of the catalyst synthesis was done by an experimental design approach (DOE) applying response surface plans with typically seven factors. The catalytic activity of the obtained materials was tested in the dehydration of D-fructose to levulinic acid (LA) and the hydrogenation of LA to γ-valerolactone (GVL). These transformations are among the key reactions in the

production of cellulose-based platform chemicals (Scheme 1). Conversion, selectivity and turn-over-number (TON) were chosen as evaluation criteria. Notably, the synthesis protocols for optimized catalysts differ significantly for both biomass-derived transformations.



Scheme 1. Transformation route of cellulose into platform chemicals. The chosen test reactions for evaluating the catalytic activity are indicated.

The application of our catalysts in the dehydration of D-fructose resulted in remarkable performances in several cases, which shows that the synthesizing procedure has a crucial influence on the observed activity. The performance of selected catalysts (bimetallic Pd/Pt-catalyst turned out to be most effective) resulted in an LA yield of up to 61%, which is one of the best results reported in the literature. Notably, the formation of humins, which are normally observed in significant amounts with common acidic catalysts, seems to be suppressed almost completely.

Under otherwise similar reaction conditions bare SBA-15 led to the formation of 5-hydroxymethylfurfural (HMF) as the major product (yield = 24%, conversion = 86%). A control experiment without the use of Pd, Pt *and* SBA-15 resulted in a lower conversion (52%) and a clearly different product composition, whereby furfural (yield = 7%) and HMF (yield = 9%) are the main products detected. Overall, these observations argue for SBA-15 being an important catalyst for HMF formation and the deposited metal particles being the crucial catalyst component for LA production.

Interestingly, a quite pronounced solvent effect was observed for our optimized catalysts: When water or 2-Me-THF were used as solvent, HMF was produced with almost complete selectivity. In contrast, ethanol (our standard solvent), acetone or THF

resulted in the highly preferred formation of LA, which suggests that the ability of the medium for water absorption plays a key role in LA production.

In the second test reaction bimetallic catalysts turned out to be most effective. After conducting an additional DOE based optimization, a GVL selectivity of 98.7% at a conversion level of 99.8% was reached, which corresponds to a TON of 1750. Experiments, in which the catalyst amount was reduced to 33 and 18% of the standardized conditions led to TON of 5200 (yield = 97.2%) and 7980 (yield = 83.4%), respectively. To the best of our knowledge these values are unprecedented.

To check the stability of the catalysts, recycling experiments were carried out. The selectivity (~ 99.5%) and the conversion (90-97%) stay almost constant after 4 consecutive runs under standardized conditions. TEM pictures of the used catalysts show only very little agglomeration, which promises good long term stability as well (Figure 2).

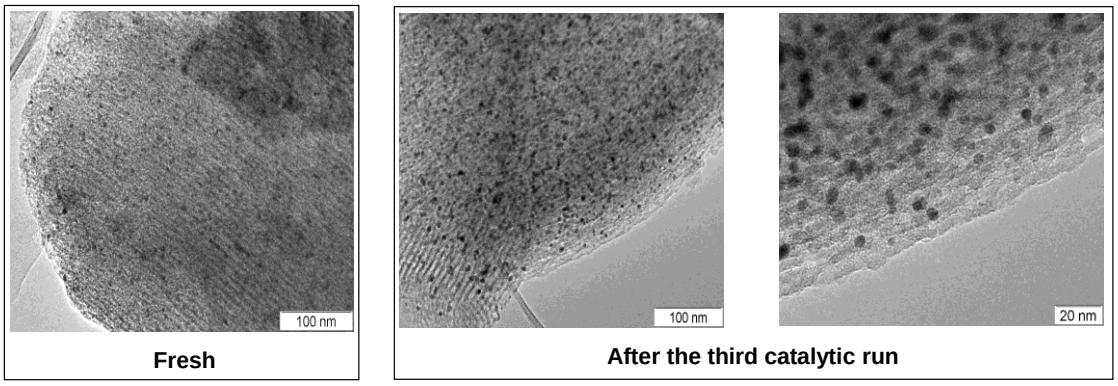


Fig. 2. TEM pictures of the fresh and the recycled catalyst.

Publications resulting from this research area: 54, 312, 413; further papers regarding other topics see publication list (page 23)

External Funding: This work was performed as part of the Cluster of Excellence "Tailor-Made Fuels from Biomass", which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities.

Cooperations: R. Palkovits, R. Rinaldi (Mülheim/Ruhr, DE)

2.2 Department of Homogeneous Catalysis

Director:

Benjamin List (born 1968)
Publications: 1, 15, 17, 18, 38, 48, 60, 74, 75, 76, 95, 117, 135, 136, 140, 147, 166, 184, 206, 216, 217, 278, 295, 300, 301, 335, 338, 347, 348, 349, 350, 364, 382, 412, 414, 415, 424, 428

Further group leaders:

Martin Klußmann (born 1974)
Publications: 265, 266, 338, 339, 375

Nuno Maulide (born 1979)
joined the Institute in January 2009
Publications: 293, 310, 311, 325, 355, 357

Klaus-Richard Pörschke (born 1949)
Publications: none

Curriculum Vitae: Benjamin List

1968	Born in Frankfurt/Main, Germany
1993	Chemistry Diploma, Freie Universität Berlin
1997	PhD, Johann Wolfgang Goethe-Universität Frankfurt
1997-1998	Postdoc, Scripps Research Institute, La Jolla, USA
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

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
1999-2010	ca. 130 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*
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*

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, expand the substrate scope of certain catalytic reactions, apply asymmetric catalysis in natural product and pharmaceutical synthesis, and study mechanisms of homogenous catalytic reactions (B. List, K.-R. Pörschke, M. Klußmann, N. Maulide).

Since leadership of the department of homogenous catalysis was taken over by Professor Benjamin List in 2005, it has grown significantly from ca. 15 members to currently > 50 members, including the groups of Professor K.-R. Pörschke, who has been a group leader at the institute since two decades now, Dr. M. Klußmann (group leader since 2007), and now also of Dr. N. Maulide, who has joined the department in 2009.

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 mechanism by which organocatalysts activate their substrates.

Furthermore, in 2005 the group has first conceptualized and then significantly advanced another approach to asymmetric catalysis, *asymmetric counteranion directed catalysis* (ACDC). Initially, merely an idea, this approach has progressed within the department but now also at other institutions around the globe, into a truly general strategy for asymmetric synthesis and has found utility in organocatalysis but also in transition metal catalysis and Lewis acid catalysis.

Research in the laboratory of **Professor Pörschke** aims at a deeper mechanistic understanding of transition metal catalyzed reactions. The group conducts fundamental research in the areas of coordination chemistry, organometallic chemistry, homogeneous catalysis, and solid state phase properties. Transition metals under focus are Ni, Pd, and Pt, which are often used in combination with main group metal compounds (Li, Mg, Al, Ge, Sn).

During the last almost four years, the group of **Dr. Klußmann** has made its name in the "hot area" of oxidative cross-couplings. They investigate reactions that allow the coupling of two C-H-fragments, establishing a C-C-unit and formally two H atoms. The substrates are activated under oxidative conditions, ideally resulting in water as the only byproduct. A breakthrough was achieved last year with the discovery of the completely metal free "Autoxidative Carbon–Carbon Bond Formation from Carbon–Hydrogen Bonds".

The group of **Dr. Maulide** was established in 2009 after its leader has obtained a prestigious and highly competitive Max-Planck Research group leader position, which is fully supported by central MPG funds. The group has diverse activities in the area of organic synthesis and catalysis. Accordingly, within a short period, the Maulide team has already published three papers in Angewandte Chemie on entirely different subjects, including a new variant of the Claisen rearrangement, Pd-catalysis, and a novel ylide transfer reaction. The group has attracted funding from various sources and is currently massively growing.

2.2.1 Research Area "Crystal Structures of Proline Derived Enamines" (B. List)

Involved: D. A. Bock, C. W. Lehmann

Objective: Within the last ten years, enamine catalysis, the catalytic activation of carbonyl compounds via enamine intermediates and a concept originally devised in our laboratory, has grown into a powerful approach to organic synthesis. Among the many different primary and secondary amine catalysts that have been developed in this field, the amino acid proline remains a privileged motif and there are literally dozens of reaction types that are catalyzed with this wonderful natural product. Proline derived enamines of aldehydes and ketones are key intermediates in the catalytic cycles of these reactions. Surprisingly though, such enamines have remained entirely hypothetical and long resisted attempts at their structural characterization. Such information however, appears to be highly valuable towards understanding the mechanistic details with which proline catalyzes carbonyl transformations. Here we report and discuss crystal structures of a series of stabilized enamines of proline and of some of its analogues.

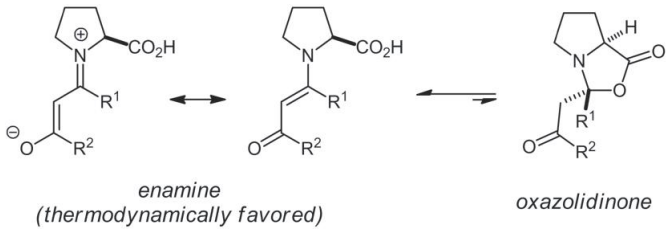
Results: The main difficulty in previous attempts at characterizing proline enamines has been the tendency of carbonyl compounds to reversibly react with proline giving oxazolidinones instead of the enamines. Rather than the enamine, thermodynamics favor the oxazolidinone constitutional isomer, in which one C—O- and one C—H-σ-bond are gained at the expense of one C—C-π-bond and one O—H-σ-bond:

enamine *oxazolidinone (thermodynamically favored)*

In view of the catalytic action of proline, oxazolidinone formations with aldehyde or ketone substrates are best described as *parasitic equilibria* since they are presumably not leading to product but inhibit its formation. While aldehyde derived "Seebach-oxazolidinones" have long been known, their ketone analogues have only recently been detected and characterized by us and later isolated also by Seebach and Eschenmoser *et al.* Interestingly, the condensation product of acetone and proline has also been detected by Metzger *et al.* using mass spectrometry. In light of our previous careful NMR-spectroscopic characterization of this adduct as an oxazolidinone, their assignment as an enamine appears to be questionable though. In addition, Seebach and Eschenmoser *et*

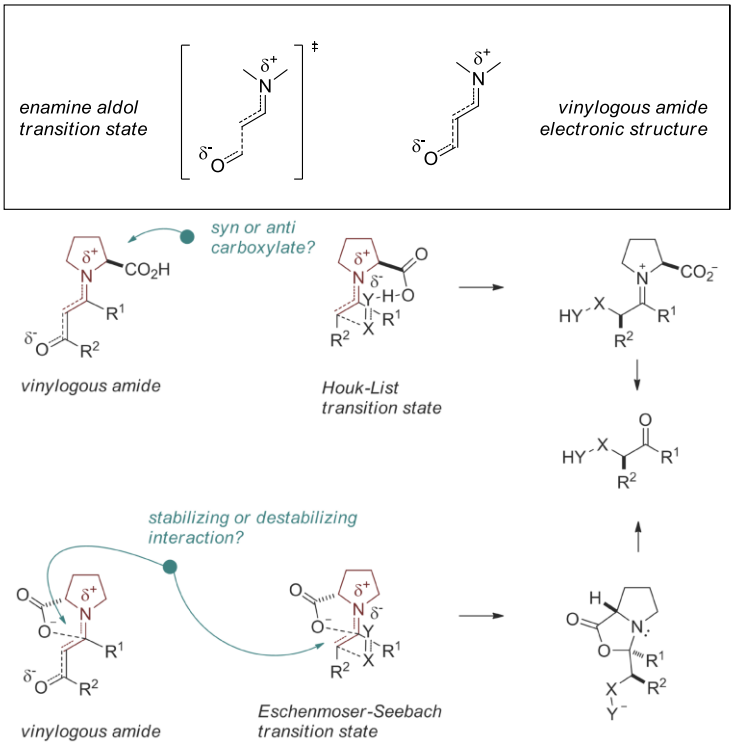
al. have partially characterized an ammonium salt of the prolyl enamine of cyclohexanone. Disappointingly though, crystallographic data on proline enamines are entirely lacking. In fact, to the best of our knowledge and based on a search of the Cambridge Structural Database (CSD, Version 5.31, Nov 2009) crystal structures of any proline derived enamines have not been reported previously.

At the outset of this work several years ago, we wondered whether or not it is possible to crystallize proline enamines that are formally derived of 1,3-dicarbonyl compounds. We hypothesized that, in contrast to the situation of the parent unconjugated system, such structures may in fact be more stable than the corresponding oxazolidinones since cyclization would interrupt conjugation of the vinylogous amide system.

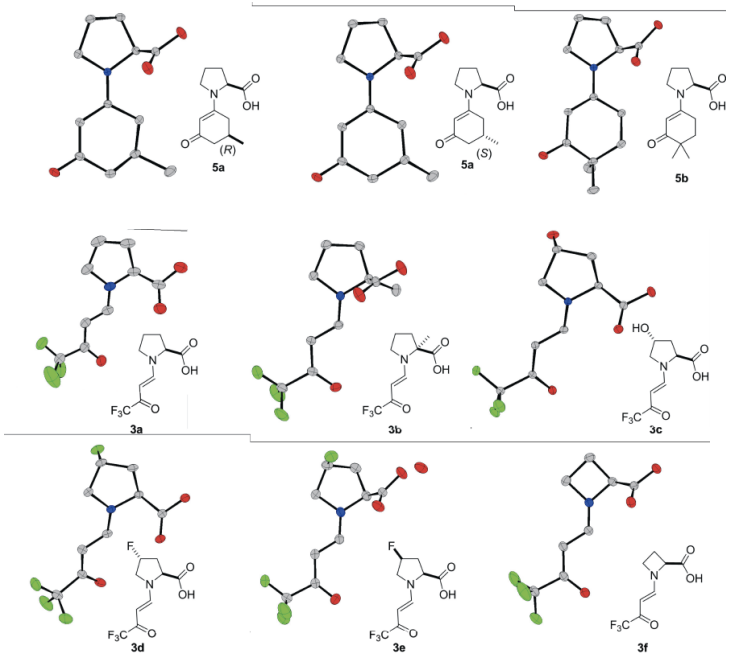


Indeed, proline derived vinylogous amides (or enaminones) have been reported previously and characterized spectroscopically as enamines. More important for the present discussion is that such vinylogous amides may be considered transition state models of a proline enamine engaging in the reaction with an electrophile. In both cases is electron density removed from the electron rich enamine-π-system. This electronic redistribution should impact the enamine geometry. For example, because of the partial iminium ion character of the vinylogous amide (and in fact of the corresponding bond-forming transition state), the sp^3-character and consequently pyramidalization at nitrogen should be reduced. Similarly, the enaminone conjugation will influence the bond-lengths of the system such that the enamine double bond will be *longer* than that expected for the analogous unconjugated proline enamine. The C—N bond of the enamine system in turn, is expected to be *shorter*, reflecting the beginning π-character of this bond. We reasoned that crystal-structural information on such vinylogous amides would provide additional valuable information on stereochemical aspects of such enamines, *i.e.* double bond configuration and *syn*- vs. *anti*-positioning of the carboxylate relative to the enamine double bond, which corresponds to an (*E*)- vs. (*Z*)-configuration at the forming iminium ion.

Additionally, following the logic outlined before, the question of how much oxazolidinone character is already developed in the transition state might potentially be answered by such structural investigations. According to a recent proposal by Eschenmoser and Seebach, the reaction of the proline enamine with an electrophile involves an anionic cyclization of the *syn*-configured carboxylate into the enamine α-carbon with concomitant bond formation at its β-carbon in the sense of an electrophile induced lactonization. This mechanism has already been discussed by Hajos before and leads directly to an oxazolidinone. If the postulated bond-formation between the carboxylate-oxygen and the enamine α-carbon in the transition state would indeed contribute to its stabilization, the question must then be asked if such an interaction should not also occur in the corresponding vinylogous amide system. Alternatively, C—O-bond formation may actually *destabilize* both the enaminone and, in fact, the corresponding transition state by interrupting conjugation.



The crystal structures of a series of enamines **3** and **5** could be elucidated successfully and yielded the solid state molecular conformations shown.

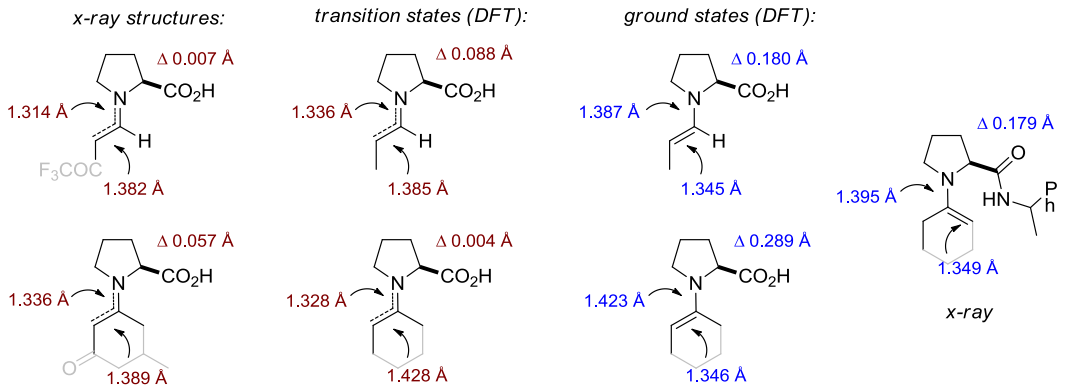


Several observations have been made: (1) Consistent with our hypothesis that resonance interruption should generally favor the enamine constitutional isomer, the corresponding oxazolidinone form is not displayed in any of the ten structures. Also, potential near attack conformations of a carboxylate oxygen engaging in a reaction with the enamine α-carbon are not observed. (2) As expected, the studied enamines exclusively display an (*E*)-geometry. (3) Of the ten structures obtained, nine display an *anti*-arrangement of the carboxylic acid and the enamine double bond. (4) All enamine structures show intermolecular hydrogen bonding interactions between the carboxylic acid and the ketone carbonyl group.

Interpreting these results in line with our original hypothesis that 1,3-dicarbonyl-derived proline enamines, to a some degree, may be viewed as transition states models of the corresponding proline-catalyzed transformations such as the aldol reaction, we notice the following: (1) The *anti*-arrangement of the (*E*)-enamine and the carboxylate, which is also required in the Houk-List transition state but stands in contrast to that suggested by Eschenmoser and Seebach *et al.*, is generally preferred in the crystal structures of the studied enamines. (2) No evidence for a positive interaction of the carboxylate with the enamine α-carbon, as suggested by Seebach and Eschenmoser for the transition state of proline catalyzed reactions has been obtained in the investigated enamine structures. (3) The intermolecular hydrogen-bonding between the carboxylate and keto groups observed in all of our crystal structures chemically resembles the intramolecular hydrogen bond proposed in the Houk-List transition state.

It is instructive to compare the obtained X-ray structures with the calculated ground and transition state structures.

As we had expected, the double bond length (1.382 Å) in the X-ray structure of proline enaminone **3a** is longer than that of the calculated enamine ground state of the proline enamine of propionaldehyde (1.345 Å) but quite similar to that in the corresponding transition state (1.385 Å).



These structural similarities are also observed in the ketone series: The enamine double bond length in compound **5a** (1.389 Å) and in the cyclohexanone Houk-transition state (1.428 Å) are significantly longer than that calculated for the corresponding ground state (1.342 Å) and also that found in an X-ray structure of a proline amide-derived cyclohexanone enamine (1.349 Å) previously obtained by Eschenmoser *et al*. Moreover, the enamine C—N-bond-lengths in the cyclohexanone series are very similar in both the structure of **5a** and the DFT-structure of the corresponding transition state further validating our transition state/enaminone analogy.

We have described the first X-ray structures of both aldehyde and ketone derived proline enaminones and compared their structures with the calculated Houk-List and the postulated Seebach-Eschenmoser transition states. Obviously, one should interpret such structures carefully and drawing conclusions on possible transition states from X-ray structures is challenging in general. Nonetheless, we note that the vast majority of the ten X-ray structures we have been able to obtain, are consistent with our previously proposed transition states of proline catalyzed aldol, Mannich-, α-amination, and-aminoxylation reactions. After the submission of this manuscript, Gschwind *et al*. have for the first time detected aldehyde-derived proline enamines by NMR spectroscopy. Remarkably, only the *anti*-conformer is observed in solution similarly to the results we report within this manuscript.

Publications resulting from this research area: 295

External Funding: Deutsche Forschungsgemeinschaft

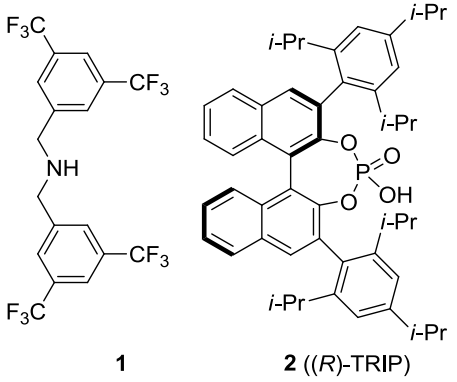
Cooperations: none

2.2.2 Research Area "Catalytic Asymmetric Epoxidation of Electron-Deficient Olefins" (B. List)

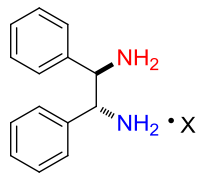
Involved: O. Lifchits, C. M. Reisinger, X. Wang

Objective: As one of the most synthetically useful transformations, the catalytic asymmetric epoxidation of olefins continues to define the state of the art in asymmetric synthesis. Despite recent advances in expanding the scope of epoxidation to challenging substrate classes, the reaction of simple cyclic and linear enones and α-branched enals has been rather limited in efficiency, selectivity, and generality. Our previous work with amine catalysis and asymmetric counteranion-directed catalysis (ACDC) demonstrated the potential of these mild yet powerful activation modes in enantioselective transformations, including the epoxidation of unbranched enals. The aim of this project was to identify catalyst systems based on primary aminocatalysis and ACDC to develop simple, efficient and highly enantioselective methodologies for the epoxidation of enones and α-branched enals.

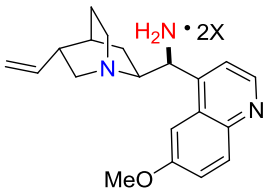
Results: Following our recent discovery that the achiral secondary amine catalyst **1** paired with a chiral phosphoric acid TRIP (**2**) effectively catalyzes the epoxidation of unbranched enals, we wished to explore other challenging substrate classes. Focusing on the epoxidation of cyclic enones **3** with hydrogen peroxide, we found that primary amines were significantly more effective in catalyzing the epoxidation of these more congested substrates. In addition, a second amine site in the catalyst proved to be essential for better enantioselectivity, presumably because it coordinates and directs hydrogen peroxide to one of the enantiofaces of the double bond. Based on these findings, two equally effective catalyst combinations **5** and **6a** were identified for the epoxidation of cyclic enones. Both catalyst salts feature a chiral bifunctional primary amine and an acid co-catalyst. While the chiral amine in the catalyst pair **5** benefits from an additional ACDC effect of the chiral acid, the readily prepared cinchona-based amine in **6a** was found to be effective with achiral co-catalyst trifluoroacetic acid (TFA). Gratifyingly**,** the pseudoenantiomeric cinchona-derived amine in catalyst pair **6b** could deliver the opposite enantiomer of the epoxide product with equal efficiency and selectivity.



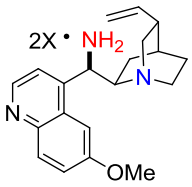
1 **2** ((*R*)-TRIP)



5 (X = (*S*)-TRIP)

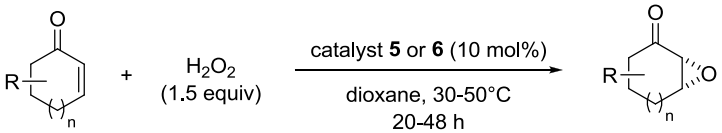


6a (X = TFA)

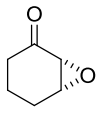


6b (X = TFA)

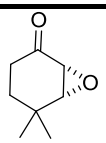
Using the optimal catalyst systems **5** and/or **6a-b** and aqueous hydrogen peroxide, a broad range of cyclic enones were epoxidized with excellent enantioselectivity.



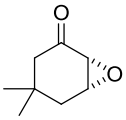
3 **4**



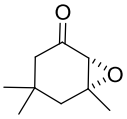
4a
cat **5**: 68%, 96:4 er
cat **6a**: 58%, 3:97 er



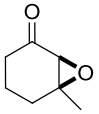
4b
cat **5**: 80%, 97:3 er



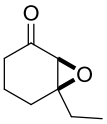
4c
cat **5**: 76%, 98:2 er



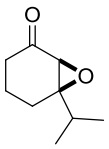
4d
cat **5**: 63%, 96:4 er



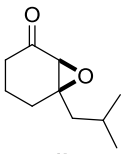
4e
cat **6a**: 70%, 98:2 er



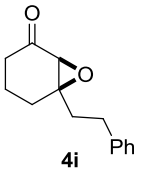
4f
cat **6a**: 73%, 98.5:1.5 er



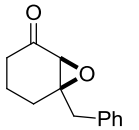
4g
cat **6a**: 79%, 99:1 er



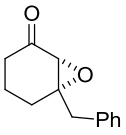
4h
cat **6a**: 73%, 98:2 er



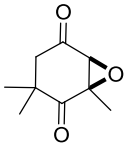
4i
cat **6a**: 84%, 98.5:1.5 er



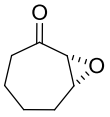
4j
cat **6a**: 78%, 99:1 er



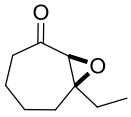
4j
cat **6b**: 77%, 98.5:1.5 er



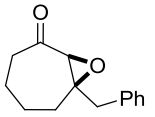
4k
cat **6a**: 49%, 96:4 er



4l
cat **5**: 82%, 99:1 er

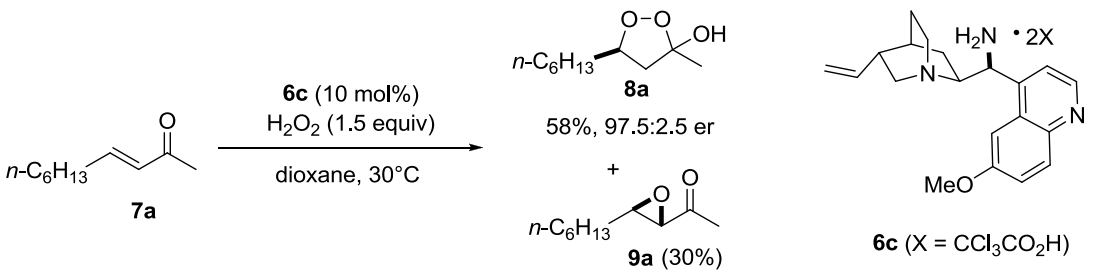


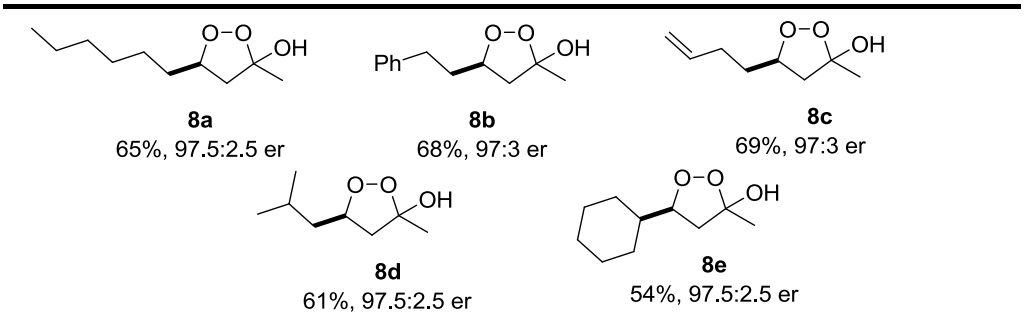
4m
cat **6a**: 85%, >99.5:0.5 er



4n
cat **6a**: 85%, >99.5:0.5 er

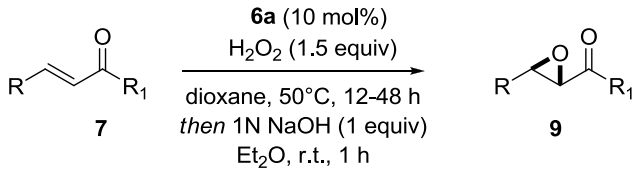
We next turned our attention to linear aliphatic enones, which have presented considerable challenges to previous methods. Remarkably, when 2-decenone **7a** was subjected to aqueous hydrogen peroxide and catalyst **6c**, peroxyhemiketal **8a** was obtained in 58% yield and 97.5:2.5 er along with 30% of the expected epoxide **9a**. Optimization of conditions allowed for the formation of a range of peroxyhemiketal products in useful yields and excellent enantioselectivities.

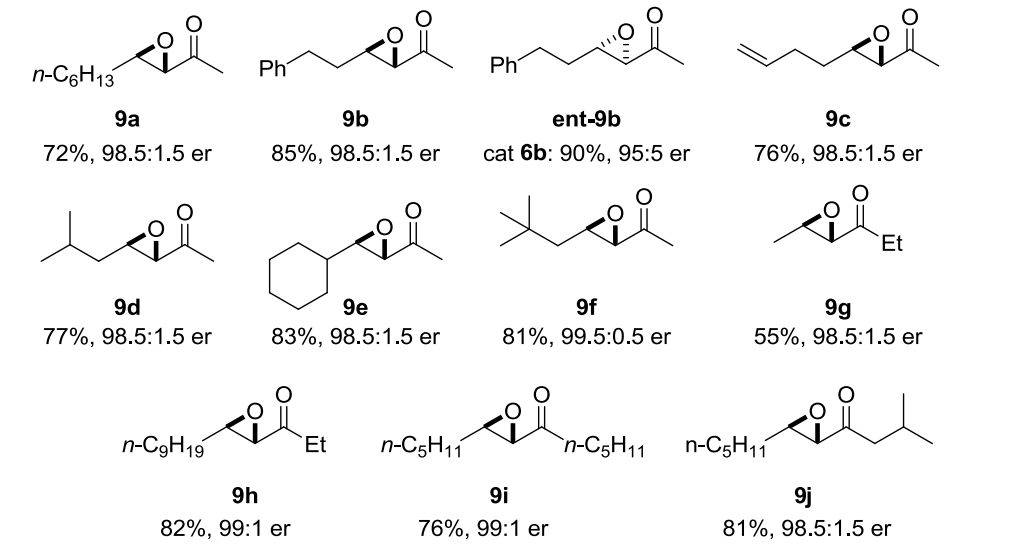




conditions: **6c** (10 mol%), H_2O_2 (3 equiv), dioxane, 32°C, 36-48 h

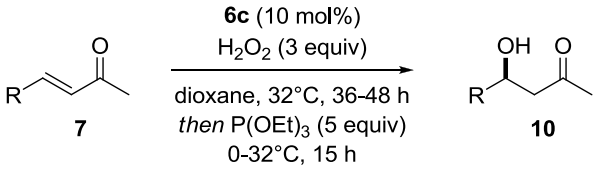
Slightly modified conditions for epoxidation followed by a basic workup provided the epoxides **9** in good yields and very high enantioselectivities.

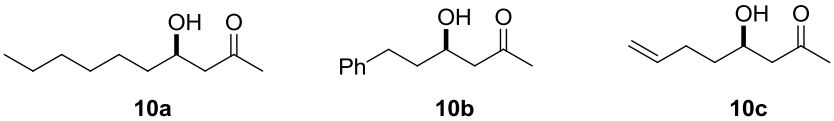




Peroxyhemiketals **8** contain a 1,2-dioxolane subunit which is present in many natural products and bioactive molecules. In addition, as a further illustration of their

usefulness, these compounds could be converted to β-hydroxyketones **10** in a one-pot operation by adding a reducing agent ($P(OEt)_3$) at the end of the reaction. This method to access β-hydroxyketones complements the asymmetric proline-catalyzed aldol reactions, in which α-unsubstituted aldehydes still present a significant challenge.





10a 59%, 97:3 er

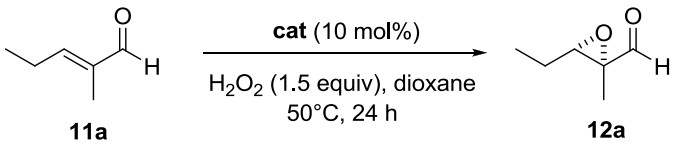
10b 53%, 96.5:3.5 er

10c 55%, 96:4 er

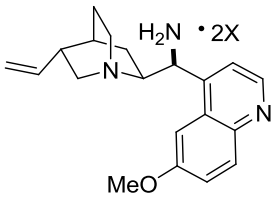
10d 56%, 96.5:3.5 er

10e 46%, 96:4 er

Recognizing the success of cinchona amine-based salts **6** in the epoxidation of sterically demanding substrates, we next examined α-branched enals, for which no direct asymmetric epoxidation methodology existed. Gratifyingly, the epoxidation of (*E*)-methylpent-2-enal **11a** with catalyst salt **6a** delivered the desired product **12a** with an encouraging er of 93:7 and dr of 75:25. Optimization of the catalyst system revealed that the additional and matched ACDC effect of (*R*)-TRIP as the acid co-catalyst dramatically improved the stereoselectivity to 99.5:0.5 er and 96:4 dr.

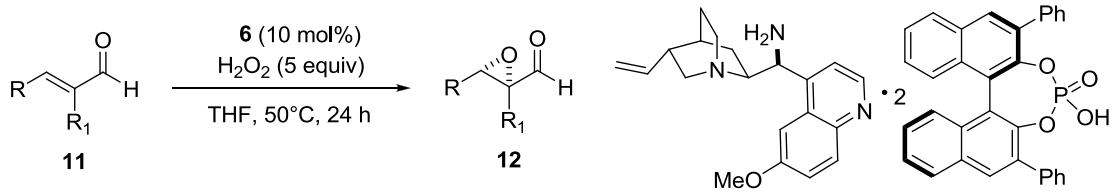


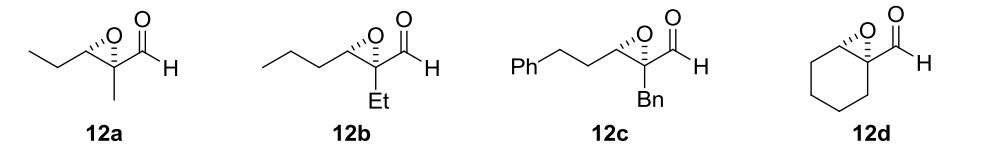
catalyst	conversion, %	er (**12a**)	dr (**12a**)
6a	38	93:7	75:25
6d	84	99.5:0.5	96:4



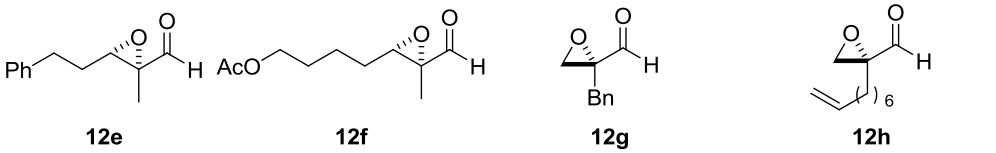
6a (X = CF_3CO_2H)
6d (X = (*R*)-TRIP)

After further optimization to achieve complete conversion, a range of α,β-disubstituted and α-substituted enals were epoxidized with good yields and consistently excellent enantioselectivity.

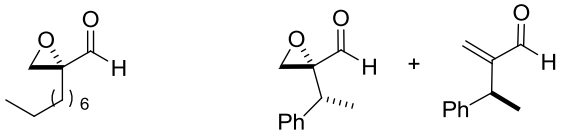




cat **6e**: 43%, 92:8 dr, 98.5:1.5 er | cat **6e**: 64%, 83:17 dr, 99:1 er | cat **6e**: 77%, 90:10 dr, 99:1 er | cat **6e**: 70%, 98.5:1.5 er



cat **6e**: 75%, 95:5 dr, 98.5:1.5 er | cat **6e**: 66%, 93:7 dr, 99:1 er | cat **6d**: 78%, 99:1 er | cat **6d**: 74%, 98.5:1.5 er



cat **6d**: 78%, 99:1 er | *kinetic resolution at 53% conversion*: cat **6d**: 44%, 96:4 er | cat **6d**: 47%, 97:3 er

In summary we developed highly enantioselective, general and operationally simple protocols for the epoxidation of hitherto challenging classes of electron-deficient olefins. Both cyclic and linear enones, as well as α-branched aldehydes could be epoxidized by employing the easily prepared cinchona-derived amine catalyst in combination with either achiral or chiral acid co-catalyst.

Publications resulting from this research area: 95,135, 348

External Funding: Deutsche Forschungsgemeinschaft; Fonds der Chemischen Industrie

Cooperations: none

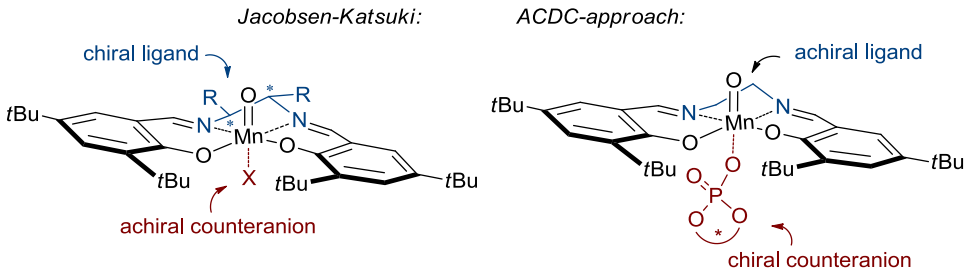
2.2.3 Research Area "Asymmetric Counteranion-Directed Transition Metal Catalysis" (B. List)

Involved: S.-H. Liao, G.-X. Jiang, Y.-W. Fang, R. Halder

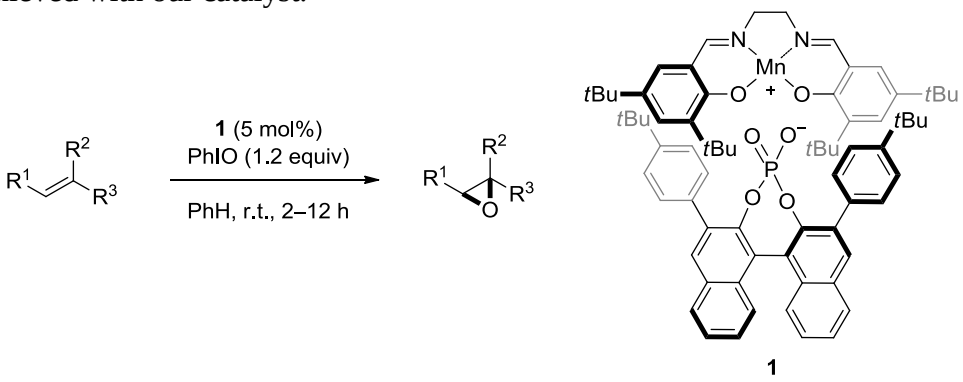
Objective: Inspired by pioneering contributions on chiral Brønsted acid mediated reactions and our own studies in aminocatalysis, a new concept for asymmetric synthesis–asymmetric counteranion-directed catalysis (ACDC) has been developed in our group. According to this concept, catalytic reactions that proceed via cationic intermediates can be performed highly enantioselectively by the incorporation of a chiral counteranion into the catalyst. After our initial proof of this concept with organocatalytic transfer hydrogenations and epoxidations, ACDC has recently been extended to transition-metal catalysis with our palladium-catalyzed Tsuji–Trost-type α-allylation of aldehydes and Toste's gold-catalyzed allene cyclizations. The aim of this project is to further explore the potential of the ACDC concept as a general strategy for asymmetric synthesis, especially in transition-metal catalyzed reactions, such as Mn-catalyzed epoxidation, Pd-catalyzed aza-Claisen rearrangement, Ru-catalyzed hydrovinylation of olefins, and Ru-catalyzed olefin metathesis.

Results:

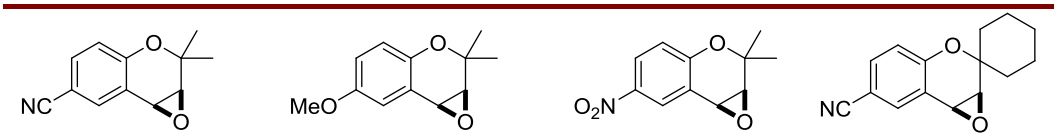
A) Stimulated by an important contribution from Kochi et al., Jacobsen and Katsuki have significantly advanced the catalytic asymmetric epoxidation of unfunctionalized alkenes by introducing chiral Mn^{III}-salen catalysts. These complexes display a broad substrate scope although certain olefin classes still fail to be converted with high enantioselectivity. Interestingly, cationic Mn-salen complexes are C_2-symmetrical and inherently chiral–even when the salen ligand itself is achiral. In case of the Jacobsen-Katsuki epoxidation, the chiral backbone of the salen ligand fixes the complex in one of the two enantiomorphic confirmations. We hypothesized that a chiral counteranion should also be able to induce a preference for one of the two enantiomorphic conformations. Specifically, chiral binol-derived phosphate anions are ideally suited for our purposes, because in addition to possibly inducing one enantiomorphic conformation of the cationic complex, these ions may also amplify the chiral microenvironment around the metal center with suitable substituents at the 3,3'-positions of the phosphates. Overall, this may lead to a new type of chiral Mn-salen catalyst with unique properties.



For the catalyst elaboration, modification on both achiral salen ligands and chiral phosphate anions was carried out, and complex **1** stood out as the most efficient Mn-salen/phosphate combination. Under optimized conditions (5 mol% catalyst, 1.2 equiv of PhIO as oxidant and benzene as solvent), various alkenes can be epoxidized smoothly at room temperature with high level of enantioselectivity. These observed stereoselectivities closely resemble those obtained with the Jacobsen catalyst, although in the cases of electron-deficient alkenes and styrene, slightly higher enantioselectivities are achieved with our catalyst.



1

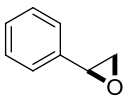


98% yield
er = 97:3

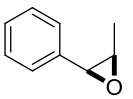
83% yield
er = 96:4

98% yield
er = 98:2

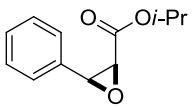
99% yield
er = 97:3



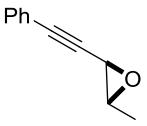
80% yield
er = 85:15



81% yield
er = 94:6 (cis)
cis/trans = 6:1



93% yield
er = 98:2 (cis)
cis/trans = 4:1

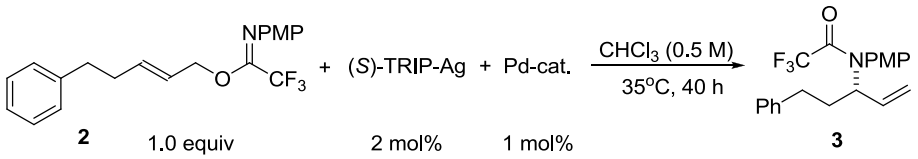


99% yield
er = 96:4 (trans)
cis/trans = 1:2

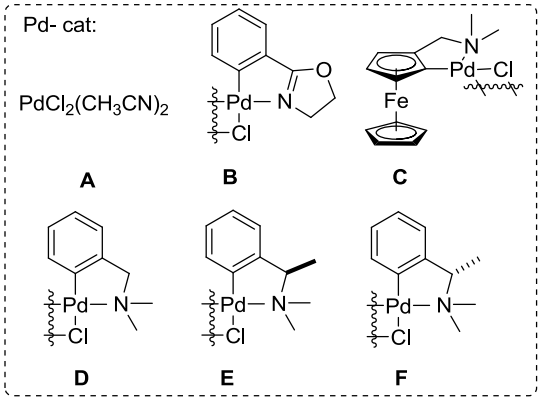
Usually, neutral donor ligands are added to the Jacobsen-Katsuki epoxidation reaction mixture to increase the reactivity and enantioselectivity, but with our catalyst system this is not necessary. The high activity of our ion-pair catalyst may result from the weakened covalent character of the sterically overloaded ("frustrated") manganese-

phophate Lewis pair. Other metal-salen/phosphate ion pair-catalyzed reactions are under investigation.

B) The asymmetric Pd^{II}-catalyzed Overman rearrangement of allylic trihaloacetimidates to allylic trihaloacetamides is an efficient approach for the transformation of allylic alcohols to less available chiral allylic amines. Great progress has been achieved with planar chiral oxazoline-based palladacycles COP-X and FOP-X, but the synthesis of these catalysts is not a trivial task. We envisioned that the replacement of the achiral counteranion (i.e. Cl^-) with a chiral phosphate anion in similar though simpler complexes could lead to a new type of catalyst, which may exhibit different activity and selectivity. After an extensive screening of several palladium complexes in combination with chiral binaphthol-derived phosphoric acid silver salt (*S*)-TRIP-Ag, we found that upon treating trifluoroacetimidate **2** with a catalytic amount of Pd complex **F** and (*S*)-TRIP-Ag, the corresponding rearrangement product **3** can be obtained in high yield and enantioselectivity. Further investigation on the substrate scope and synthetic application of the reaction is underway in our laboratory.

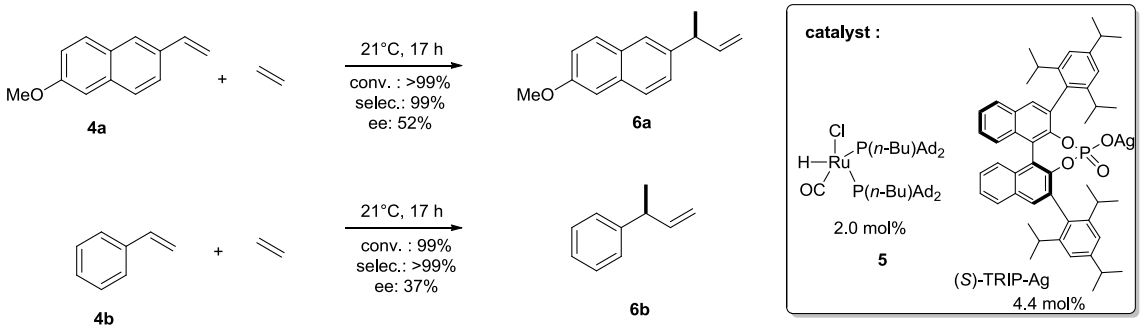


Entry	Pd-cat.	Yield (%)	e.r.
1	A	20	53.1 : 46.9
2	B	94	68.0 : 32.0
3	C	93	92.8 : 7.2
4	D	94	97.3 : 2.7
5	E	96	94.5 : 5.5
6	**F**	**93**	**98.3 : 1.7**
7	F (no Ag salt)	99	50.0 : 50.0
8	(only Ag salt, no Pd)	0	---



C) The asymmetric hydrovinylation of olefins is one of a handful of catalytic asymmetric reactions that uses only feedstock carbon sources for the synthesis of valuable fine chemical intermediates. For the asymmetric hydrovinylation, all successful catalysts are based on Ni complexes incorporating chiral ligands such as azaphospholane, phosphinite, and phosphoramidite. Inspired by the reported results, initially, we extended our ACDC concept to Ni-catalysis but only low enantioselectivity

was achieved. Considering the excellent reactivity and efficiency of Ru-H catalyzed hydrovinylation, we ventured into Ru-ACDC-type catalysis for the development of an asymmetric process. In the presence of a catalytic amount of achiral ruthenium complex **5** and (*S*)-TRIP-Ag, treatment of aromatic olefins **4a, 4b** with ethylene provided the corresponding products **6a** and **6b** in high yields, excellent regioselectivities and promising enantioselectivities. This is the first example of an asymmetric hydrovinylation of olefins using ruthenium catalysis.



Publications resulting from this research area: 347

External Funding: China Scholarship Council Fellowship (S.-H. Liao)

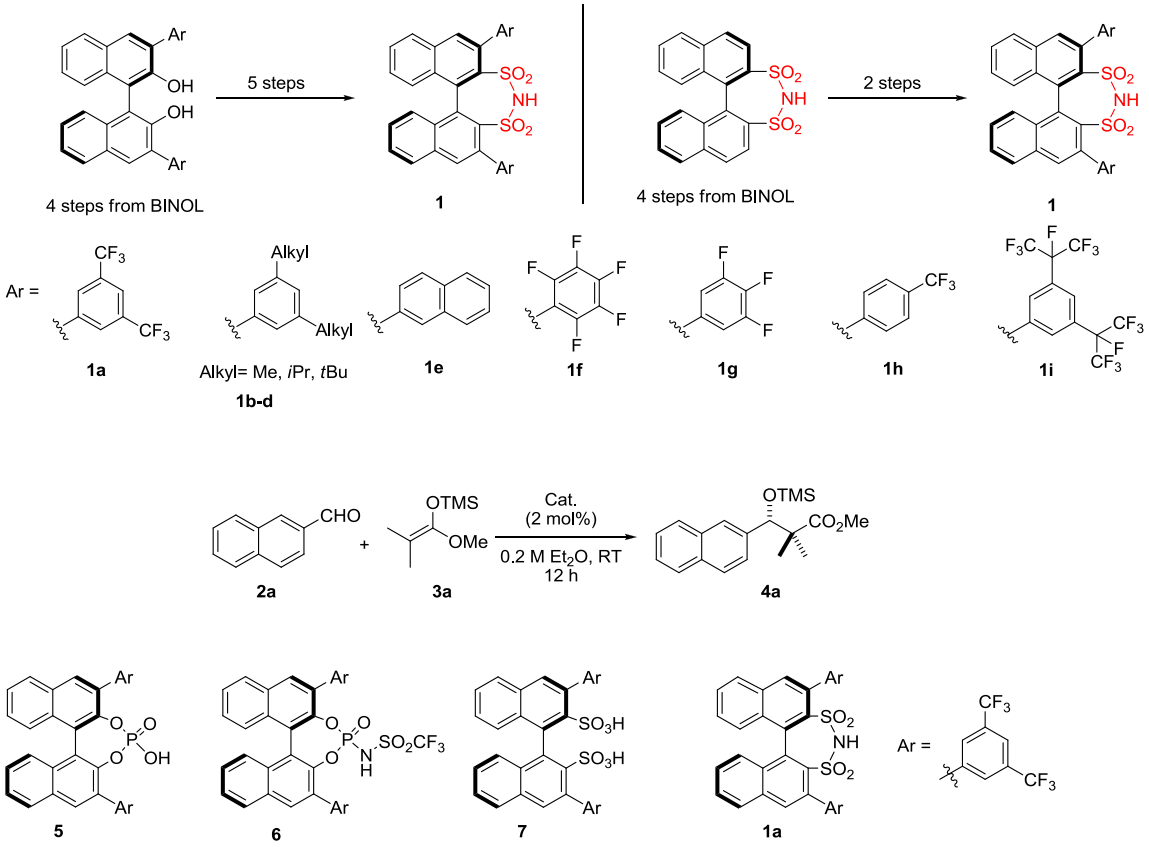
Cooperations: none

2.2.4 Research Area "Lewis Acid Organocatalysis" (B. List)

Involved: F. Lay, Pi. García-García, L. Ratjen, Pa. García-García, K. Rabalakos

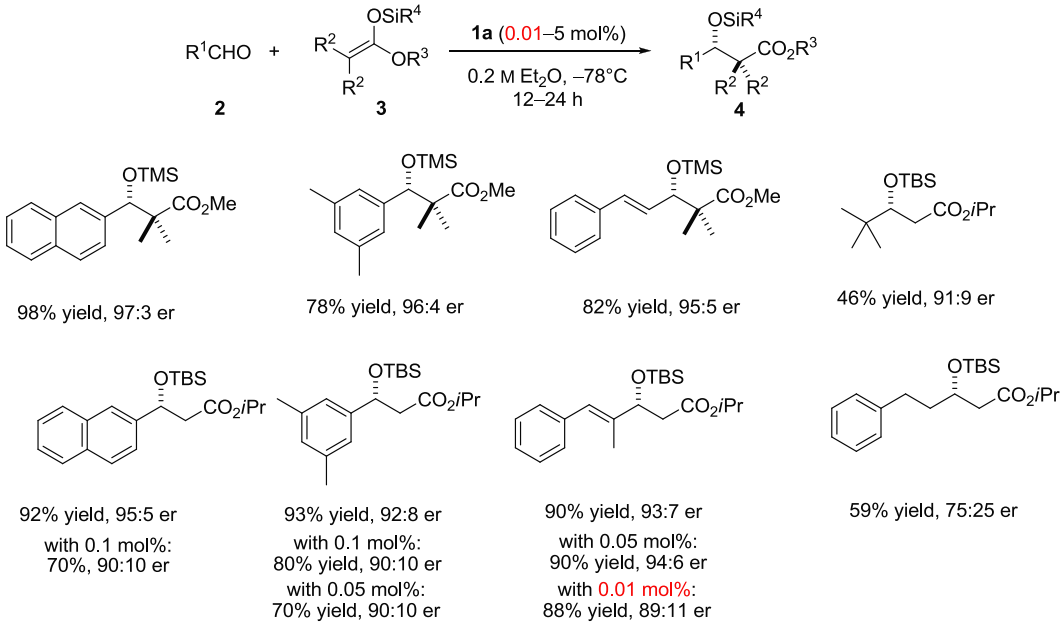
Objective: Organocatalysts function by donating or removing electrons or protons, defining four distinct activation modes: Brønsted base catalysis, Brønsted acid catalysis, Lewis base catalysis, and Lewis acid catalysis. While the vast majority of organocatalysts, including many amines, carbenes, and phosphines, act as Lewis bases, Brønsted acid and base organocatalysis is also growing strongly. Remarkably though, the one area that has been left almost completely unexplored is that of *organic Lewis acid catalysis*. Of particular interest in our laboratory has been the asymmetric *Mukaiyama* aldol reaction, of which most asymmetric variations still require high catalyst loadings of typically 20 mol%. The reason for this high loading is that an achiral yet *catalytically competent* second species is generated during the reaction: a silylium ion equivalent, which can be released if the terminating aldolate silylation step is relatively slow. Inspired by the fact that bistriflimide (Tf_2NH) is a powerful achiral *Mukaiyama* aldol pre-catalyst generating the highly reactive Lewis acid Tf_2NTMS as the actual catalyst, and encouraged by our recently introduced concept of asymmetric counteranion direct catalysis (*ACDC*), the aim of this project has been the development of chiral disulfonimides as chiral Tf_2NH equivalents and their application in enantioselective *Mukaiyama* aldol reactions. Potentially, our approach could offer solutions to the problems encountered in conventional asymmetric Lewis acid catalysis.

Results: In the initially developed synthesis of chiral binaphthyl-based disulfonimides 3,3'-diaryl substituted (*R*)-BINOL derivatives were used as starting materials. An obvious drawback of this route has been the nine chemical operations required for every 3,3'-diaryl substituted disulfonimide. In the second route, the unsubstituted disulfonimide, readily available on a multigram scale from (*R*)-BINOL, is converted into 3,3'-diaryl substituted disulfonimides via a metalation, halogenation, cross-coupling sequence leading to more than twenty different 3,3'-diaryl substituted disulfonimides.



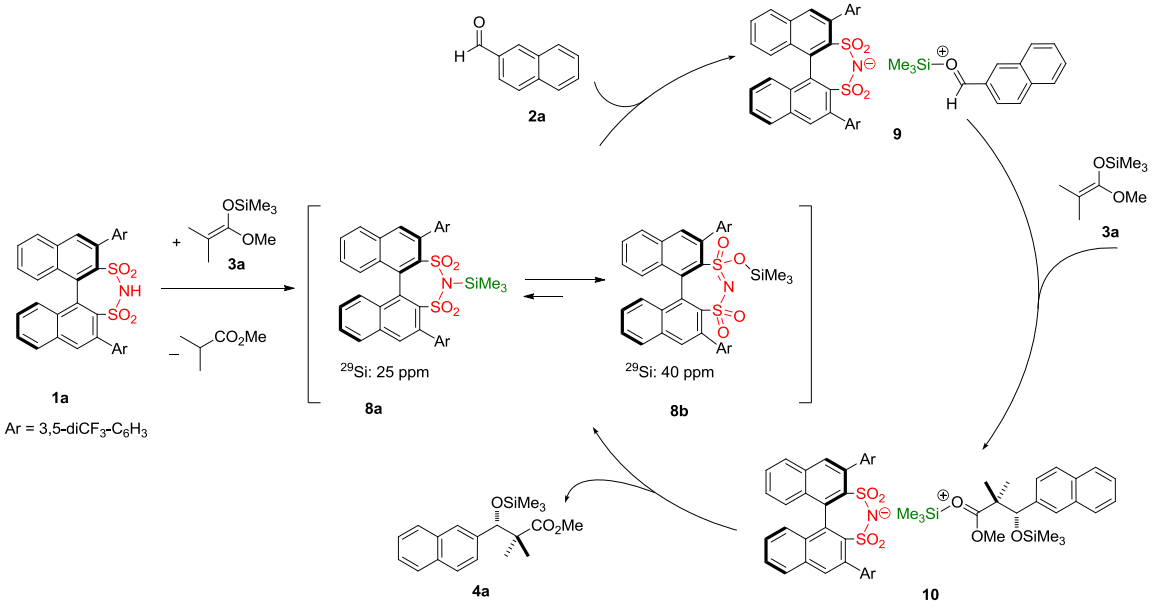
To our delight we found that in contrast to previously developed chiral Brønsted acid catalysts **5**-**7**, chiral binaphthyl-derived disulfonimides showed strong catalytic activity in the *Mukaiyama* aldol reaction. After catalyst screening and optimization of reaction conditions it was found that pre-catalyst **1a** yielded the highest enantioselectivities in Et_2O at −78°C.

Entry	Catalyst	Yield [%]	er
1	**1a**	< 99	90:10
2	**5**	< 2	-
3	**6**	< 2	-
4	**7**	> 2	-



The reaction is well suited for isobutyrate derived ketene acetals, which react with various aromatic aldehydes giving the corresponding aldol products in high yields and enantioselectivities (≥ 95:5 er). An α,β-unsaturated aldehyde could also be employed with the same nucleophile giving the desired product in good yield and with an enantiomeric ratio of 97:3. Even the more challenging acetate derived ketene acetal could be used and upon reaction with different aromatic and α,β-unsaturated aldehydes the corresponding products were obtained in excellent yields and high enantioselectivities (≥ 95:5 er). In the case of 2-naphthaldehyde, 3,5-dimethoxybenzaldehyde, and (*E*)-α-methylcinnamaldehyde, we also investigated the effect of lowering the catalyst loading on the outcome of the reaction. An amount of only 0.1 mol% turned out to be sufficient to give the desired products in good to excellent yields while maintaining high enantioselectivity. Even lower catalyst amounts can be used with good results and the α-methylcinnamaldehyde derived product was obtained in high yield and an enantiomeric ratio of 88:12 with a remarkably low catalyst loading of 0.01 mol%. Finally, aliphatic aldehydes were also tested and provided pivaldehyde and hydrocinnamaldehyde derived products with good yields and reasonable enantioselectivities (≥ 75:25 er).

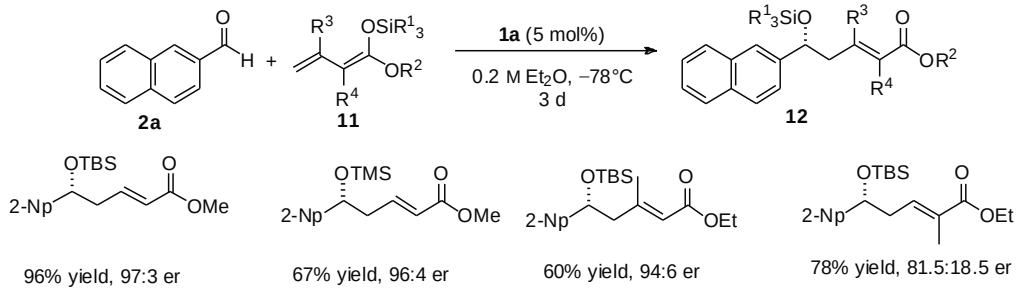
Interestingly, the aldol process is indeed promoted even in the presence of 2,6-di-*tert*-butyl-4-methyl pyridine. This base is known to inhibit any Brønsted acid catalysis and has previously been used to differentiate between Lewis acid- and Brønsted acid-catalyzed pathways. Mechanistically, we propose the reaction to proceed *via* a silylated imide **8**, which is generated upon initial reaction of catalyst **1a** with the ketene acetal. We could demonstrate by ^{1}H-NMR that the ketene acetal **3a** rapidly silylates the catalyst and a more detailed analysis of the *in situ* generated species by NOESY-^{1}H-NMR, ^{29}Si-NMR, and ^{15}N-NMR with ^{15}N enriched **1a**, actually revealed the existence of *N*-*O*-silylotropy. To date it is not clear if *N*-silyl imide **8a,** *O*-silyl imide **8b,** or both are catalytically active species. Aldehyde activation is then realized via silyl transfer from silylated imide **8**, generating an oxonium ion. Asymmetric induction occurs via stereochemical communication within ion pair **9**, consisting of the disulfonimide anion and the *O*-silylated oxonium cation. Its reaction with the ketene acetal then provides the *Mukaiyama* aldol product via ion pair intermediate **10**.



Thus, rather than trying to fight the silylium-catalysis pathway by using a large amount of another competing chiral Lewis acid, as has been tried so hard before, our approach capitalizes on the high inherent silylium-reactivity. Since the chiral disulfonimide counteranion is part of a close contact ion pair, also in the transition state, asymmetric induction is achieved.

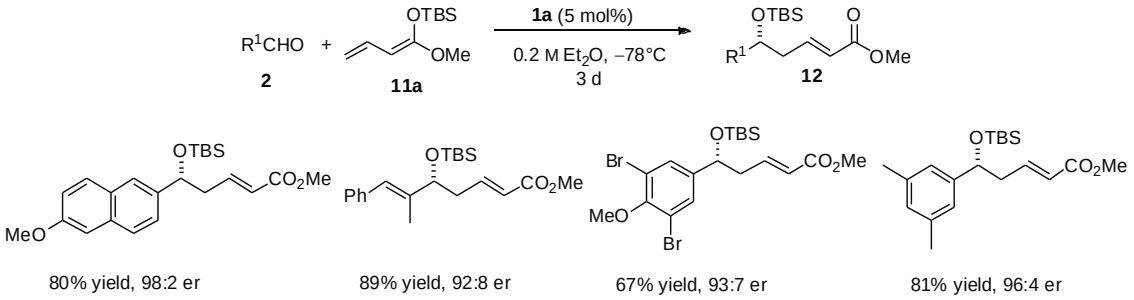
Furthermore, binaphthyl-derived disulfonimide **1a** was also very successfully employed in vinylogous *Mukaiyama* aldol reactions. Studying the influence of the silyl group and the ester substituent in various vinylogous nucleophiles **11** revealed that the silyl group

had only little influence on the reaction outcome, while the ester substituent proved to be important in terms of reactivity. The methyl ester showed high reactivity and delivered products with high isolated yields, while increasing the ester bulkiness



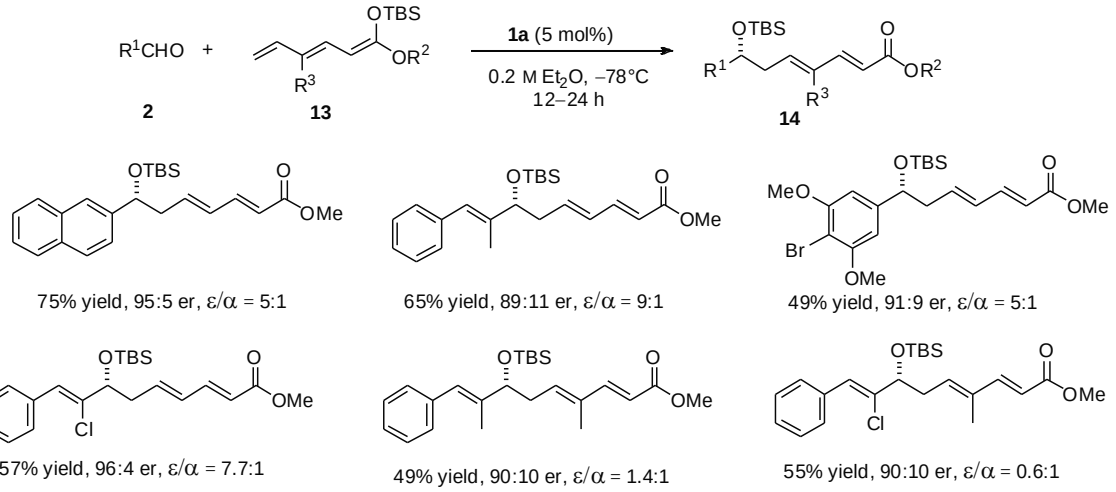
towards a *tert*-butyl group significantly reduced the yields. Introduction of substituents in nucleophiles **11** revealed, that a substituent in β-position is well tolerated, whereas substitution in the α-position furnished the product **12** in somewhat decreased enantioselectivity. All reactions had γ/α-ratios higher than 50:1.

A preliminary evaluation of the aldehyde **2** scope revealed that electron-rich or neutral aromatic aldehydes clearly provide superior results, but electron-poor substrates still enable the reaction to occur, furnishing good enantioselectivities and γ/α-ratios higher than 40:1.



Moreover, our catalytic system could be employed in the previously unexplored bisvinylogous version of the *Mukaiyama* aldol reaction furnishing α,β,γ,δ-unsaturated esters **14** in a single step. The system is particularly suited for aromatic and cinnamaldehyde derivatives, furnishing the desired products **14** in high enantioselectivities and good yields. The introduction of a methyl group (**13**, R^3 = Me), gave products in good enantioselectivities but somewhat lower yields. As predicted by DFT-calculations, the terminal ε-selectivity (up to 9:1) proved to be less distinct compared to the γ-selectivity in the vinylogous systems.

In summary, a highly efficient and enantioselective *Mukaiyama* aldol reaction has been developed with turnover numbers of up to 8,800. Moreover, we have developed



efficient and easily applicable, disulfonimide-catalyzed vinylogous and bisvinylogous *Mukaiyama* aldol reactions. These extended aldolizations display good to excellent enantioselectivities and have a remarkably broad ketene acetal scope. Highly enantioselective catalytic asymmetric bisvinylogous aldol reactions of any type have previously been unknown. The proposed mechanism suggests a general solution to problems of asymmetric Lewis acid catalysis, associated with non-enantioselective "background" reactions promoted by the achiral R_3Si-cation.

Publications resulting from this research area: 364, 382, 424

External Funding: Sanofi-Aventis (L. Ratjen); Deutsche Forschungsgemeinschaft (SPP 1179, Organocatalysis); Alexander von Humboldt Foundation (Stipend to K. Rabalakos); Spanish Ministerio de Educación y Ciencia (Fellowship to Pi. García-García and Pa. García-García)

Cooperations: E. Y.-X. Chen (Fort Collins, USA); V. Dalla (Le Havre, FR); D. Trauner (Munich, DE); A. Fürstner (Mülheim/Ruhr, DE)

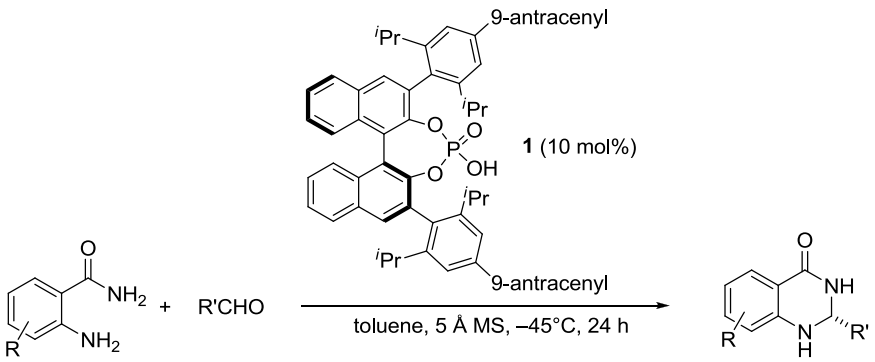
2.2.5 Research Area "Catalytic Asymmetric Acetalizations" (B. List)

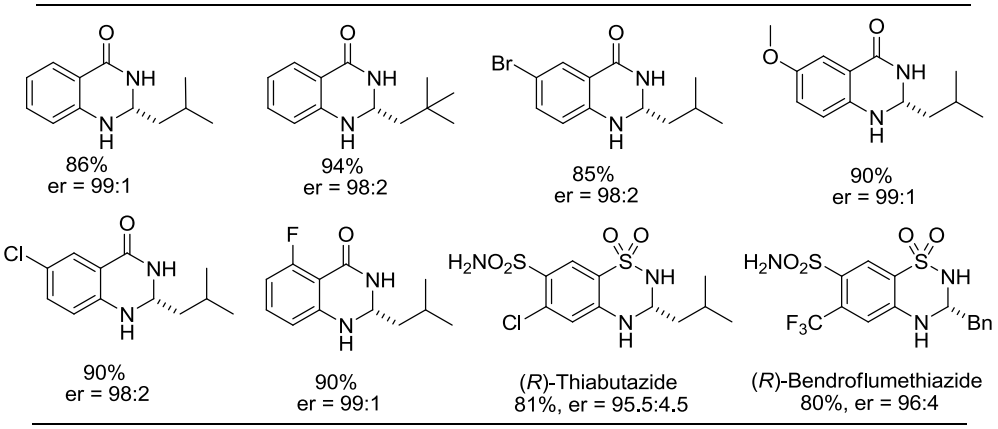
Involved: X. Cheng, S. Vellalath, I. Čorić, S. Müller

Objective: Stereogenic acetals are ubiquitous in natural products, ranging from simple carbohydrates to complex spiroketal polyketides. Controlling their relative and absolute configuration can be extremely important. For example, starch and cellulose only vary in the configuration at their anomeric acetal stereocenter. The importance of chiral acetals is further illustrated by their occurrence in a variety of chiral pharmaceuticals and their potential as diastereocontrolling elements in organic synthesis. Nevertheless, methods for the enantioselective synthesis of stereogenic acetals are very limited and usually based on chiral starting materials or reagents.

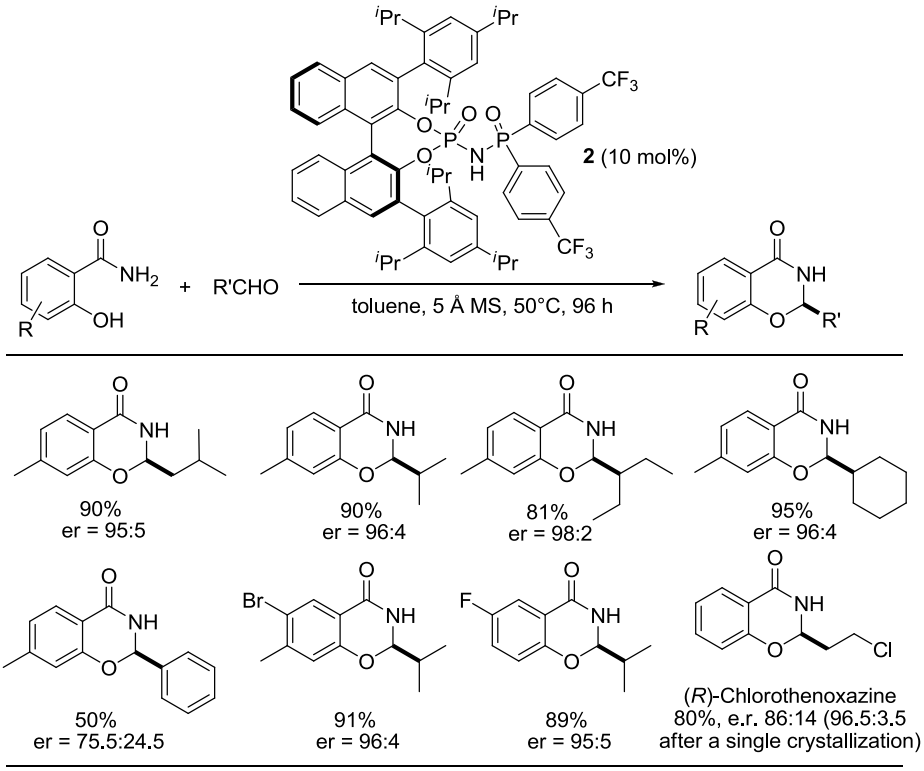
The aim of this project is the development of catalytic and highly enantioselective acetalization reactions resulting in formation of *N*, *N*-, *N*,*O*-, and *O*,*O*-acetals.

Results: As part of our interest in asymmetric acetalization reactions, we have developed direct enantioselective syntheses of cyclic *N*,*N*- and *N*,*O*-acetals from aldehydes. In a condensation reaction of *o*-aminobenzamides and aliphatic aldehydes phosphoric acid catalyst **1**, which we have previously developed in our group, delivered chiral *N*,*N*-acetals in high yield and with high enantioselectivity. The methodology has been applied to the first asymmetric synthesis of several antihypertensive aminal drugs including (*R*)-Thiabutazide.

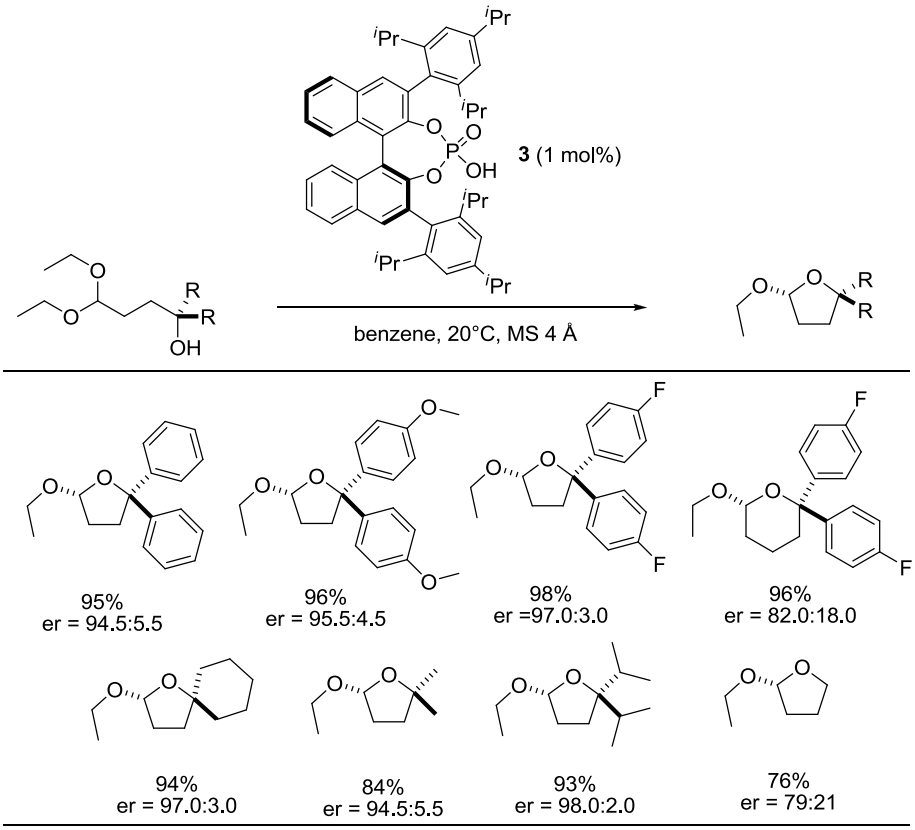




A structurally related condensation reaction of *o*-hydroxybenzamides and aliphatic aldehydes to benzoxazinones proved to be very challenging when we investigated a variety of established chiral catalysts. Therefore we embarked on the development of a new chiral Brønsted acid catalyst for the direct asymmetric synthesis of *N*,*O*-acetals from aldehydes. An *N*-phosphinyl phosphoramide has been designed as a new motif for asymmetric Brønsted acid catalysis. Readily accessible catalyst **2** proved to be highly efficient and enantioselective in catalyzing the first direct asymmetric *N*,*O*-acetalization of aldehydes. The synthetic utility of this methodology was demonstrated with the first catalytic asymmetric synthesis of the analgesic pharmaceutical (*R*)-chlorothenoxazine.

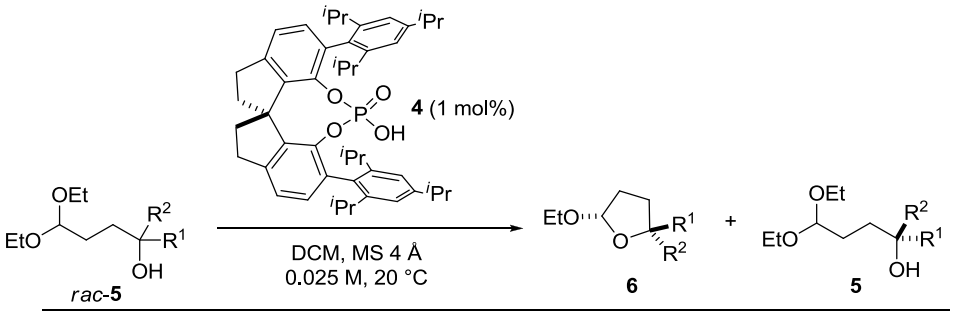


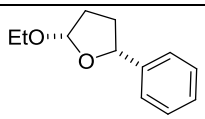
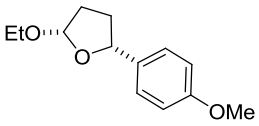
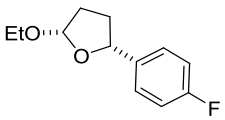
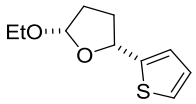
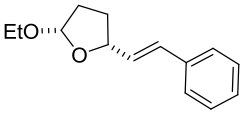
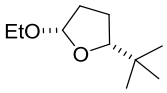
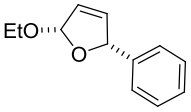
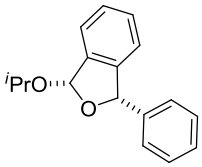
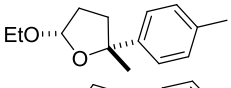
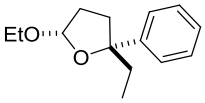
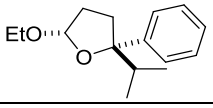
O,O-Acetals presented an additional challenge as enantioselective additions to oxocarbenium ion intermediates that could potentially lead to chiral *O,O*-acetals, are much less explored compared to additions of nucleophiles to imines. We envisioned a catalytic enantioselective synthesis of this fundamental functional group in organic chemistry via a transacetalization reaction. The chiral phosphoric acid TRIP (**3**) was found to be an efficient and highly enantioselective catalyst for intramolecular transacetalization reaction of hydroxyacetals enabling the asymmetric synthesis of acetals with the acetal carbon as the only stereogenic center. In addition, to the best of our knowledge, this reaction represents the first example of phosphoric acid catalyzed enantioselective addition of nucleophiles to simple *O,O*-acetals.

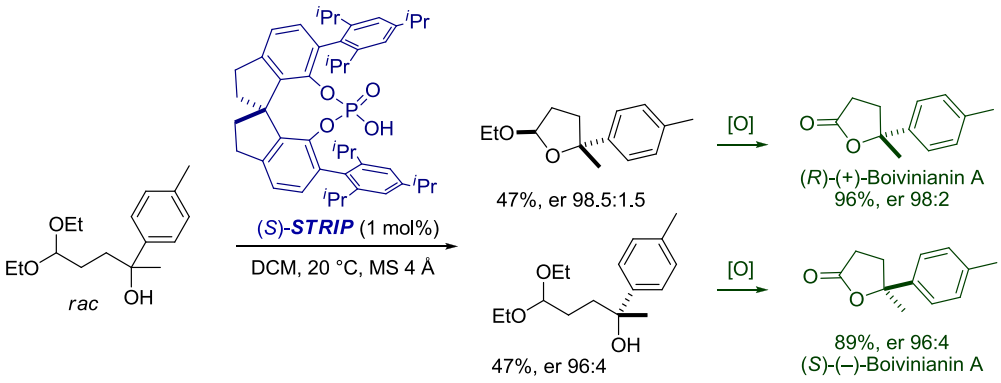


Further expanding on the asymmetric transacetalization reaction we have recently developed a superbly enantioselective kinetic resolution of homoaldol acetals **5** that is catalyzed by *STRIP* (**4**) representing a new class of phosphoric acid catalyst. Our kinetic resolution is a very atom economic method that, unlike common alternative resolution methods, does not require any stoichiometric reagents, and forms ethanol as the only byproduct. The acetal group in cyclic acetals **6** can be easily modified, e.g. oxidized, reduced or substituted giving access to enantioenriched tetrahydrofuranes and γ-

butyrolactones. The current method is applicable to the resolution of a wide range of secondary and tertiary homoaldols.



entry	conv. (time)	**6**	er **6**	dr **6**	er **5**
1	55% (18 h)		97:3	13:1	98.5:1.5
2	55% (16 h)		97:3	12:1	98:2
3	54% (14 h)		96.5:3.5	13:1	97.5:2.5
6	53% (14 h)		97.5:2.5	19:1	98.5:1.5
7	56% (14 h)		98:2	8:1	98:2
8	55% (4 h)		93.5:6.5	19:1	98:2
10	54% (1 h)		89:11	> 50:1	95:5
11	55% (12 h)		89.5:10.5	44:1	96.5:3.5
13	55% (10 h)		98.5:1.5	9:1	96:4
14	55% (12 h)		98.5:1.5	9:1	98.5:1.5
15	55% (28 h)		97.5:2.5	7:1	92:8



This approach could be utilized in a short synthesis of both enantiomers of boivinianin A, illustrating the power of our methodology to access and utilize both homoaldol kinetic resolution products.

In summary, we have developed efficient organocatalytic asymmetric direct *N*,*N*- and *N*,*O*-acetalizations of aldehydes. For *N*,*O*-acetalization a chiral *N*-phosphinyl phosphoramide was developed as a novel powerful Brønsted acid motif. The synthesis of *O*,*O*-acetals was accomplished via a catalytic asymmetric transacetalization reaction, which represents the first example of phosphoric acid catalyzed enantioselective addition of nucleophiles to simple *O*,*O*-acetals. The asymmetric transacetalization was subsequently applied to the highly enantioselective resolution of acetal protected aldehyde homoaldols catalyzed by a newly designed spirocyclic phosphoric acid STRIP.

Publications resulting from this research area: 18, 300, 301, 412

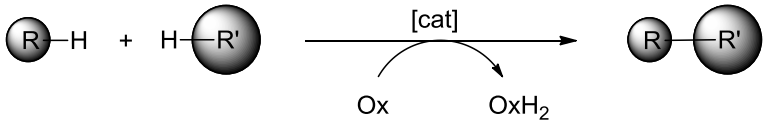
External funding: Deutsche Forschungsgemeinschaft; Alexander von Humboldt Foundation; Fonds der Chemischen Industrie

Cooperations: none

2.2.6 Research Area "Oxidative Coupling Reactions for the Formation of Carbon-Carbon Bonds" (M. Klußmann)

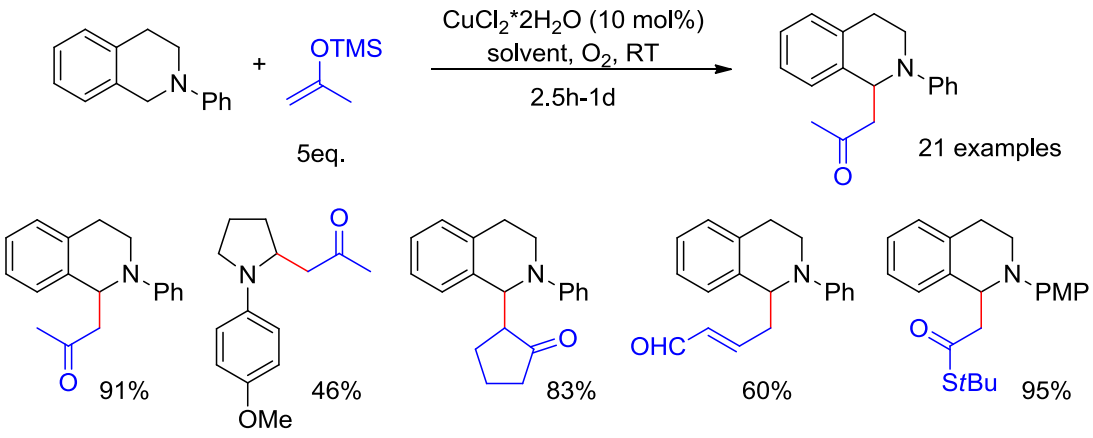
Involved: E. Böß, Á. Pintér, A. Sud, D. Sureshkumar

Objective: The activation of carbon-hydrogen bonds for chemical synthesis is a longstanding goal in the chemical community. The direct substitution of hydrogen in C-H bonds by the desired fragment creates interesting synthetic alternatives to the more common multi-step approach of first introducing reactive functional groups. Instead, only one step is needed and very simple substrates can be used, as C-H bonds are basically ubiquitous in organic compounds. The transformation of two C–H bonds into a new C-C bond can be achieved by oxidative coupling, requiring a stoichiometric amount of an oxidizing reagent or a catalyst together with a terminal oxidant:

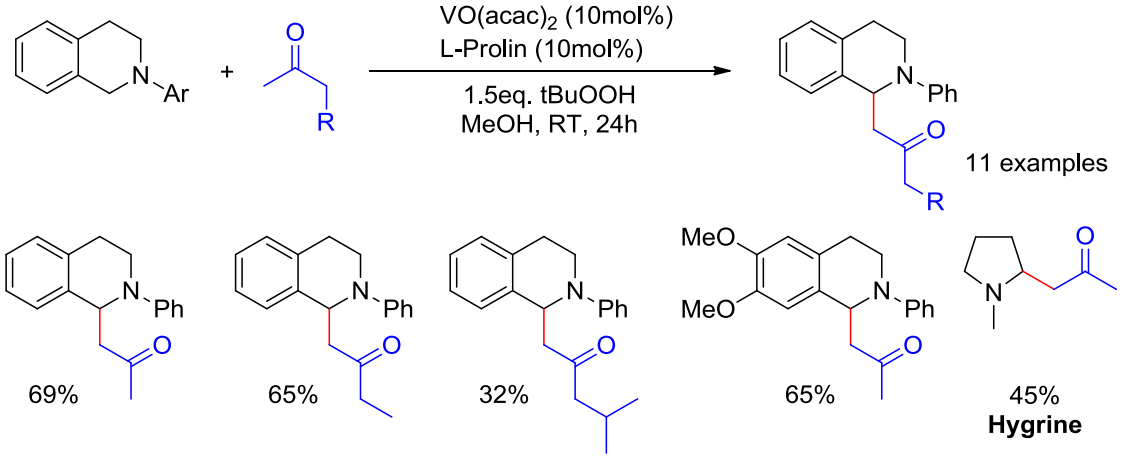


Many of these reactions, however, still need harsh conditions, expensive noble metal catalysts or synthetic oxidants, producing unwanted cost and waste. We aimed to develop oxidative coupling reactions for the formation of C-C bonds using mild conditions and preferably elemental oxygen as oxidant to create more sustainable methods for organic synthesis.

Results: We have developed two different methods for the coupling of tertiary amines with ketones using transition metal catalysis. Using copper catalysis, amines can be oxidatively coupled with silyl enolates or ketene acetals, furnishing amino-ketones, aldehydes and esters. The reaction requires only a simple copper salt and elemental oxygen; it proceeds fast at ambient temperature and generally gives high yields:

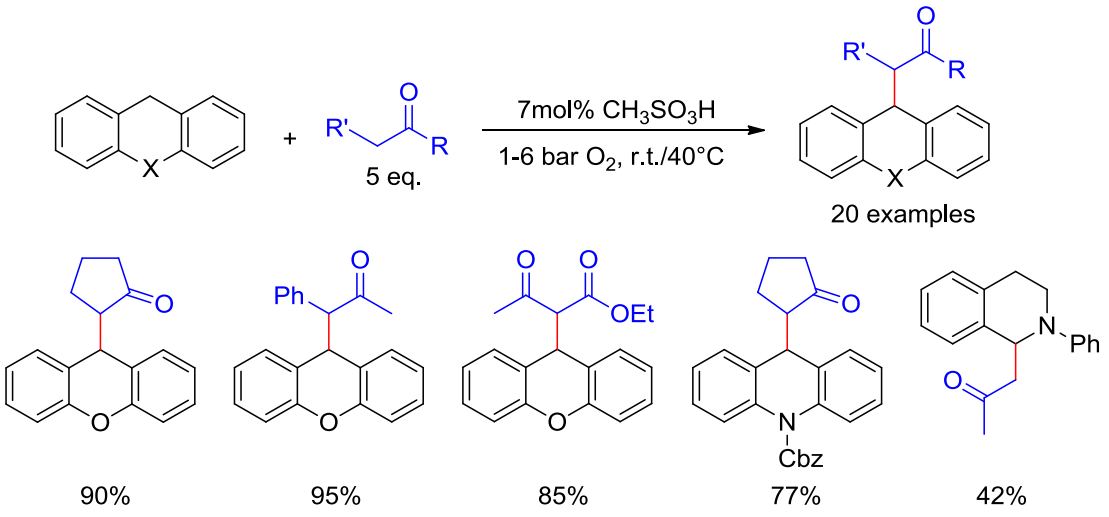


In order to utilize free ketones instead of preformed enolates, we developed a combined metal- and organocatalysis approach. The combination of a simple vanadium complex and *tert*-butyl hydroperoxide was used to oxidatively activate tertiary amines while proline was used to activate ketone nucleophiles via enamine catalysis, resulting in an oxidative Mannich-type reaction. This method could be applied to the one-step total synthesis of the alkaloid hygrine.



Attempts at performing these reactions stereoselectively have failed so far, giving at best an enantiomeric excess of 17% with a prolinol-derivative as chiral organocatalyst.

Recently, we have discovered a surprising oxidative coupling that proceeds without any redox-active catalyst. Xanthene, acridanes and tetrahydroisoquinolines are coupled with ketones or activated esters simply by stirring the substrates without additional solvents under oxygen in the presence of catalytic amounts of a strong Brønsted acid like methanesulfonic acid:



The reactions are believed to proceed via hydroperoxides formed by autoxidation, which would then undergo acid-catalyzed substitution reactions with the carbonyl

nucleophiles. Accordingly, we have termed this reaction “autoxidative coupling”. Its unprecedented simplicity and sustainability could serve as a model for future developments of green cross-coupling reactions.

Publications resulting from this research area: 265, 266, 339, 375

External funding: Alexander von Humboldt Foundation (stipend to D. Sureshkumar); Fonds der Chemischen Industrie

Cooperations: none

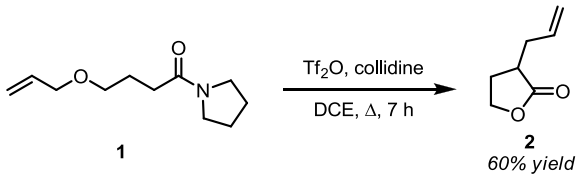
2.2.7 Research Area "Electrophilic Activation of Amides / Pericyclic Reactions of Keteniminium Derivatives" (N. Maulide)

Involved: C. Madelaine, D. Petkova, V. Valerio, M. Winzen

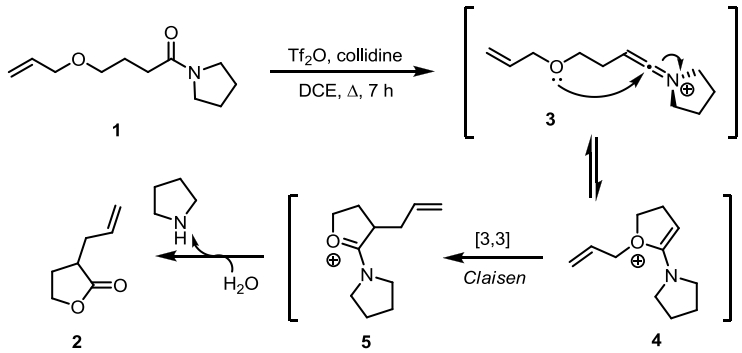
Objective: The selective activation of amides by interaction with suitable electrophilic reagents allows access to novel reactivity manifolds and opens up intriguing perspectives in synthesis. In particular, the *in situ* preparation of keteniminium salts for subsequent [2+2] cycloadditions is a well-known transformation, although the chemistry of those intermediates is scarcely explored beyond four-membered ring formation.

The aim of this project is the development of new pericyclic cascade transformations of keteniminium salts generated *via* electrophilic activation of amides.

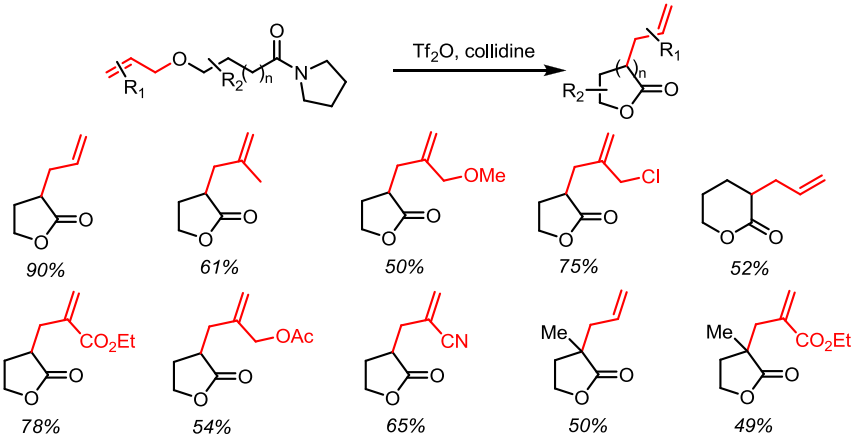
Results: This area of research is predicated on our original observation that electrophilic activation of the γ-alkoxyamide **1** under the typical conditions for generation of an intermediate keteniminium salt (triflic anhydride and a base) did not lead to the anticipated [2+2] cycloadduct. Instead, we were surprised to observe the *exclusive* formation of α-allyl butyrolactone **2**.



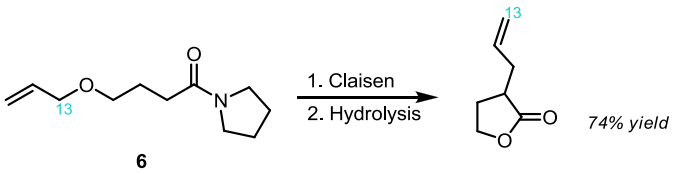
Mechanistically, we assume the reaction to proceed as depicted below. Accordingly, after initial activation of the amide carbonyl by the electrophilic reagent, elimination to form keteniminium **3** probably takes place. The enhanced electrophilicity of this intermediate then triggers an unusual ether nucleophilic addition step, which may be reversible. This step, however, generates a vinyl-allyl-oxonium **4** which is ideally poised to undergo a [3,3]-sigmatropic rearrangement. Such a reorganization should lead to the stabilized carbenium ion **5**, hydrolysis of which then accounts for the formation of lactone **2**.



We have developed this transformation into a general synthesis of γ-butyro- and δ-valerolactones. As shown, the mild conditions of this rearrangement tolerated a variety of functional groups, including ester, nitrile and halide moieties. The selective activation of the amide functional group of the starting materials in the presence of the latter moieties highlights the chemoselectivity of this procedure.

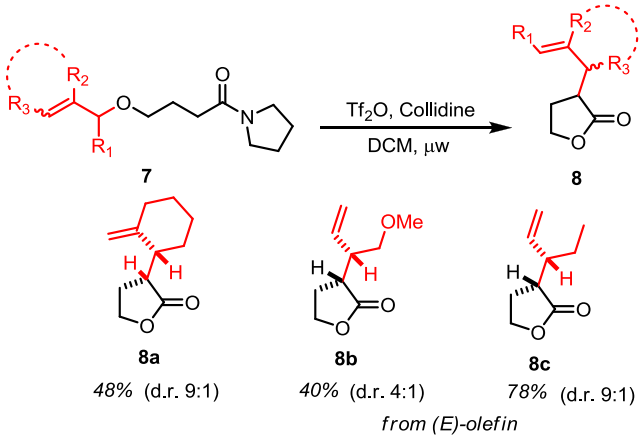


Allylic inversion was unambiguously established through rearrangement of the ^{13}C-labelled amide **6**.



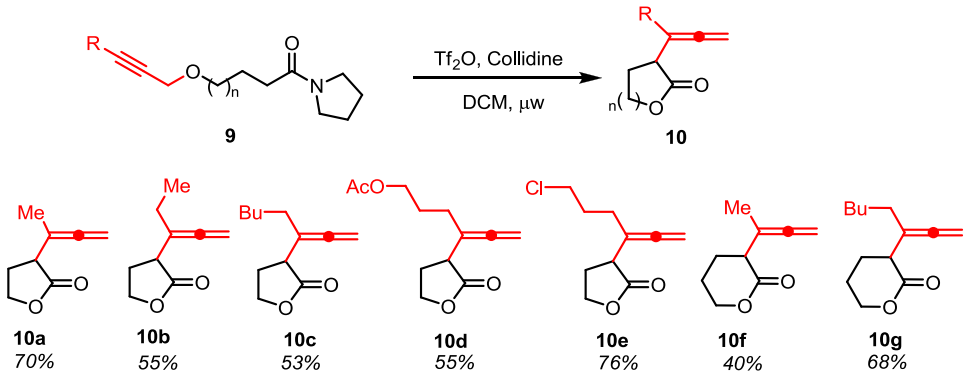
6

This unequivocal result suggested opportunities for preparation of diastereoenriched lactones with challenging reaction patterns. Indeed, when the readily available (*E*)-amides **7a** and **7b-c** were employed in the reaction, high diastereoselectivities for the formation of products **8a** and **8b-c** were observed.



In addition, subjection of propargyl ether-containing amides **9** to the reaction conditions resulted in smooth rearrangement to α-allenyl lactones **10** in moderate to very good yields. As before, the reaction tolerated a broad variety of functional groups, including

esters and halides. It is particularly noteworthy that none of the lactones **10** were known in the chemical literature prior to our studies.



In summary, we have developed a novel Claisen-like rearrangement of keteniminium intermediates generated through electrophilic amide activation. Future work will focus on the broadening of the concepts presented herein to more complex cascade rearrangements.

Publications resulting from this research area: 355

External funding: Deutsche Forschungsgemeinschaft; Alexander von Humboldt Foundation (stipend to C. Madelaine)

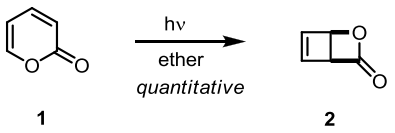
Cooperations: L. Veiros (Lisbon, PT)

2.2.8 Research Area "Stereoselective Synthesis of Cyclobutenes" (N. Maulide)

Involved: D. Audisio, F. Frébault, M. Luparia, M. T. Oliveira, U. Specht, E. Wöstefeld

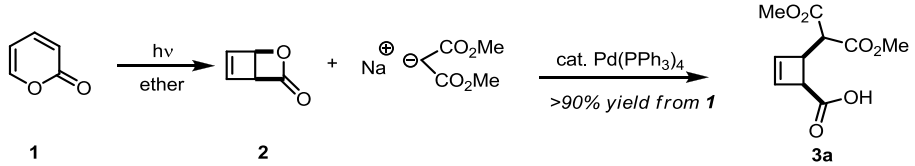
Objective: The preparation of small rings has been a pervasive topic in organic synthesis ever since chemists realized the potentialities and fascinating properties associated with their inherent ring strain. Furthermore, the number of isolated natural products which contain, embedded in their core structure, a cyclopropane or cyclobutane does not cease to grow. Nevertheless, there is a serious lack of general methodologies for the preparation of optically active functionalized cyclobutane derivatives. This is even more so when one considers cyclobut**e**nes, uniquely attractive building blocks due to the synthetic versatility associated with the presence of the additional carbon-carbon double bond embedded in the four membered ring.
The aim of this project is the development of new strategies for the stereoselective preparation of versatile cyclobutene building blocks starting from 2-pyrone.

Results: 2-Pyrone **1** is known to undergo photomediated isomerization to the unstable oxabicyclo[2.2.0]hexane **2**. Historically, this reaction has been the subject of considerable scrutiny, since it still constitutes the surest path to the synthesis of the elusive anti-aromatic compound cyclobutadiene (*via* decarboxylation of **2**).



1 **2**

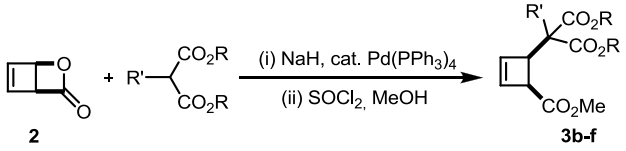
This project has its origins on our realization that compound **2** is, structurally, an allylic ester susceptible of ionization by a suitable zero-valent, electron-rich transition metal. We have achieved the first catalytic, stereoselective transformations of **2** that suggest a versatile synthesis of functionalized cyclobutenes in only two operations from 2-pyrone. In preliminary experiments, we found that treatment of **2** with sodium dimethylmalonate in the presence of 5 mol% $Pd(PPh_3)_4$ led to a nearly quantitative yield of the *cis*-cyclobutene carboxylic acid **3a** as a single diastereomer. The structure of **3a** was confirmed unequivocally by X-ray analysis.



1 **2** **3a**

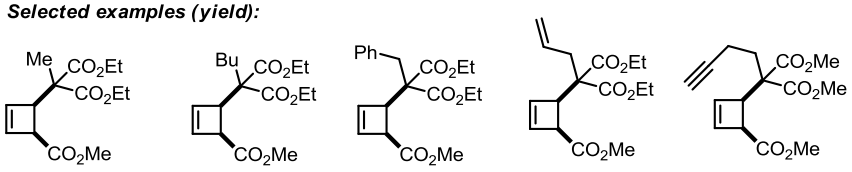
Following optimization of the reaction conditions, the scope for this transformation was evaluated. As depicted below, a variety of active methylene compounds could be used

as nucleophilic partners. The corresponding cyclobutene carboxylic acids (or the derived methyl esters) were formed in good to excellent yields.



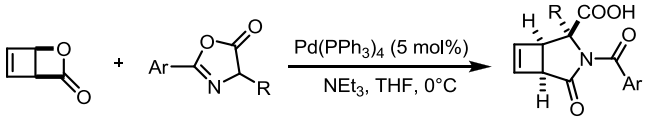
2 **3b-f**

Selected examples (yield):



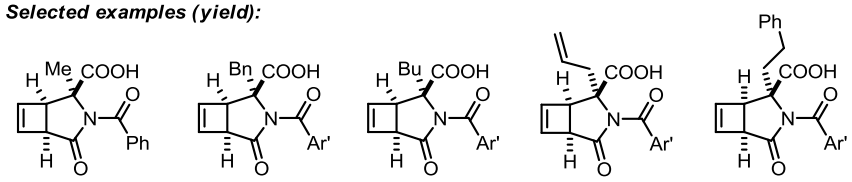
3b (80%) **3c** (74%) **3d** (83%) **3e** (76%) **3f** (88%)

In addition, we found that azlactones of the general structure **4** also function as competent nucleophiles in this process. Incidentally, the products obtained were not the expected alkylated acids but rather the rearranged azabicycles **5**. The structure of **5a** was confirmed unambiguously by X-ray analysis.



1 **4** **5**

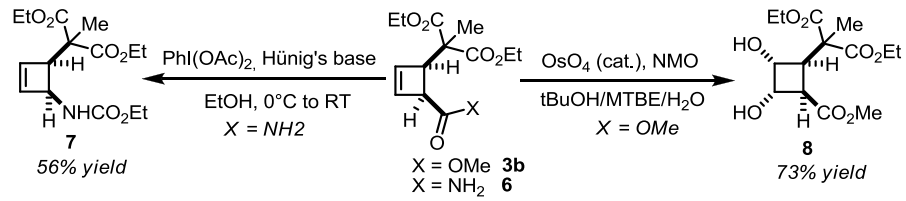
Selected examples (yield):



5a 57% **5b** 46% **5c** 57% **5d** 56% **5e** 47%

Ar' = (p-NO2)C6H4

The adducts formed through this simple reaction sequence proved amenable to a variety of transformations, exploiting the latent reactivity of the functional groups generated. For instance, the strained cyclobutene double bond of **3b** could be easily dihydroxylated in good yield, affording the tetrasubstituted cyclobutane **8** with complete control of all four stereogenic centers. Aiming at biologically relevant scaffolds, the amide derivative **6** smoothly underwent Hofmann rearrangement to the novel constrained, fully protected cyclobutene-γ-amino acid **7**.



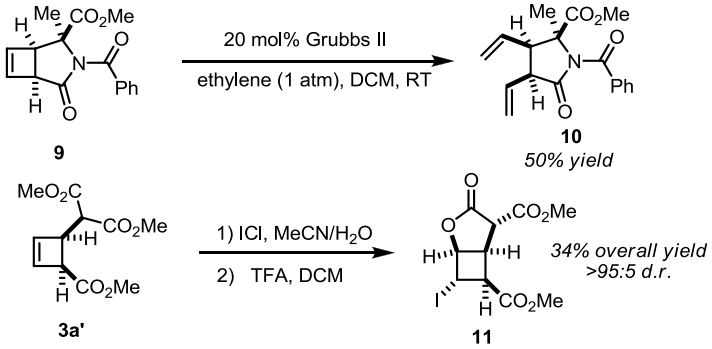
7 *56% yield*

X = OMe **3b**
X = NH_2 **6**

8 *73% yield*

Other manipulations further showcase the synthetic advantage deriving from the cyclobutene double bond and hint at potential applications of this method in total synthesis. Thus, ROM/CM of azabicycle **9** under an atmosphere of ethylene (1 atm) promoted by Grubbs' second generation catalyst afforded the diastereopure pyrrolidinone **10**, reminiscent of kainic and domoic acid derivatives.

On the other hand, a two-step halolactonization of triester **3a'** led to compound **11**, possessing the core structure of Pestalotiopsin A. It is testament to the power of this approach that synthetically relevant compounds can be derived from 2-pyrone in no more than three straightforward synthetic operations.



In summary, we have developed a new and concise synthesis of functionalized cyclobutenes. The overall process reported here combines the efficiency of clean, highly efficient photochemical reactions with the powerful selectivity that can be imparted by metal catalysis and should find broad applications in synthesis. Current and future work will focus on broadening the scope of this and other related methodologies.

Publications resulting from this research area: 310, 311

External funding: Deutsche Forschungsgemeinschaft; Alexander von Humboldt Foundation (stipend to M. Luparia)

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

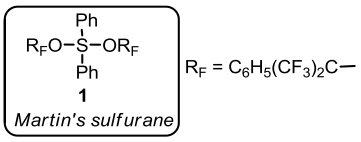
2.2.9 Research Area "Sulphur Chemistry Revisited / New Ylide Transfer Reactions" (N. Maulide)

Involved: X. Huang

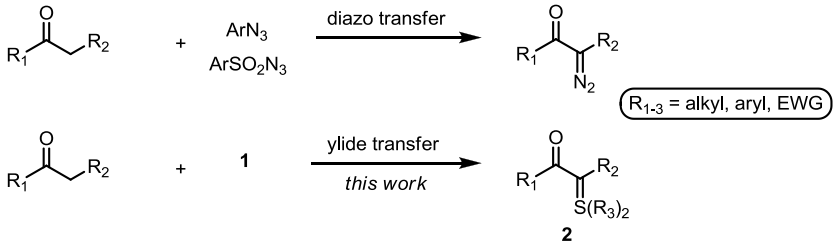
Objective: Sulfur ylides occupy a prominent place among so-called "textbook reagents" in organic chemistry. Their use as connective reagents for the preparation of small rings (the *Corey-Chaykosvky* reactions) and in cascade cyclizations is well established in the literature. Recently, they have garnered interest as potential carbene donors for metal complexes, presenting clear advantages when compared to the diazo compounds that are almost ubiquitously employed in that role. Nevertheless, their synthesis is still a multi(≥ 2)step procedure and applications in transition metal catalysis remain limited.

The aim of this project is the development of a new concept of "ylide transfer" to carbonyl derivatives and heteroaromatic compounds that directly delivers sulfur ylides in a single step.

Results: Martin's sulfurane **1**, named after the scientist who first prepared it in 1971, is widely used as a reagent for dehydration of alcohols in organic synthesis.

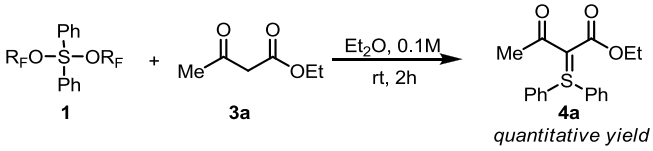


We speculated that **1** might behave as an ylide transfer reagent to suitable carbonyl derivatives, thus yielding diphenylsulfonium ylides (**2**, R^3=Ph) in a single step.

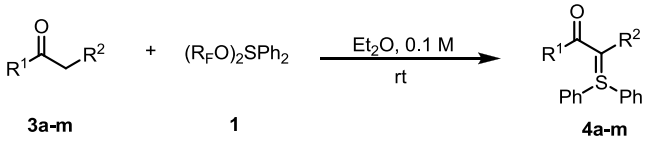


If successful, this would constitute an interesting novel concept of "ylide transfer", the long-awaited analogue of the well-known "diazo transfer" family of reactions.

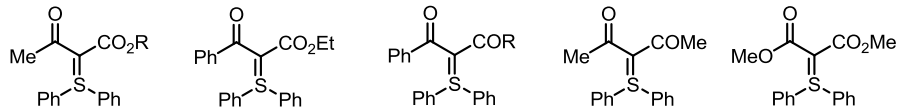
In initial experiments, we were delighted to find that **1** reacts with ethyl acetoacetate **3a** to afford the sulfur ylide **4a** in quantitative yield (structure confirmed by X-ray analysis). The striking simplicity of this reaction stimulated us to investigate it further.

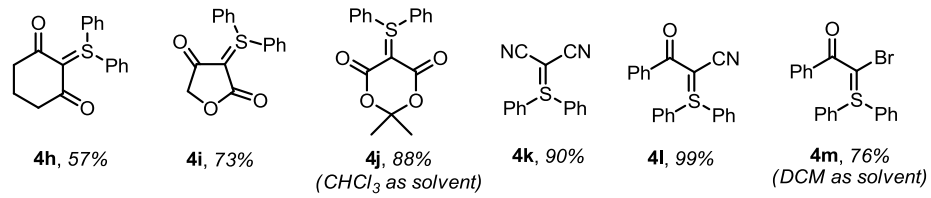


Additional experiments verified the generality of this observation. As displayed below, different active methylene compounds **3a-m** successfully underwent the reaction, affording the corresponding sulfur ylides **4a-m** in excellent yields. Notably, this transfer process was successful with β-ketoesters, β-diketones and even diesters.



Selected examples:

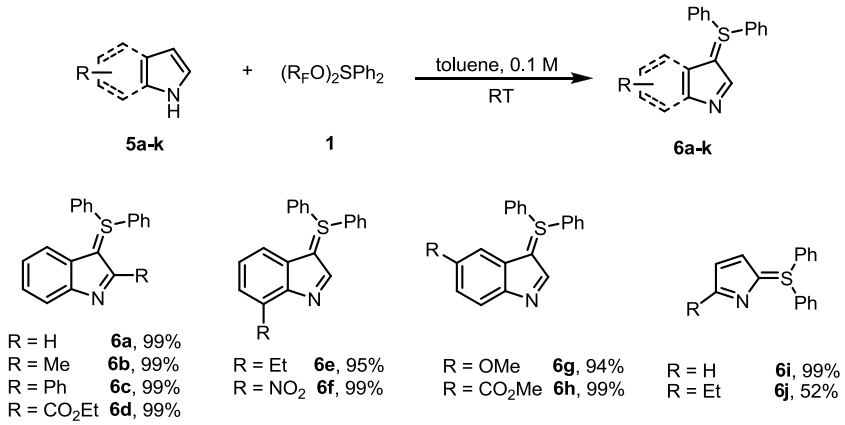




Dimethylmalonate **3g** afforded the corresponding ylide **4g** in very high yield. Cyclic diketones and diesters **3h-j** also responded well to this reaction, as did nitriles **4k-l**. The α-bromoketone **3m** merits special notice, as related compounds have been accessed only by cumbersome bromination/deprotonation of the corresponding, non-halogenated ylides. In contrast, ylide **4m** is directly available from bromoacetophenone in a single step using this procedure.

We further speculated that **1** might be capable of "Friedel-Crafts-like" dearomatization of suitable heterocycles. In the event, we discovered that indoles **5** reacted smoothly with **1** within 2 hours at room temperature, affording the corresponding indole-3-sulfonium ylides in excellent yields. As can be seen, this reaction appears to possess a broad scope. Indoles **5a-h** bearing a notable scope of substituents ranging from electron-donating to electroneutral and strong electron-withdrawing were perfectly tolerated.

Moreover, considerable flexibility is allowed regarding the substituent locus. All the ylides **6a-h** were obtained in quantitative yields.



In addition, pyrrole **5i** and its derivative **5j** also performed competently in this reaction. As might be expected, pyrrole 2-sulfonium ylides **6i-j** were obtained as the exclusive regioisomers. The robustness of this reaction is further apparent from the ease of scale-up: indole derivative **5d** was easily converted to the corresponding sulfonium ylide (**6d**) on a multigram scale.

In summary, we have developed a new ylide transfer reaction. This process allows a direct, operationally simple synthesis of sulfur ylides from active methylene compounds and heteroaromatics and provides a powerful sulfur equivalent to the well-known diazo transfer reactions. The readily available sulfurane **1** and its exquisite reactivity under particularly mild conditions were decisive to achieve this goal. Indeed, **1** appears uniquely suited to direct, high-yielding syntheses of sulfur ylides and the reactions described herein should find broad applications in synthesis. Further work focuses on detailed study of the fascinating structures of the ylides synthesized and their applications in catalysis.

Publications resulting from this research area: 325

External funding: none

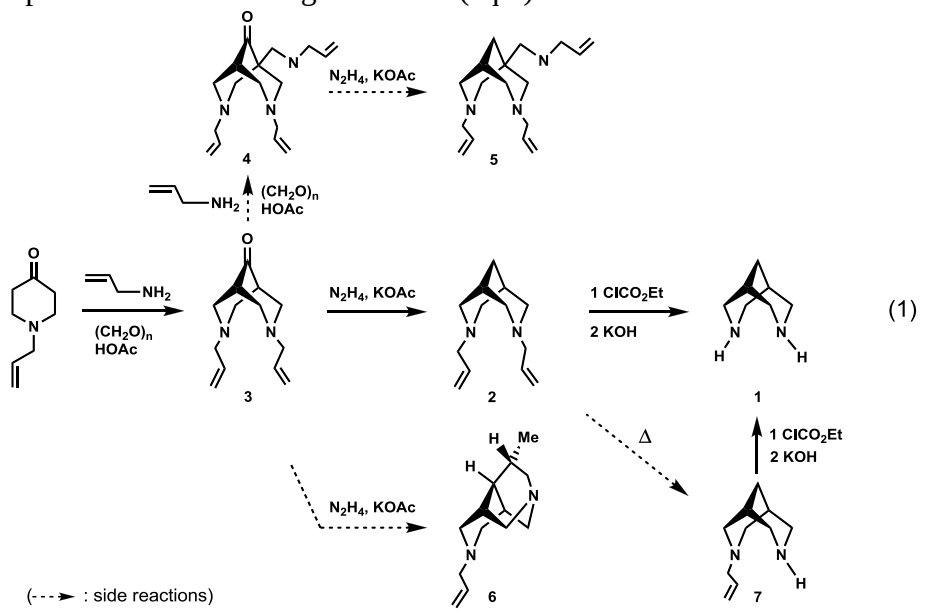
Cooperations: R. Goddard (Mülheim/Ruhr, DE)

2.2.10 Research Area "Immobilization of Bispidine Complexes" (K.-R. Pörschke)

Involved: H. Cui, R. Goddard, U. Blumenthal

Objective: We are interested in the synthesis of substituted bispidine complexes (bispidine = 3,7-diazabicyclo[3.3.1]nonane) and their immobilization on textile fibers as part of a joint project with the German Institute for Textile Research North West (DTNW). The project addresses the question as to whether bispidines are suitable ligands for heterogenization of metal complexes for catalytic purposes. Our contribution to this 2-year project is the synthesis and characterization of various bispidine complexes, which are handed over to DTNW for heterogenization on the textile fibers.

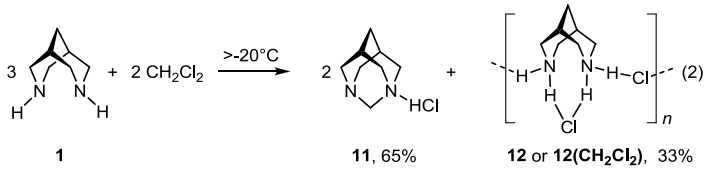
Results: Stimulated by previous experience in the chemistry of *N*,*N*′-dimethyl-bispidine and its nickel(0) complexes (*JACS* **1997**, *119*, 7992), we looked at the syntheses of the parent bispidine (**1**) and *N*,*N*′-diallyl-bispidine (**2**) in more detail. *N*-Allyl-piperidone reacts in a twofold Mannich reaction with formaldehyde and allylamine to give *N*,*N*′-diallyl-bispidinone **3** and some **4**. Wolff-Kishner reduction affords mainly **2** (and some **5**), although an internal cyclization to give tricyclic **6** and partial thermal deallylation generating **7** may also occur. Full deallylation of **2** and **7** yields the parent **1**. We have separated pure **1** and **2** on multigram scales (eq 1).



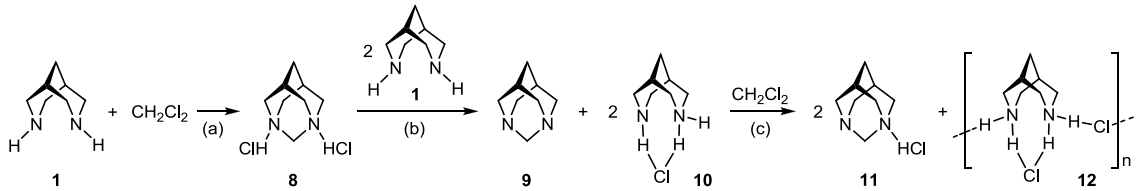
(1)

It turns out that halocarbons are not suited as solvents for reactions of bispidines with inorganic metal salts. It is instructive to look at the reaction of **1** with CH_2Cl_2, which starts as low as > –30°C and which, by nucleophilic substitution of both chloride ions in CH_2Cl_2, results in rapid methylation of **1** to give 1,3-diazaadamantane hydrochloride, $C_8H_{14}N_2$ (HCl) (**11**, 65%), as the main and soluble product. In addition, bispidine bis-

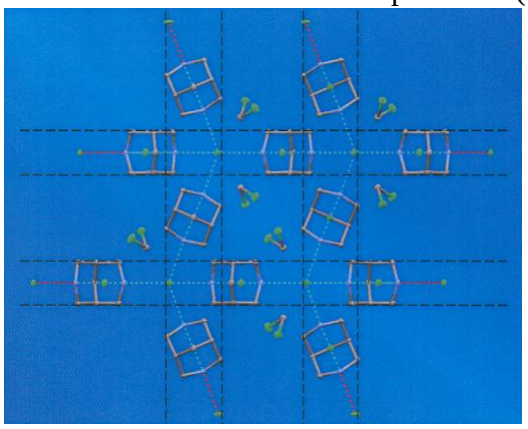
(hydrochloride) crystallizes as an insoluble solid (33%), either kinetically controlled (most frequently) in form of the CH_2Cl_2 solute $[C_7H_{12}(NH_2)_2Cl]Cl{\cdot}CH_2Cl_2$ (**12(CH$_2$Cl$_2$)**) or thermodynamically controlled as solute-free $[C_7H_{12}(NH_2)_2Cl]Cl$ (**12**). Interestingly, **12** and **12(CH$_2$Cl$_2$)** can crystallize simultaneously from the same batch. Under vacuum (20°C), **12(CH$_2$Cl$_2$)** irreversibly loses CH_2Cl_2 to give solvent-free **12**.



Principal intermediate of the synthesis reaction is the 1:1 addition product 1,3-diazaadamantane bis(hydrochloride), $C_8H_{14}N_2(HCl)_2$ (**8**), representing the starting point of a *series of three cascading acid–base reactions*. These involve **1** (a,b), 1,3-diazaadamantane, $C_8H_{14}N_2$ (**9**, c), and bispidine mono(hydrochloride), $C_7H_{12}(NH)_2(HCl)$ (**10**, reacting with itself; c) as bases in a sequence of decreasing basicity.

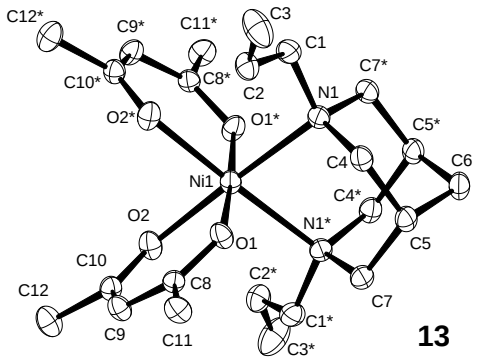


The soluble product **11**, containing one undissociated HCl, is monomeric in the crystal (space group $P2_1/m$, No. 11). Insoluble **12** (*Pbca*, No. 61) and **12(CH$_2$Cl$_2$)** (*Pbcm*, No. 57) consist of infinite zigzag chains of alternating $[C_7H_{12}(NH_2)_2Cl]^+$ cations and Cl^- anions, linked via NH···Cl···HN bridges. The chains in **12** are all uniform and parallel. In contrast, **12(CH$_2$Cl$_2$)** comprises *two types of chains* in a *supramolecular structure*, with different sheets of equivalent and parallel chains stacked crosswise to one another and the CH_2Cl_2 solute molecules located at interstitial positions (see drawing).

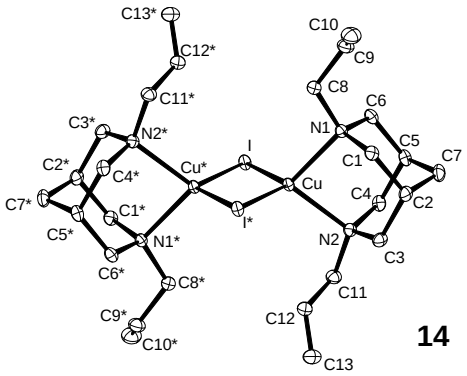


We learnt that in many cases DMF (instead of CH_2Cl_2) is a suitable solvent for reactions of **1** with transition metal salts. A series of Pt(II) complexes with **1** have been prepared and, inter alia, crystallographically characterized. These are not further discussed here.

N,*N*′-Diallyl-bispidine (**2**) reacts with $Ni(acac)_2$ and CuI to quantitatively afford $(C_7H_{12}N_2allyl_2)Ni(acac)_2$ (**13**, blue cubes; *C*2/*c*, No 15) and dimeric $\{(C_7H_{12}N_2allyl_2)$-$Cu(\mu\text{-}I)\}_2$ (**14**, white needles; *P*21/*c*, No 14). Attempts to synthesize a related Cu(II) complex resulted in its reduction to also yield **14**. Complexes **13** and **14** have been successfully immobilized on a polyester fiber by photolysis of the fiber and radical reaction with the *N*-allyl functions. Metal bleeding of the so heterogenized bispidine complexes appears insignificant.

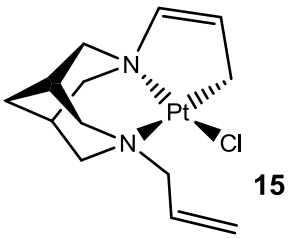


13



14

Reaction of (1,5-hexadiene)$PtCl_2$ with **2** was impaired by an engagement of the *N*-allyl functional group of the bispidine. Displacement of 1,5-hexadiene by **2** affords the expected $(C_7H_{12}N_2allyl_2)PtCl_2$ only as an intermediate, since one *N*-allyl ligand subsequently loses a proton from its NCH_2 group and eliminates HCl. As a result, the C=C bond is shifted and $\{C_7H_{12}N_2(allyl)(CH{=}CH{-}CH_2)\}PtCl$ (**15**) is formed, in which the bispidine is anchored to a σ-allyl ligand, forming a new tridentate ligand to Pt(II).



15

Publications resulting from this research area: none

External funding: Ministry of Economy and Technology (BMWi)

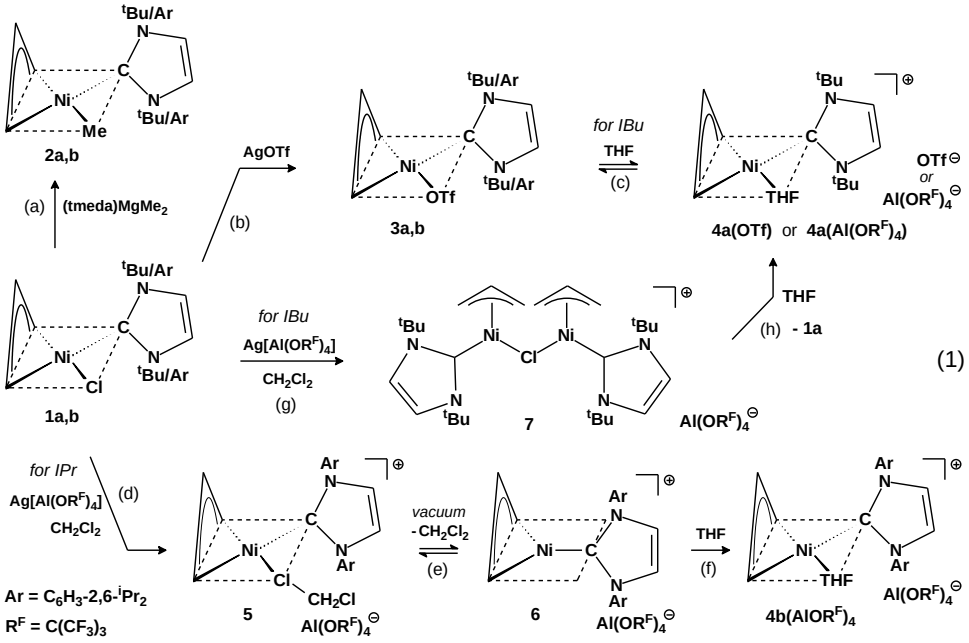
Cooperations: K. Opwis, T. Mayer-Gall (Krefeld, DE)

2.2.11 Research Area "NHC-modified Ni(II) Complexes" (K.-R. Pörschke)

Involved: R. Greven, R. Goddard, W. Ben Mustapha

Objective: Transition metal complexes having *N*-heterocyclic carbene ligands (NHC, Arduengo carbenes) have been widely investigated in recent years. NHCs are superior to phosphines in many aspects and their complexes have found numerous applications in coordination chemistry and catalysis. We have studied the properties of 16-e (π-allyl)Ni(NHC)X and 18-e CpNi(NHC)X complexes, in which X is either hydride, methyl, solvent, or a weakly or non-coordinating ligand. A long-term objective is the generation of coordinatively unsaturated species such as 12-e $[(NHC)NiH]^+X^-$ and $[(NHC)NiCH_3]^+X^-$, in which the Ni–H and Ni–CH_3 functional groups are modified by a single (bulky) carbene ligand. The study continues our previous work on related Pd compounds (*Organometallics* **2005**, *24*, 439; **2007**, *26*, 3236).

Results: The complexes (η^3-C_3H_5)Ni(NHC)Cl (**1a,b**) (NHC = C{N(^{t}Bu)CH}$_2$ (IBu, **a**) and C{N(C_6H_3-2,6-^{i}Pr$_2$)CH}$_2$ (IPr, **b**)) react with (tmeda)$MgMe_2$ to give (η^3-C_3H_5)Ni-(NHC)Me (**2a,b**) in 85% yield (eq 1a). While **2a,b** are stable at ambient temperature, even in air, the corresponding hydrides are still elusive. The reaction of **1a,b** with AgOTf to give (η^3-C_3H_5)Ni(NHC)OTf (**3a,b**) is solvent dependent: synthesis of (η^3-C_3H_5)Ni(IPr)OTf (**3b**) proceeds in THF, whereas decomposition occurs in CH_2Cl_2. In contrast, (η^3-C_3H_5)Ni(IBu)OTf (**3a**) can be prepared in CH_2Cl_2 but partially dissociates in THF to give the ionic solvate [(η^3-C_3H_5)Ni(IBu)(THF)]OTf (**4a(OTf)**) (eq 1b,c).

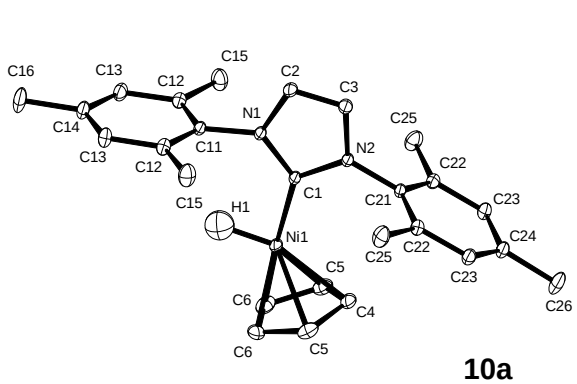


(1)

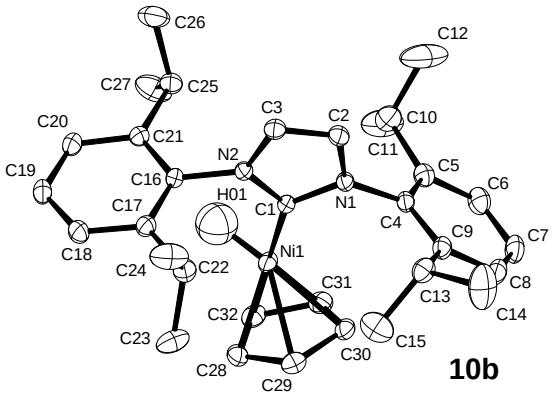
(η^3-C_3H_5)Ni(IPr)Cl (**1b**) reacts with 1 equiv of Ag[Al(OR^F)$_4$] (R^F = C(CF$_3$)$_3$) in CH_2Cl_2 to yield ionic [(η^3-C_3H_5)Ni(IPr)(CH_2Cl_2)][Al(OR^F)$_4$] (**5**), in which the CH_2Cl_2 ligand is labile (eq 1d). According to NMR, the structure of **5** is chiral (C_1) at –80°C. Nevertheless, the IPr ligand has local C_2 symmetry due to rotation about the Ni–$C_{carbene}$ bond. At –30°C syn–syn,anti–anti H-exchange of the allyl protons takes place, leading to an overall C_s symmetry of the complex (local symmetry of IPr is now C_{2v}). The spectra indicate an apparent "π-allyl rotation" and are best explained by reversible dissociation of CH_2Cl_2 and formation of a Y-shape 14-e [(η^3-C_3H_5)Ni(IPr)]$^+$ intermediate/transition state, resulting in transposition of the CH_2Cl_2 and IPr ligands. In fact, at ambient temperature under vacuum **5** releases CH_2Cl_2 to afford isolable [(η^3-C_3H_5)Ni(IPr)]-[Al(OR^F)$_4$] (**6**) (eq 1e). Solid **6** exemplifies a complex of the type [RNi(NHC)]$^+$X$^-$, R representing a 4-e donor. Dissolution of **6** in CH_2Cl_2 restores **5**, while in THF the stable [(η^3-C_3H_5)Ni(IPr)(THF)][Al(OR^F)$_4$] (**4b(Al(OR^F)$_4$)**) (eq 1f) is formed.

(η^3-C_3H_5)Ni(IBu)Cl (**1a**), having the bulkier IBu ligand, reacts with only ½ equiv of Ag[Al(OR^F)$_4$] in CH_2Cl_2 to form dinuclear [{(η^3-C_3H_5)Ni(IBu)}$_2$(μ-Cl)][Al(OR^F)$_4$] (**7**) (eq 1g). **7** represents a mixture of diastereomers (the two Ni centers have the same or opposite chirality) and, as such, is stable at room temperature, which rules out π–σ-allyl isomerization. Upon addition of THF dinuclear **7** splits into **1a** and [(η^3-C_3H_5)-Ni(IBu)(THF)][Al(OR^F)$_4$] (**4a(Al(OR^F)$_4$)**) (eq 1h).

Replacing the π-allyl group with cyclopentadienyl, we have also reacted Cowley's (η^5-C_5H_5)Ni(NHC)Cl (**8a,b**) (NHC = C{N(C_6H_2-2,4,6-Me$_3$)CH}$_2$ (IMes, **a**), C{N(C_6H_3-2,6-^{i}Pr$_2$)CH}$_2$ (IPr, **b**)) with (tmeda)MgMe$_2$ and $LiAlH_4$ to afford 18-e (η^5-C_5H_5)Ni-(NHC)Me (**9a,b**) and (η^5-C_5H_5)Ni(NHC)H (**10a,b**) in high yields (eq 2a,b). (η^5-C_5H_5)-Ni(IBu)Cl, as a possible starting compound, remains unknown. As for the Ni–methyl complexes **9a,b**, the Ni–hydrides **10a,b** are thermally rather stable and furnish in the EI mass spectra (≥ 110°C) the molecular ions M$^+$ in high intensities. According to X-ray structure determinations of **10a,b**, the geometry at Ni is pseudo-trigonal planar. Intere-

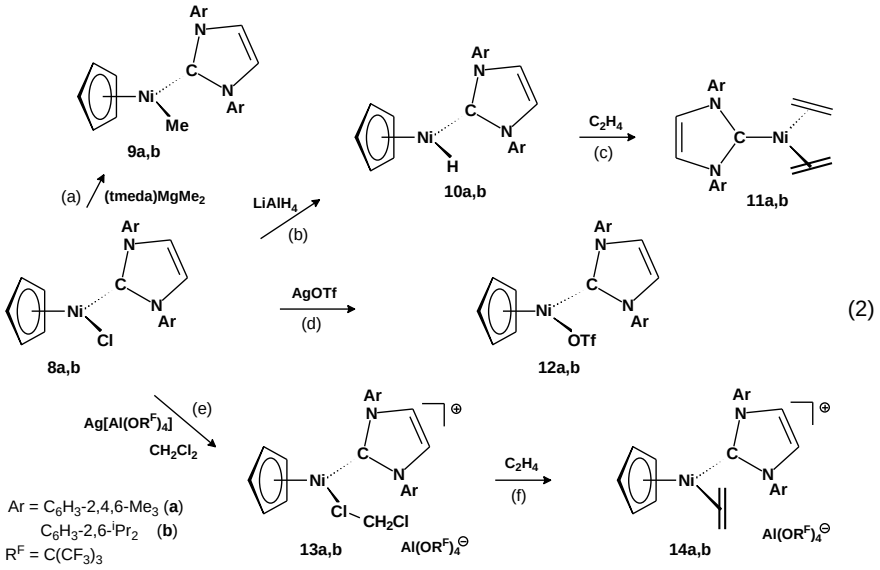


10a



10b

stingly, in **10a** the imidazole ring lies exactly in the coordination plane (which is in fact a mirror plane), in contrast to all other known (η^3-C_3H_5)Ni(NHC)X and (η^5-C_5H_5)Ni-(NHC)X complexes. In **10b**, having the bulkier IPr ligand, the interplanar angle between the imidazole and coordination planes is 35°.



10a,b react slowly with ethene (2 days) to afford, by elimination of CpEt, the Ni(0) complexes (NHC)Ni(C_2H_4)$_2$ (**11a,b**) (eq 2c). Dissolution of **10a,b** in CH_2Cl_2 at ambient temperature leads to recovery of **8a,b**. **8a,b** reacts with AgOTf to give (η^3-C_3H_5)-Ni(NHC)(OTf) (**12a,b**) (eq 2d) and with Ag[Al(OR^F)$_4$] in CH_2Cl_2 (−78°C) to afford ionic [(η^5-C_5H_5)Ni(NHC)(CH_2Cl_2)][Al(OR^F)$_4$] (**13a,b**). Displacement of CH_2Cl_2 in **13a,b** by ethene gives rise to [(η^5-C_5H_5)Ni(NHC)(C_2H_4)][Al(OR^F)$_4$] (**14a,b**) (eq 2e,f).

Publications resulting from this research area: none

External funding: none

Cooperation: none

2.3 Department of Heterogeneous Catalysis

Director:

Ferdi Schüth (born 1960)
Publications: 4, 5, 9, 11, 40, 52, 57, 58, 68, 79, 80, 97, 98, 99, 103, 104, 107, 108, 109, 110, 111, 112, 113, 126, 127, 128, 129,137, 146, 154, 159, 162, 172, 203, 204, 221, 223, 224, 226, 229, 244, 245, 250, 251, 252, 256, 263, 264, 269, 272, 274, 276, 277, 282, 302, 306, 307, 308, 313, 314, 316, 330, 331, 332, 345, 351, 352, 353, 354, 360, 369, 373, 379, 380, 390, 391, 394, 395, 396, 397, 427

Further group leaders:

An-Hui Lu (born 1972)
left the Institute in June 2009
Publications: 5, 57, 58, 162, 274, 306, 307, 308, 331, 352, 353, 354

Frank Marlow (born 1960)
Publications: 53, 82, 120, 194, 208, 212

Regina Palkovits (born 1980)
joined the Institute in January 2008
Publications: 73, 79, 97, 98, 99, 146, 223, 224, 225, 226, 341, 368, 369, 370, 371, 372, 373, 391, 408

Roberto Rinaldi (born 1979)
group leader since July 2009
Publications: 97, 98, 99, 242, 243, 244, 245, 328, 352, 359, 360, 370, 390, 391

Wolfgang Schmidt (born 1962)
Publications: 19, 46, 79, 100, 131, 132, 192, 226, 253, 254, 315, 331, 332, 352, 389, 394

Oliver Trapp (born 1973)
left the Institute in September 2008
Publications: 121, 122, 123, 124, 125, 163, 411

Other publications: 25, 44, 49, 50, 55, 56, 66, 81, 138, 148, 152, 160, 169, 175, 186, 199, 201, 211, 257, 296, 324, 346, 416

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

Other Activities / Committees

1995-1997	Managing Director of the Institute of Inorganic Chemistry, Frankfurt University
1995-2001	Coordinator of the DFG-Schwerpunktprogramm "Nanoporous Crystals"
1994	Member of the Dechema Arbeitsausschuss "Heterogene Katalyse"
1995-2005	Member of the Dechema Arbeitsausschuss "Zeolithe"
1996-2004	Member of the Dechema Arbeitsausschuss "Mikroreaktionstechnik"
1996-	Member of the Editorial Board, *Microporous Materials*
1998	Member of the Editorial Board, *Advanced Materials*
1998-2005	Chairman of the Dechema Arbeitsausschuss "Zeolithe"
1999-	Founder, Chairman of the Board and of the Scientific Advisory Board hte AG
1999-2005	Member of the Kuratorium, *Nachrichten aus der Chemie*
2000-	Member of the Dechema Board of Governors
2000-	Member of the Selection Committee for the Humboldt Award
2001-	Member of the IZA-Council
2001-	Chairman of the IZA Commission on Mesoporous Materials
2001-2006	Member of the Editorial Board, *Chemistry of Materials*
2002-	Member of the IMMA-Council
2002-2007	Member of the Selection Committee Heinz Maier-Leibniz Award
2003-2005	Managing Director of the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr
2003-2007	Member of the Deutsche Forschungsgemeinschaft Senate Commission for SFB
2003-2010	Chairman of the Selection Committee, Alexander von Humboldt Award
2003-	Member of the Editorial Board "QSAR-Combinatorial Science"
2003-	Member of the International Expert Commission Elitenetzwerk Bayern
2004-2008	Member of the Kuratorium Universität Duisburg-Essen
2004-	Member of the Editorial Board, *Chemical Communications*
2004-	Member of the Scientific Commission of the State of Niedersachsen
2004-	Member of the GDCh Board of Governors
2004-	Chairman of the Dechema Forschungsausschuss "Chemical Reaction Engineering"
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
2007-	Vice-President of the Deutsche Forschungsgemeinschaft (DFG)
2009-	Vice-Chairman of the Scientific Council of the Max Planck Society
2009-	Vice-Chairman of Dechema
2009-	Member of the Supervisory Board of the Karlsruhe Institute of Technology (KIT)

Research in the Department of Heterogeneous Catalysis

The department of Heterogeneous Catalysis has seen substantial personnel change over the last three years, which is, however, fully intended. While the Institute plans stability with respect to the heads of departments, the positions of most 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 guarantees the influx of new ideas and approaches on a regular basis, since leaving group leader positions are filled typically by scientists from outside. Continuity of the work is ascertained by the director of the department (F. Schüth) and few senior scientists on permanent positions, either as group leaders or staff scientists (F. Marlow, W. Schmidt, C. Weidenthaler).

Due to the high importance of restructuring our energy system, research in this direction is considered to be highly important by the director of the department. This has not led to a change in the general approach to catalysis, i.e. exploitation of porosity and nano-structuring. However, the target reactions which are being studied are more and more related to energy questions. Several of the research directions of the department have not drastically changed, but naturally evolved and flourished. These include investigations of fundamentals of solids formation, porous solids, nanostructured catalysts and optical properties of solids. But in addition to these, some new developments were initiated, which broadened the scope of the research. There are strongly intensified efforts in the field of biomass conversion, which are pursued in the groups of F. Schüth, R. Palkovits and R. Rinaldi, and a new activity in the group of F. Schüth on porous polymer catalysts, which is predominantly funded since 2010 by an ERC Advanced Grant. The activities in the field of ordered mesoporous materials have been downsized to some extent. It is felt that such materials have reached a certain degree of maturity and thus are now part of the regular toolbox of catalysis. Some challenges still remain, but the overall importance has decreased. The investigation of complex hydrides has shifted in focus: while previously this direction was dominated by the goal to find novel storage materials for applications in cars, primarily based on $NaAlH_4$ and partially driven by the long and substantial interaction with Opel, it is now oriented more towards fundamental questions of discovering new hydride materials.

Over the reporting period, altogether six groups were active in the department, although not all of them over the whole period. In fact, the only groups which were in full operation between 2008 and 2010 were the group of F. Schüth (director) and that of

F. Marlow. O. Trapp left the Institute in September 2008 to become a professor at Heidelberg University. He was succeeded by R. Palkovits, who, in turn, also moved on to a new challenge as a professor at RWTH Aachen in October 2010. However, she and her group will continue to pursue research in the Institute until approximately middle of 2011, since the lab space at RWTH is still being created. A potential successor of R. Palkovits has already been identified: H. Tüysüz had graduated from the group of F. Schüth in 2009 and is presently post-doc in the group of P. D. Yang at Berkeley. He has expressed interest in returning to Mülheim in 2011. A.-H. Lu was appointed professor at Dalian University of Technology in the middle of 2009. He was succeeded by R. Rinaldi, who had been a post-doc in the department before. R. Rinaldi has been awarded a Sofja Kovalevskaja prize in 2010 which makes him financially almost fully independent. Finally, due to the high quality research and his visible scientific profile, W. Schmidt was promoted to group leader in the reporting period, so that there are now five groups (including the one of the director) in the department. In addition to the groups listed above, B. Bogdanović who sadly passed away in 2010, was still associated with the department to support the work on hydrogen storage materials, while the day-to-day activities of the hydrogen storage team were coordinated by M. Felderhoff. Substantial independent research has also been carried out by C. Weidenthaler in the field of advanced XRD methods in catalysis research and J. Kornatowski, who has supplied tailored samples of specific molecular sieve crystals to a number of cooperating groups.

A major thrust of the department is development of novel synthetic methods for nano-structured materials with predominant applications in catalysis. A strong focus in the reporting period was placed on the combination of colloidal synthesis of nanoparticles, creation of defined pore systems and different templating concepts. This combination has allowed the development of catalysts structured at will on the nanoscale, in order to introduce novel functionality. This line of research has led to the synthesis of various complex composite catalysts which are, for instance, sinter stable, or are superparamagnetic, so that they can be magnetically separated and recycled. The expertise built up in this line of research has also led to the synthesis of other interesting materials, such as mesostructured magnetic oxides of different composition which were explored in cooperation with the Zabel-group at Bochum University. Also materials with interesting optical properties are synthesized and studied, and the group of F. Marlow has proved to be instrumental in obtaining deeper insight in the exciting properties of such systems. The activities in the field of optical materials have also

repercussions on the catalysis oriented research, since a new line of work on photocatalysis is expected to develop over the next years.

Most of the reactions studied are now in the wider field of energy catalysis. There is a number of projects for the conversion of biomass to fuels and other value-added products, including hydrolytic and hydrogenolytic depolymerization of cellulose, and different sugar-transformation reactions, such as to hydroxymethylfurfural or different furan derivates. Moreover, R. Rinaldi is ramping up a program on lignin conversion, and glycerol as an abundant byproduct of Biodiesel fuel production is explored with respect to its catalytic conversion. Other energy-related projects are in the field of synthesis gas chemistry, methane activation via solid-catalyzed Periana-type chemistry, and ammonia decomposition for the generation of CO_x-free hydrogen as fuel cell feed.

While most of the general research themes pursued in the department are covered in the individual reports on the research areas, some of the activities do not fall into one of the categories. These include, for instance, studies on high throughput experimentation, in which some still lacking experimental techniques have been developed and artificial intelligence methods have been further explored. However, high throughput experimentation has become a routine tool by now, and thus no special report will be devoted to this topic. Results on such projects that do not fall into one of the research areas described can be found in the complete list of publications.

A powerful new analytical method, HR-SEM, in the microscopy group has boosted the capabilities of the department to obtain unprecedented insight in the structure of ordered mesoporous materials and other solid catalysts. In close collaboration with other analytical departments, in-situ XRD techniques were further developed and exploited in several projects, and the very interesting work on the use of ESI mass spectrometry for the study of nucleating solutions has been further pursued, especially adding MS-MS techniques to the toolbox in order to obtain structural information.

The groups of the department are not only participating in internal cooperations, but are also integrated in intensive external cooperation networks, either through formal or informal cooperation. These cooperations include an EU network of excellence (IDECAT), BMBF and AIF grants, integration into the nano-energy program at the University Duisburg-Essen, and participation of the department in DFG Schwerpunktprogrammen (priority programs) and Sonderforschungsbereichen (centers of excellence). Notably, the department is also a member of the cluster of excellence

(CoE) “Tailor-made fuels from biomass” at RWTH Aachen which proved to be a stepping stone for R. Palkovits, who is now professor in Aachen. The CoE is also highly important for R. Rinaldi, who runs a very successful project as part of the cluster. For the next round of proposals in the framework of the Excellence Initiative, the department is partner in one cluster proposal at the Universität Duisburg-Essen and two at the Ruhr-Universität Bochum.

In addition to the integration in bigger networks, there are many bilateral research projects between research groups, and funded cooperation projects with industrial companies. Especially fruitful was the cooperation with Osamu Terasaki, who was affiliated to the department as an Alexander von Humboldt Senior Award winner during the reporting period. This has enhanced the capabilities for high level electron microscopy analysis substantially. The department is also a node in the Max Planck International Research School SURMAT. The work of the members of the department has been recognized by a number of awards and distinctions, several of which contribute to the third-party funding of the activities. Most notable are the ERC Advanced Grant to F. Schüth (€ 1.76 M), the Robert Bosch Junior Professorship to R. Palkovits (€ 1 M) and the Sofja Kovalevskaja Award of R. Rinaldi (€ 1.54 M). Other awards to different members of the department are listed in a separate section.

2.3.1 Research Area "Understanding the Synthesis of Solid Catalysts" (F. Schüth)

Involved: A. Kempter, I. Lim, B. B. Schaack, S. S. Wang

Objective: Understanding the fundamental processes during the synthesis of solids is essential for a rational design of catalysts. In this group of projects we develop the tools to study the early stages of solids formation from solution and apply them to problems of the department. This group of projects is of a rather fundamental character with a correspondingly long time scale.

Results: Electrospray Ionization Mass Spectrometry (ESI-MS) had already been discussed in the last report as a very powerful tool for the study of pre-nucleating and nucleating solutions. First time-resolved studies had been described in the last report. Since then, significant progress has been made, both with respect to insight in the systems studied and the methodology.

Germanium containing zeolites have been in the focus of the attention, as they have attracted very high interest due to the work of primarily the Corma-group who was successful in the synthesis of a number of highly interesting novel structures with ultra-large pores. In order to understand the formation and the relevant factors governing the synthesis of such materials, several germanium containing zeolites have been analyzed with ESI MS techniques. It was found that immediately before the detection of the first solid particles by light scattering, oligomers are present in solution that are also structural elements

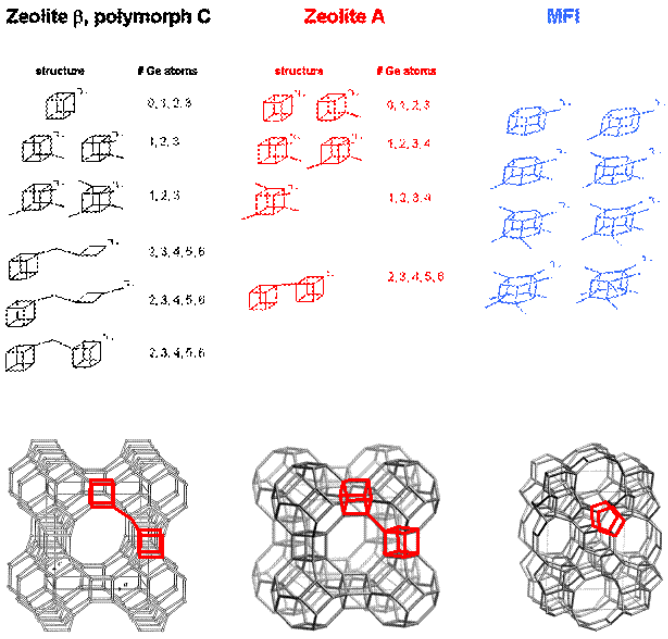


Fig. 1. Top: selected oligomeric species detected immediately before solids formation in different zeolite synthesis systems. For zeolite beta and zeolite A, several germanium atoms were found in the oligomers due to the high germanium content of the systems, in the MFI system, the germanium concentration is low, so that each oligomer contained one germanium atom at most. Bottom: sections from the corresponding structures, with characteristic elements highlighted in red.

in the final zeolite structures of the specific synthesis system (Figure 1). In the system which results in the formation of zeolite beta, double four-ring units bridged by a single silicate moiety were detected immediately before nucleation, for zeolite A-synthesis directly linked double four-rings were found, whereas in the synthesis of Ge-containing MFI-type material double five-ring units are present. While the double five-rings are not exactly secondary building units of MFI, the five-rings, which are characteristic for MFI-type materials are already formed in solution. These results demonstrate that building blocks found in the final structure of the zeolite are also favored species in solution, and nucleation of the solid seems to occur when the concentration of the relevant species has exceeded a certain concentration.

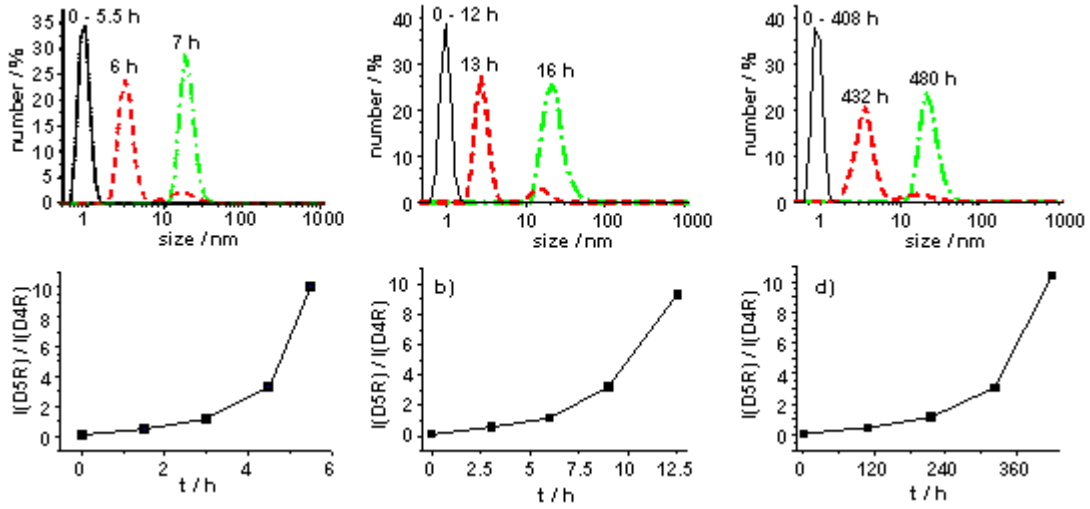


Fig. 2. Nucleation of Al-MFI at different temperatures (170°C left, 100°C middle, 40°C right). Top: particle size distribution determined by light scattering. Bottom: ratio between double-five ring silicate species and double-four ring silicate species over synthesis time determined by ESI MS.

This is even more convincingly seen in a study in which the formation of Al-MFI was studied at different temperatures. Depending on the temperature, the formation of the first solid (detected by light scattering) occurs at very different times, i.e. after only about 5 h at 170°C, after about 12 h at 100°C, and only after 400 h at 40°C. Interestingly, initially a high concentration of the stable cubic octamer silicate was formed under all conditions, but the concentration of this species decreased on expense of double five-ring species. At all temperatures, the first solid particles were detected by light scattering, when the ratio of double five-rings to double four-rings reached about 10 (Figure 2). This suggests that the double five-ring species is crucial for the formation of the MFI structure, and that solids formation requires a certain concentration of such species. The mysterious “induction time” observed in zeolite crystallization – and in the

formation of other solids from solution – is thus necessary for the decisive species for crystallization to build up.

This analysis, however, required not only the determination of sum formula of the detected species which is straightforward in mass spectrometry, but also the elucidation of the structures of the species. This was achieved by MS-MS experiments, in which species of one mass were first isolated in an ion trap and fragmented by collisions with inert species. The mass resolved analysis of the formed fragments in a second mass filter then allows conclusions on the structures of the initial species. Using such methods, it was possible to obtain insight in the distribution of heteroelements in the different oligomers formed in solution. It could, for instance, be shown that the Loewenstein-rule (no Al-O-Al linkages in zeolites) was obeyed to a large extent for the solution species, but that a minor fraction of the alumosilicate oligomers in solution did in fact violate this rule. Germanium was found with a maximum number of three per cubic octamer, species with four germanium octamers were not detected.

EXAFS is routinely used in cooperation with the group of J. D. Grunwaldt for the study of catalyst formation. Especially the synthesis of copper nanoparticles was investigated in detail, using different synthetic routes. It could be shown that an identical low-temperature intermediate was formed, irrespective of the initial precursor, which explains the low influence of the precursor and the low extent of tuning which is possible in the synthesis of copper nanoparticles by the Bönnemann route. These experiments did not only give important hints for the synthesis of size controlled copper clusters, but also extended the range of possibilities of the EXAFS technique in this cooperation.

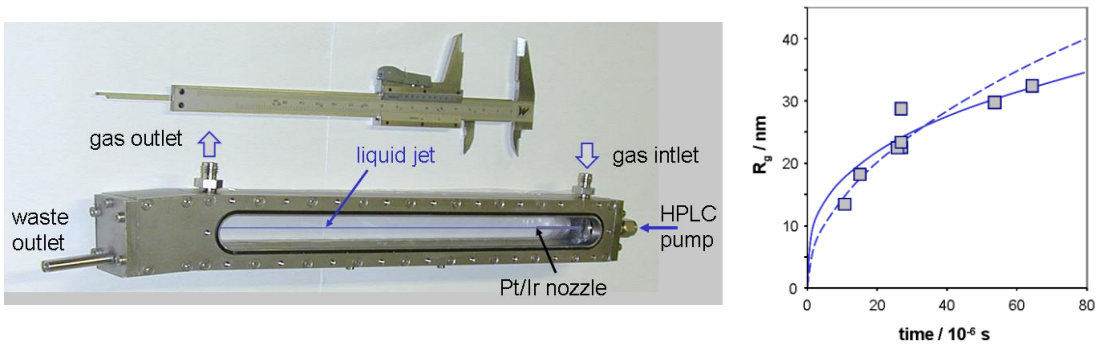


Fig. 3. Jet reactor for accessing extremely short precipitation times (left). The solution enters the chamber from the right, the synchrotron radiation beam passes perpendicularly through the transparent windows. Right: Particle radii calculated from the SAXS data at different reaction times for the injection of a 1 M Zn^{2+} solution in a 1/3 H_2S/N_2 atmosphere.

For accessing very short reaction times in the formation of solids, tubular reactor concepts were used already repeatedly in the past by the group. However, due to mixing problems, these approaches are typically restricted to time scales longer than several milliseconds. For the analysis of reactions which are faster, a jet reactor has been developed, in which a precursor solution is injected through a pinhole into a reactive gas atmosphere, in the case studied, a Zn^{2+} solution was injected into a H_2S atmosphere (Figure 3). Using synchrotron radiation, this setup allowed recording small angle scattering data at time scales down to several microseconds. It could be shown that on this time scale, ZnS formation is a diffusion controlled process, no obvious nucleation threshold was detected for the conditions studied.

Publications resulting from this research area: 4, 103, 250, 251, 252, 269, 394

External Funding: Deutsche Forschungsgemeinschaft (SFB 558); Leibniz Award

Cooperations: H. Amenitsch (Graz, AT); A. Corma (Valencia, ES); A. Erdem-Sentalar (Istanbul, TR); J. D. Grunwaldt (Zürich, CH); M. Lindén (Abo, FI); W. Schmidt, W. Schrader (Mülheim, DE)

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

Involved: P. A. Bazula, M. J. Benitez, T. Klasen, J. Kornatowski, W. C. Li, Y. Liu, Y. Meng, J. J. Nitz, F. Richter, E. L. Salabas, B. B. Schaack, M. Schwickardi, Q. Tong, H. Tüysüz, C. Weidenthaler

Objective: In this group of projects we are investigating and developing novel pathways for the synthesis of high surface area materials. The focus of the work is on oxides and carbon-based materials. The latter materials were, to a large extent, explored in the group of A.-H. Lu but after he took over the professor position at Dalian activities were reintegrated into the group of F. Schüth. Several projects are pursued in cooperation between these groups. The major synthetic methods still rely on different templating approaches, but also other techniques, such as sol-gel synthesis, are being used. While the main reason for the synthesis of high surface area materials is catalysis, other application areas, such as sorption or magnetism, are being explored as well. There is a natural interaction between the projects in this research area with the field of nanoengineered catalysts, since many of the high surface area materials synthesized are subsequently used as components for the fabrication of designed composites.

Results: Most activities related to zeolites have now been transferred to the group of W. Schmidt and will be subject of a separate report. Several projects are continuing in cooperation between the two groups. For instance, size-tailored zeolites were synthesized in close collaboration with him and then used for the dehydration of glycerol to acrolein. It was clearly shown that the reaction is strongly mass transfer limited. Optimum zeolites are thus those with high acid site concentration and small particle sizes.

Ordered mesoporous materials, synthesized either by solution processes or by nanocasting, are still subject of intensive investigations of the department. The investigation of the interesting magnetic properties of nanoscaled antiferromagnetic solids was continued in cooperation with the Zabel-group in Bochum. Using magnetic fingerprinting techniques, the dilute-antiferromagnet-in-a-field model was identified as the best description of the magnetic properties.

There is still a need to explore additional synthetic routes and create hitherto inaccessible compositions. For the solution based processes, non-oxide materials are especially interesting, and the synthesis of ordered mesoporous polymers and carbons – obtained after carbonization of such polymers – is explored in connection with the use

of such high surface area polymers in biomass conversion processes. With respect to novel compositions, a range of mixed metal oxides of the spinel structure has been synthesized by adapted nanocasting processes. The compositions created include $Cu_{1.1}Mn_{1.9}O_4$, $CuCr_2O_4$, $CuCo_2O_4$, $NiCo_2O_4$ and $CoFe_2O_4$. These mixed metal oxides are interesting in catalysis for a number of reasons. They are highly active, noble metal free CO oxidation catalysts (the Cu-Mn-oxide resembles the well known Hopcalite catalyst), which partly are active already at room temperature. Moreover, the metal ions, especially the cobalt ions, are located in different coordination environments and are differently charged in the different compounds, and the analysis of these otherwise very similar materials gives important information on the active species in CO oxidation. An interesting synthetic method for the creation of ordered mesoporous oxides with novel framework composition was discovered in the alcohol-reduction of oxides with higher oxidation states. Thus, CoO could be synthesized by the reduction of Co_3O_4 with glycerol and other alcohols at temperatures around 300°C, similarly, Fe_3O_4 was obtained from Fe_2O_3. This process seems to be generic and can probably be extended to other oxides as well. Surprisingly, this reduction process was not only interesting with respect to the oxide. In looking at the reaction products which had formed from glycerol, it was discovered that allyl alcohol was produced with significant yields of up to 25%. The mechanism is unclear, yet, but probably involves a hydrogen transfer from either glycerol or a reaction intermediate.

A very exciting development with respect to the analysis of ordered mesoporous materials was the establishment of high resolution scanning electron microscopy (HR-SEM). The combination of the high structural quality of the materials synthesized and the unrivaled resolution of the Hitachi S-5500 microscope allowed the recording of images revealing unprecedented details of the surface structures of ordered mesoporous materials (Figure 1).

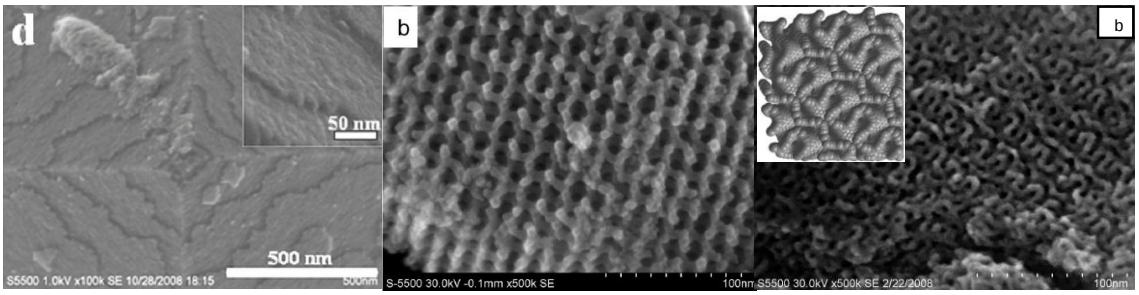


Fig. 1. HR-SEM images of different ordered mesostructured materials. Left: surface details of a FDU-16 crystal. The spherical micelles from which it grows are visible in the insert. Middle: nanocast Co_3O_4. Only one pore system of the parent KIT-6 is replicated. Right: ordered mesoporous silica KIT-6. Insert shows image simulation of a cut through the gyroid structure parallel to the 211 plane.

High surface area porous polymers have moved into the focus of the research of the department in the last years. This class of potential catalysts seems to be underexplored, primarily due to their low thermal stability. However, biomass conversion which is expected to increase in importance in the future, often proceeds at low temperatures in aqueous environment. Polymers seem to be highly suitable for application under such conditions. Therefore, a program to explore the synthesis and catalytic properties of such materials has been initiated and is meanwhile funded by an Advanced Grant of the ERC. Several pathways are explored for the synthesis of porous polymers. These include soft and hard templating approaches, sol-gel synthesis, and different types of phase separation processes. Several polymeric materials have already been prepared with high surface area and porosity. These include engineering polymers, such as polyetheretherketone (PEEK), which could be obtained with surface areas exceeding 100 m^2/g by a templating process with silica, which was leached after polymer infiltration, or poly-divinylbenzene which was polymerized in the pores of silica gel and could thus be produced with surface areas exceeding 500 m^2/g. Figure 2 shows a HR-SEM image of such a sample after removal of the silica with dilute NaOH solution. Also resorcinol-formaldehyde gels have been synthesized with surface areas of several hundred square meters per gram. While the latter material is mostly only used as a precursor for high surface area carbon, it has also been functionalized with acidic groups or noble metal particles for the production of catalysts based on the polymer.

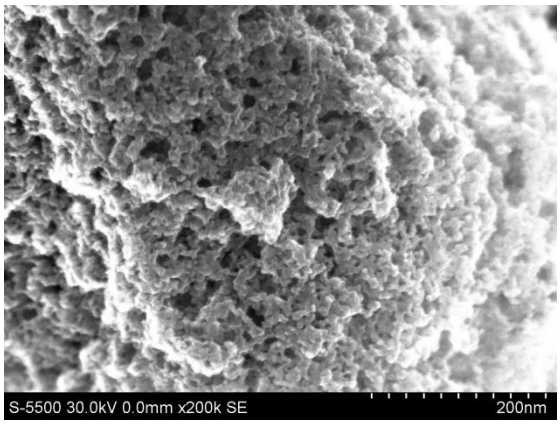


Fig. 2. HR-SEM image of a highly porous poly-divinylbenzene obtained by nanocasting from silica gel.

Such porous polymers are also the precursors for many kinds of porous carbon materials which are intensively studied in the department. An important prerequisite for the production of carbon is a high carbonization yield of the polymer, so that not all polymeric precursors are suitable for the synthesis of high surface area carbon. Very good precursors are condensation products of aromatic alcohols and formaldehyde, but also polyfurfuryl alcohol, as used in the synthesis of ordered carbons of the CMK-3 type, is often employed. Such ordered carbons were studied intensively, and in connection with the nanoengineering of catalysts, the surface functionalization of CMK-5 has been studied in depth. Using strategies, in which part of the pore system of CMK-

5 was blocked, selective functionalization of only one pore system was possible, which is an important step on the way to a carbon catalyst with different functionality selectively placed in each of the two pore systems of the CMK-5.

Carbon hollow spheres are interesting targets for different applications, such as matrix for electrode materials or as support for electrocatalysts. One approach for the synthesis of multilayer carbon vesicles relies on the use of aqueous emulsion synthesis starting from resol, tetraethoxysilane, Pluronics F127 and 1,3,5-trimethylbenzene as cosolvent. From such synthesis systems, multilayer polymer-silica vesicles in the size range of several 100 µm can be obtained. Calcination leads to the formation of carbon-silica vesicles, from which pure carbon multilayer vesicles can be prepared by leaching of the silica.

More interesting for applications, in which electronic conductivity is relevant, is a synthetic approach which results in the formation of graphitic hollow spheres. If 2,4-dihydroxybenzoic acid is polymerized with formaldehyde in the presence of lysine and the surfactant F127, a homogeneous spherical product is obtained. Suspending the initially solid polymer spheres in water for several hours leads to the formation of hollow polymer spheres, which can be carbonized to hollow spheres of amorphous carbon or, after introduction of iron species as graphitization catalyst, to graphitic carbon. These materials are presently being explored both as fuel cell catalysts and as matrix for the synthesis of iron phosphate electrode materials for Li ion batteries.

One problem for the highly porous carbon materials synthesized via organic sol-gel processes with subsequent carbonization is the complex synthetic procedure. The synthesis requires long reaction times and solvent exchange in order to retain the pore system of the initially formed organogel. In addition, while such materials are interesting catalyst supports, their properties as adsorbents are often inferior to many other carbon based materials due to the lack of microporosity. By careful fine-tuning of each synthesis step and an additional steam activation step it was possible to solve both problems. The overall preparation time could be shortened from more than two weeks to one day, and the activation step introduces a high fraction of micropores.

Fig. 3. Pilot-scale production of micro/meso-porous carbon aerogel. Here the production of the resorcinol-formaldehyde precursor gel is shown.

The resulting microporous carbon aerogel has excellent adsorption properties. Many of the undesirable components of cigarette smoke could be successfully removed under standard smoking conditions, and the new material outperformed standard coconut shell activated carbon by a wide margin. Due to these promising results the material was scaled-up to the 10 kg scale (Figure 3), and pilot tests are currently under way to explore the commercial potential of this promising material.

Publications resulting from this research area: 5, 9, 55, 56, 57, 58, 126, 127, 128, 129, 137, 148, 154, 162, 221, 282, 313, 314, 331, 352, 353, 395

External Funding: European Research Council Grant; IMPRS SURMAT; industry

Cooperations: C. Lehmann (Mülheim, DE); A.-H. Lu, W. C. Li (Dalian, CN); H. Zabel (Bochum, DE); Y. Wang, D. Y. Zhao (Shanghai, CN)

2.3.3 Research Area "Nanoengineered Catalysts" (F. Schüth / A.-H. Lu)

Involved: C. Baltes, M. Comotti, A. Dangwal Pandey, M. Feyen, C. Galeano, J. L. Galilea, R. Güttel, C. J. Jia, Y. Liu, Y. Meng, C. Neudeck, J.-J. Nitz, R. Palkovits, E. Passas-Lagos, M. Paul, K. Schlichte, M. Schwickardi, M. Soorholtz, G. Streukens, H. Tüysüz, G. H. Wang, S. S. Wang, C. Weidenthaler

Objective: The exciting developments in various fields, i.e. the controlled synthesis of metal or metal oxide nanoparticles, exact tailoring of porosity in many different porous solids, different templating and nanocasting concepts, together with unforeseen advances in electron microscopy, have made it possible to exactly tailor solid catalysts down to the nanometer scale. This means that particle sizes can exactly be predetermined, as well as the localization of different chemical functionalities. The success of these approaches is so substantial, that one can truly speak about "nanoengineering" of solid catalysts. This research field is so exciting and successful that it was one of the biggest groups of projects pursued in the department in the reporting period.

Results: Core-shell systems or yolk-shell systems (the core is located in a void which in turn is encapsulated by a shell) are very interesting, since such architectures can stabilize the core against sintering or corrosion. Such systems had already been introduced in the last report. At that time, a pathway for the generation of gold, encapsulated by a hollow zirconia shell, had been described, and the extremely high thermal stability of the composite had been proven: the system could be heated to 800°C without any sintering of the gold colloids in the core of the zirconia shells. This basis has now been extended into many different directions: the composition of the shell has been changed, as well as the size of the hollow spheres. Also the core materials have been modified, and the sizes of the gold cores in the zirconia shells can be adjusted. Some of the methods used will be highlighted here, more information can be found in the publications cited.

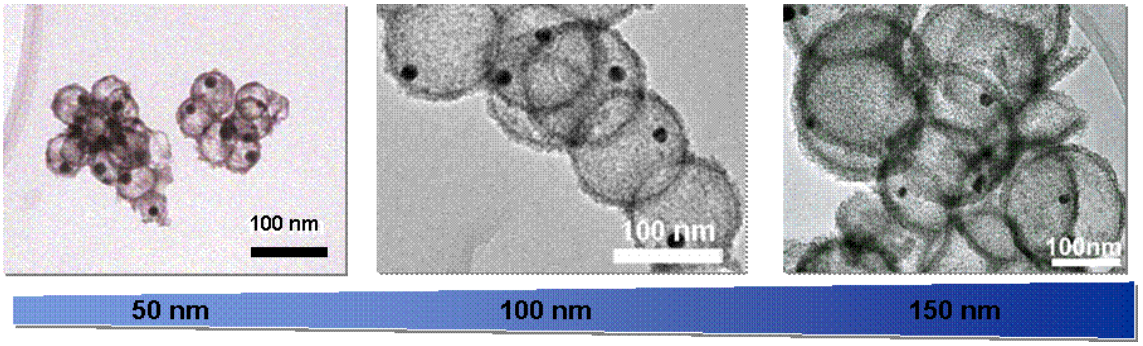


Fig. 1. Differently sized hollow zirconia spheres, each encapsulating a single gold particle. The size of the zirconia hollow spheres is determined by the amount of tetraethoxysilane which is used in the modified Stöber synthesis of the silica sacrificial template.

The modification of the size of the hollow spheres is relatively straightforward. The gold nanoparticles act – after proper functionalization with a surfactant – as the nucleation centers for silica in a modified Stöber process. After the growth of the silica spheres, the final coating with zirconia is applied, before the silica sacrificial template is leached. Due to this mechanism, the size of the silica spheres – and thus the resulting zirconia hollow spheres – can be tuned by the amount of tetraethoxysilane in the Stöber process. Figure 1 shows the range of sizes of the zirconia shells which is relatively easily accessible via this method.

Some shell materials can be synthesized by a similar method as the original zirconia shell (titania, ceria). However, other shells are less easily accessible, although they would be very interesting for the synthesis of catalytic materials. Carbon is an interesting catalyst and catalyst support, and thus a pathway was developed for the encapsulation of metal nanoparticles in hollow carbon shells. The route is slightly more complex: the pores in the zirconia coating of the previously described system are infiltrated with a carbonizable polymer before dissolution of the silica sacrificial template. After carbonization, both the silica and the zirconia are dissolved, resulting in a metal particle in a carbon shell. In the course of this development, it was found that a porous silica shell on the impervious silica template is even more suitable for the formation of the porous carbon (Figure 2).

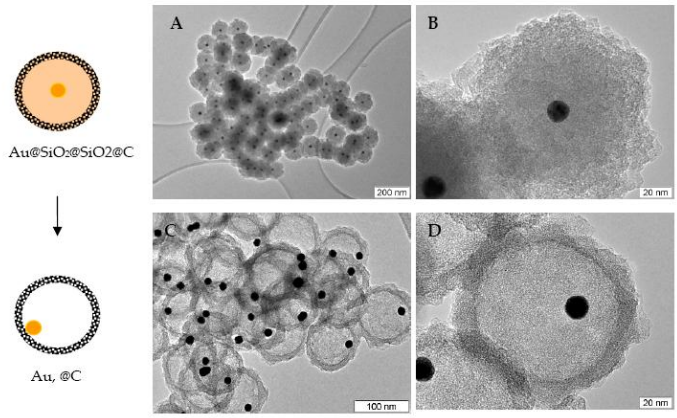


Fig. 2. Carbon encapsulated gold nanoparticles. The synthesis starts with gold particles which are coated with an impervious silica sphere, then with a porous silica shell. The pores in this shell are filled with a polymer which is carbonized (top). After leaching of the silica, the final product (bottom) is obtained.

In numerous experiments it has been established that the 15 nm sized gold cores produced by the Turkevich method are ideal for the encapsulation. However, smaller gold particles are more interesting for catalytic applications, as also shown in many experiments, both by our group and by others. Decreasing the size of the gold cores was therefore an attractive target. It was found that under certain conditions the silica shells are not fully impervious, but that the gold can be leached out. Aqua regia is suitable for this leaching process, and the gold can be fully removed, leaving a 15 nm sized void in the center of the silica spheres (which can, incidentally, be filled with another metal).

However, partial leaching results in complete loss of activity for CO oxidation, due to the chlorine which acts as a catalyst poison. Thus, gold was leached with cyanide solution. Here the concentration can be adjusted according to the stoichiometry of the reaction so that target gold sizes could be achieved. Using this pathway, gold particle sizes between 5 and 15 nm were accessible, and in CO oxidation it could be shown that in this particle size range the catalytic activity is independent of particle size, i.e. the TOF does not change. On the other hand, it was shown that titania doping of the gold cores led to a strong increase in catalytic activity. Catalysts in which 15 nm sized gold particles were modified with small amounts of titania had catalytic activities which typically are observed only for highly active catalysts with gold particles in the size range below 5 nm. This demonstrates the strongly modifying effect which the support has on the activity of gold catalysts. A non-interacting support, such as the carbon described above, incidentally leads to catalytic activities which are much lower than the activities of the zirconia encapsulated gold particles.

The question of the support effect on the catalytic activities of small gold particles has been intensively studied in the reporting period. Since these gold particles are deposited by the colloidal deposition method, a high degree of control is exerted over the formation of the gold particles. Many different novel support materials have been studied, and with MgO and $Mg(OH)_2$ as support, the most active catalysts so far reported have been synthesized. At a space velocity of 80,000 ml $g^{-1}h^{-1}$, full conversion was reached even at temperatures as low as –90°C. The activity is very dependent on the moisture present in the system, as had been reported before for other catalysts as well. However, this high activity is lost at temperature around 0°C, before full conversion is again reached at 180°C. This behavior is attributed to the presence of an active oxygen species at low temperature, which, however, is desorbed upon heating, overcompensating the rate increase of the surface reaction, and thus leading to the negative apparent activation energy.

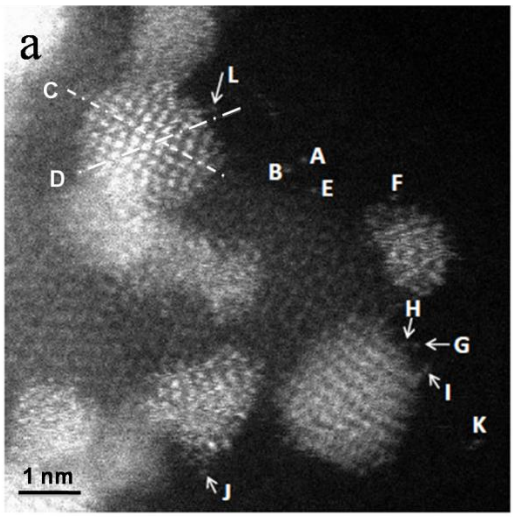


Fig. 3. HAADF-STEM images of colloidally deposited gold particles on iron oxide. The labelled atoms are single gold atoms produced in the TEM analysis and can be used for intensity calibration. Along the lines, the particles are up to 3-4 layers thick.

In the literature, it had been suggested that highly active catalysts based on iron oxide require the presence of bilayer, sub-nm sized gold species. Since the colloidal deposition method should exclude the formation of such small gold species, catalysts were synthesized

by this method for comparison. These catalysts were found to have similar activities – based on catalyst mass – as the catalysts which had the bilayer gold structure. The colloidally deposited catalysts were extensively characterized by HAADF-STEM, and the presence of small gold clusters could be excluded. Gold particles were typically four-layer particles, as proven by simulation of the electron microscopy images.

It was also shown in the reporting period that the presence of gold is not necessary for high activity CO-oxidation catalysts. Nanocasted and highly porous Co_3O_4 was found to be as active as gold-based catalysts, and if the cobalt oxide was additionally modified with silica, the activity was even higher. By now, a number of other – typically spinel-type – mesoporous catalysts with high CO oxidation activity has been identified. By synthesizing different, specifically tailored spinel-type oxides with cobalt selectively placed on tetrahedral or octahedral sites, it could be shown that both Co^{2+} and Co^{3+} can lead to high catalytic activity, in contrast to reports in the literature.

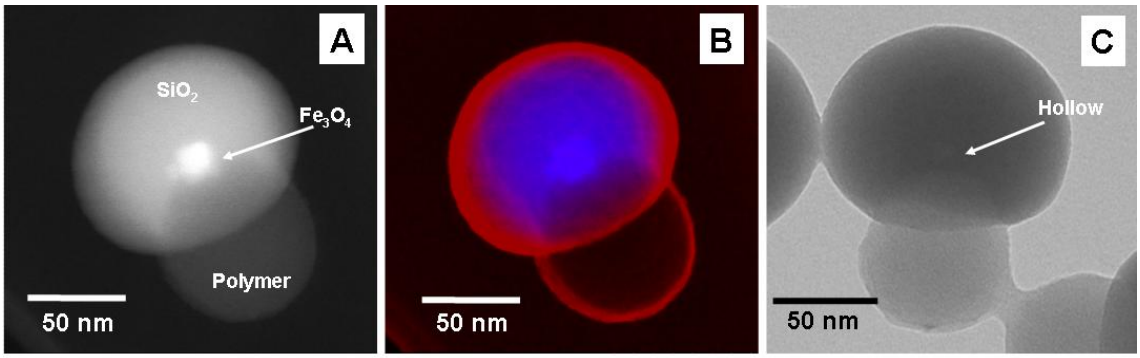


Fig. 4. (a) Dark field STEM image of the mushroom structure, obtained by growth of poly(styrene-co-divinylbenzene) on iron oxide, followed by a second growth of silica. (b) Overlay of SEM and dark-field STEM of the same structure. (c) STEM image of same material after HCl leaching, the iron oxide particles are dissolved and a corresponding void is left.

Core-shell catalysts can also be produced starting from oxide cores. If iron oxides are used, the resulting material can have superparamagnetic or ferromagnetic properties, depending on the size and exact composition of the cores. Growth of specific shells can be induced by similar methods as for the gold cores. For each system, however, specific conditions have to be established. Iron oxides can ideally be coated with polymer, for instance, poly(styrene-co-divinylbenzene). The divinylbenzene moiety of the copolymer provides the crosslinking and thus mechanical stability. Based on this composite – an iron oxide core and the polymer shell – further functionalized solids can be produced. Sulfonation of the polymer creates acidic sites, and the resulting material is an acidic catalyst which can be recycled after magnetic separation. More complex composites can be created after an additional coating of the iron oxide/polymer core-shell system with an additional layer of silica. If the iron oxide core is not covered completely with the polymer, the silica nucleates on the iron oxide still exposed, resulting in the formation

of "mushroom" structures. These can be further modified, for instance, by carbonization of the polymer part or by selective leaching of the iron oxide cores.

Iron oxides can also be encapsulated in the pores of ordered mesoporous materials. In order to check what degree of control can be achieved with respect to localization of particles in such pore systems, an iron oxide/CMK-5 material has been synthesized with the iron oxide exclusively deposited in the inside of the carbon tubes (Figure 5). This

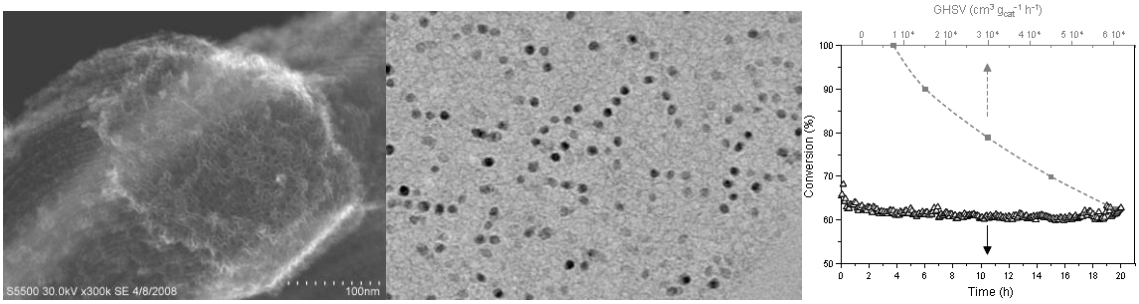


Fig. 5. Left: HR-SEM of CMK-5, the pore openings of the carbon tubes with 6 nm internal diameter can clearly be seen. Middle: TEM of microtomed γ-Fe_2O_3/CMK-5, the sample was cut perpendicular to the channel axes. Left: Performance of the system in decomposition of pure ammonia. Such catalysts have very high stability and excellent activity.

system, incidentally, turned out to be an excellent catalyst for ammonia decomposition. For the selective deposition of iron oxide in the tubes, first the inside of the pores of SBA-15 was coated with polyfurfurylalcohol which was then pyrolized to result in formation of a carbon coating. The pores in the silica-carbon composite were filled with iron nitrate solution and heated to 1000°C, resulting in the formation of γ-Fe_2O_3 particles inside the carbon tubes. Leaching with dilute NaOH removed the silica and opened up an additional pore system. Detailed XRD analysis of this system and other iron-based catalysts ex-situ and in-situ revealed that under reaction conditions iron nitride phases are formed, the exact composition of which depends on the reaction conditions.

Based on a high surface area carbon material, another highly interesting catalyst system was fabricated. In the group of Markus Antonietti it had been discovered that pyrolysis of dicyanopyridine under certain conditions results in the formation of a high surface area carbon-nitrogen material. The idealized structure of this material contains fragments which resemble the bipyrimidyl-motif of the ligands in the molecular Periana catalyst for methane oxidation with sulfur trioxide in oleum to methylbisulfate. This triggered the idea of constructing a solid analogon of the Periana-system. Various pathways for introducing platinum into the C-N-material were explored, but it was found that already simple impregnation led to strong binding of platinum to the solid (Figure 6). Different analytical methods revealed that the platinum is most probably

atomically dispersed in the solid and that most binding sites are occupied with platinum centers. The activity of the resulting solid per platinum site is in the same range as for the molecular counterpart, but the solid catalyst can be recycled without loss in activity.

Publications resulting from this research area: 46, 146, 203, 223, 224, 226, 263, 264, 272, 274, 277, 302, 306, 307, 308, 316, 330, 332, 345, 351, 354, 369, 373, 427

External Funding: Deutsche Forschungsgemeinschaft (SFB 558); Leibniz award; industry

Cooperations: M. Antonietti (Golm, DE); C. Christensen (Lyngby, DK); M. Muhler (Bochum, DE); O. Terasaki (Stockholm, SE); R. Schlögl (Berlin, DE); C. W. Lehmann, R. Palkovits, W. Schmidt, (Mülheim/Ruhr, DE)

2.3.4 Research Area "Hydrides for Hydrogen and Energy Storage" (F. Schüth)

Involved: J. Döring, M. Felderhoff, S. Grabbe, K. Hauschild, R. Pawelke, K. Peinecke, A. Pommerin, W. Schmidt, H. Y. Shao, N. Spielkamp, G. Streukens, C. Weidenthaler, B. Zibrowius

Objective: Hydrides, especially complex light metal hydrides, are intensively studied, both for their attractive properties as potential hydrogen storage materials and for fundamental reasons, since relatively little is known about many of these seemingly simple materials. In the past, the work had been primarily concentrated on doped $NaAlH_4$ as storage material, in cooperation with Opel. However, the stoichiometry does not allow reaching the target storage densities with this material. The scope of the work has therefore been broadened substantially, in order to explore the chemistry of complex hydrides more widely, to further develop synthesis methods – most notably mechanochemical methods, such as ball-milling – , and to study the suitability of different hydride systems also as heat storage materials.

Results: One-step synthesis of complex hydrides by ball-milling methods was in the center of the attention during the last reporting period. While some studies were still carried out on the $NaAlH_4$ system for use in miniaturized fuel cells and for scale-up, work has been expanded to other hydrides, especially to rare earth aluminum hydrides. Also methodical developments were pursued: ball milling is the most often used method for the synthesis of hydrides. However, under the conditions of ball milling, unstable hydrides decompose almost invariably, due to the high energy transferred. This has severely hampered the synthesis of novel, unstable hydrides up to now. Since many hydrides, which are unstable at room temperature, are thermodynamically stable at lower temperatures, cryo-milling was developed for the synthesis of such materials. Thus, different alanates (Li, Na, K) could directly be synthesized from the corresponding binary metal hydride and alane (Figure 1). At room temperature, milling of AlH_3 leads to rapid decomposition to aluminum metal and hydrogen. This method is now being explored for the synthesis of other complex hydrides. Ball milling is also highly suitable for the synthesis of other compounds. $NaAlD_4$, required for neutron diffraction studies, is not easily synthesized by conventional methods. Ball milling, on the other hand, allows easy access to this compound according to equation (1):

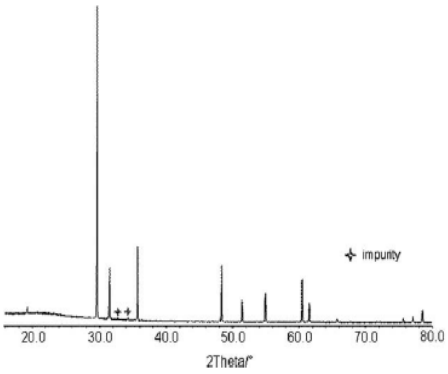


Fig. 1. X-ray diffraction pattern of $NaAlH_4$, synthesized at –196°C from NaH and AlH_3.

$$LiAlD_4 + NaF \rightarrow NaAlD_4 + LiF \qquad (1)$$

The corresponding potassium compound can also be synthesized following this route, but surprisingly, $Ca(AlD_4)_2$ and $Mg(AlD_4)_2$ did not form, although thermodynamically possible. Ball milling was also explored for the synthesis of other compounds, such as in the preparation of ternary potassium transition metal halides. Several halides, some of which hitherto not reported, could by produced in a very simple manner.

The extension of the ball milling technique had originally started with the doping of $NaAlH_4$ with titanium as decomposition catalyst. It was also used for the doping with other catalysts, such as cerium or scandium, which are among the most effective catalysts for the dehydrogenation/hydrogenation reaction.

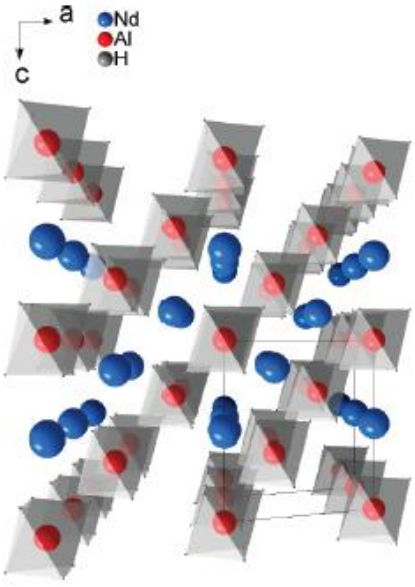


Fig. 2. Crystal structure of $NdAlH_6$ in projection along [010]. Hydrogen positions were not refined.

Especially the cerium doped system was found to be promising, since the resulting material has fast kinetics as well as stable cycling properties. The successful doping reaction with rare earth compounds initiated attempts at the synthesis of the pure rare earth aluminum hydrides. These were successful for RE = La, Ce, Pr, and Nd. In a metathesis reaction of the rare earth chlorides $RECl_3$ with $NaAlH_4$, isostructural solids were obtained for all rare earth compounds, judging from the XRD patterns. However, structure solution directly from the powder patterns proved to be difficult. Nevertheless, after quantum chemical structure calculations, the powder patterns could be refined and plausible structures could be suggested (Figure 2). The hydrogen content of the materials is too low for technical applications. Nevertheless, it is remarkable that a new structural motif in aluminum hydrides could still be discovered in spite of the tremendous amount of work invested in this field.

After several years of basic research in the field of complex sodium aluminum hydride, the focus is presently on small demonstration projects. In cooperation with ZBT and IUTA the integration of a $NaAlH_4$ storage tank into the thermal loop of a HT-PEM cell was shown for the first time. This is now extended to the usage of complex metal hydride systems for the decoupling of heat and electricity generation with PEM fuel cells for single family houses.

Since the storage capacities of all the aluminum hydrides studied so far fall short of the requirements of the automotive industry, also other hydrides were included in the study.

One of the more promising materials – and long studied in the institute by B. Bogdanović since the 1980s – is MgH_2. This can be obtained in nanostructured form, if it is first reacted with anthracene and then with catalytic amounts of $TiCl_4$. Subsequent hydrogenation then leads to the formation of the final nanostructured and titanium-catalyzed MgH_2. The hydrogen release for this nanostructured and titanium-containing MgH_2 occurs at temperatures more than 100°C lower than for the bulk material. Whether this is due to the nanostructuring, the titanium, or both is unclear, yet.

The original target application for MgH_2 was heat storage. The hydrogenation/ dehydrogenation reaction is associated with an enthalpy change of 0.9 kWh kg^{-1}, rather high compared to other materials. Since the temperature range in which MgH_2 operates corresponds closely to the range relevant to concentrating solar thermal power plants, work has been initiated to explore the use of metal hydrides in such power plants.

Complex hydrides as catalysts for hydrogenation reactions of unsaturated bonds in organic molecules have also intensively been studied. However, while in the liquid phase such reactions were successful, as shown for the case of stilbene, gas-phase reactions proved to be very difficult. The hydrogenation of 1,3-butadiene was studied as test reaction, and while the complex hydrides were moderately active, no remarkable selectivities were observed, and reproducibility problems associated with a very sensitive catalyst slowed down progress. Due to the unimpressive catalytic properties and the problems described, this line of research was eventually terminated.

Publications resulting from this research area: 11, 25, 80, 81, 159, 160, 172, 175, 229, 263, 276, 379, 380

External Funding: GM/Opel; AIF; BMBF; Energieforschung NRW

Cooperations: A. Heinzel, S. Peil, J. Wartmann (Duisburg, DE); M. Fichtner (Karlsruhe, DE); M. Dornheim (Geesthacht, DE); C. Wolverton (Evanston, USA)

2.3.5 Research Area "Nanostructured Optical Materials" (F. Marlow)

Involved: R. Brinkmann, D. Schunk, C. Mendive, Muldarisnur, I. Popa, P. Sharifi

Objective: Nanostructures with length scales in the order of the wavelength of light have specific effects on electromagnetic fields. Photonic crystals are highly ordered versions of them. Synthesis, modification, and characterization of such materials are investigated in this research area in order to develop novel functional materials.

Results: The self-assembly of well-ordered macroporous materials, especially of artificial opals, was investigated in this research area. This method is one basic approach to photonic crystals which are potential key materials for future optical technologies. The refinement and understanding of one of the currently known opal fabrication methods was the focus of the research.

As reported in a former report we have developed a new efficient technique for opal fabrication. This method exploits capillary forces and is much easier to handle than the known methods. Our method delivers large-area, homogeneous opal layers with a controlled crack structure. The cracks are typical defects for all kinds of artificial opal layers. Besides the cracks, also the opal lattice turned out to be strongly aligned in opals fabricated by our method (Figure 1). This is considered as an important step to mono-crystalline opals which are, up to now, not existing. The current opal films can be understood as intergrowth structures of two different fcc lattices.

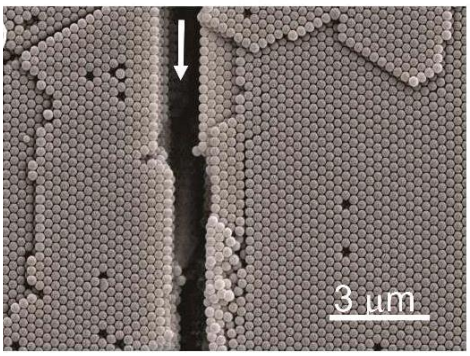


Fig. 1. SEM picture of an opal fabricated by the capillary deposition method (CDM). The white arrow is the growth direction.

The detailed understanding of the opal self-assembly process is another topic of our research. The opal formation is divided into two temporal phases: the wet assembly and the drying. Both are of relevance for the quality of the opals. We have followed the second phase in-situ by optical spectroscopy and found slow rearrangement processes during and after water removal. It takes some hours till the final nanosphere arrangement is formed.

To improve our knowledge on the lattice disturbances we have performed neutron scattering experiments at the GKSS Geestacht. Our results deliver a further strong indication that the opal films fabricated by CDM consist of an intergrowth structure of two lattices only. Rocking curves have shown long-range lattice deformations described by a mosaic model. Theses deformations of less than 3° in the lattice directions have been quantified for the first time.

Inverse opals fabricated by a sol-gel technique turned out to feature much stronger deformations. The crystal parts fluctuate by about 11° against the mean lattice orientation. These deformations exclude a number of applications of these special photonic crystals such as the use of slow photon effects. Therefore, the search for self-assembled photonic crystals different from traditional artificial opals (other inorganic materials) and avoiding inversion steps have been started.

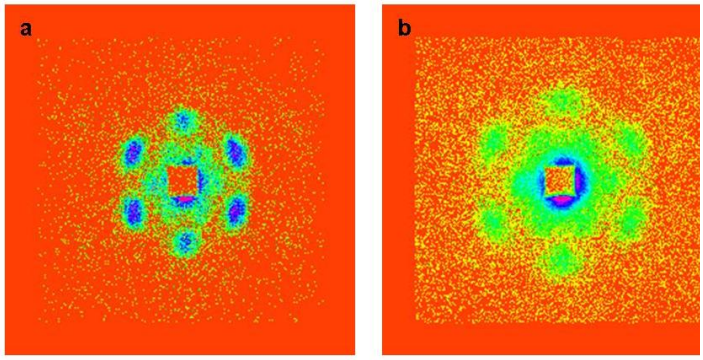


Fig. 2. Diffraction pattern for an opal film made by 264 nm polystyrene spheres (a) and for a TiO_2 inverse opal film (b) fabricated from a template as in Fig. 1a. The position of the peaks delivers lattice constants of 360 and 269 nm, respectively.

Publications resulting from this research area: 53, 82, 120, 194, 208, 212

External funding: International Max Planck Research School for Surface and Interface Engineering in Advanced Materials (IMPRS-SurMat); Nano Energy Technology Center (NETZ)

Cooperations: H. Zabel (Bochum, DE); H. Eckerlebe (Geestacht, DE); H. Wiggers / C. Schulz (Duisburg, DE); E. Mazur (Harvard, USA); T. Voss (Bremen, DE); M. Tiemann (Gießen, DE); M. Rohwerder (Düsseldorf, DE)

2.3.6 Research Area "Solid Catalysts and Reaction Systems for Utilization of Cellulose and Sugars" (R. Palkovits)

Involved: A. Ruppert, K. Tajvidi, S. Zhou, K. Pupovac, M. Kükrek, M. Mischner, W. Hofstadt

Objective: Lignocellulose presents a potential future carbon source for production of fuels and chemicals. The high density of functional groups opens numerous possibilities for tailored chemical transformations to novel target molecules. With regard to catalysis, however, this over-functionalization makes high demands on catalyst and process development. Today's refineries are based on gas phase processes at high temperatures introducing functionality into non-polar feedstocks. In contrast, transformations based on lignocellulose require liquid phase processes in polar solvents at rather low temperatures. Several projects were designed to tackle these challenges focusing on the development of suitable solid catalysts and reaction systems for the efficient utilization of cellulose, sugars and polyols.

Results: One of the major challenges with regard to the development of catalysts and processes for the efficient transformation of cellulose refers to the fact that cellulose is hardly soluble in any conventional solvent complicating utilization of solid catalysts. Ionic liquids, especially based on alkyl imidazolium salts, dissolve cellulose on a molecular level. Consequently, various attempts have been made to hydrolyse cellulose to glucose or 5-hydroxymethylfurfural (5-HMF) in ionic liquids applying mineral and organic acids or metal salts. However, separation of such reaction products from polar ionic liquids is challenging because glucose and 5-HMF are difficult to extract and not thermally stable. An alternative is the depolymerization of cellulose to cello-oligomers in ionic liquids catalyzed by acidic ion exchange resins or via slow addition of conventional molecular acids. Therein, the slow release of protons into the reaction solution renders a controlled depolymerization to cello-oligomers of narrow degree of polymerization possible. Such cello-oligomers can be precipitated by simple addition of water and show a significantly accelerated enzymatic hydrolysis to glucose.

Concerning the direct transformation of cellulose or sugars into potential platform molecules, not only separation of such products from ionic liquids, but also selectivity to certain target molecules becomes an issue. In addition to hydrolysis of cellulose to glucose and further dehydration to 5-HMF, re-hydration to levulinic acid or formation of humins via polymerization reactions occur. Reactive extraction presents an approach

to address both issues separation and selectivity. Therefore, two-phase systems were designed based on dehydration of fructose or glucose to 5-HMF in a polar solvent, including water or the acidic ionic liquid 1-H-4-methylimidazolium chloride [MIM]Cl, and continuous extraction of 5-HMF in an organic layer with subsequent conversion into products of lower polarity (Figure 1). In a first step, the individual reactions have been investigated. Concerning the polar phase, dehydration is carried out either in pure [MIM]Cl serving as both solvent and acid catalyst or in aqueous phase adding a suitable solid acid. With regard to dehydration in [MIM]Cl, water management is essential. Without water removal, 5-HMF yields remain low, while reduced pressure enforces formation of humins. In contrast, a simple air stream through the solution results in full conversion and 95% selectivity for 5-HMF after 5 h at 90°C. With regard to efficient dehydration in aqueous phase, temperatures above 140°C and solid acids with appropriate concentration and strength of acid sites are required. Especially, surface functionalized silica and carbon materials showed promising results and further attempts will be made to identify correlations between the properties of the materials and their activity in sugar dehydration. Suitable transformations with regard to the organic layer include oxidation to furan-2,5-dialdehyde (A), a potential monomer for polymer production, hydrogenolysis to 2,5-dimethylfuran or 2,5-dimethyltetrahydrofuran (B), which are discussed as biofuels, or aldol condensation with suitable aldehydes (C), e.g. acetone, towards synthesis of chemical building blocks. The extracting solvent has not only to allow proper phase separation with the polar phase and sufficient solubility of 5-HMF, but also to be suitable for the attempted further conversion. Current investigations focus not only on the design of reaction systems, but also on the development of suitable catalysts, including solid acid and solid base materials for such coupled reactions. Therein, first studies of combined reaction systems emphasized that sugar

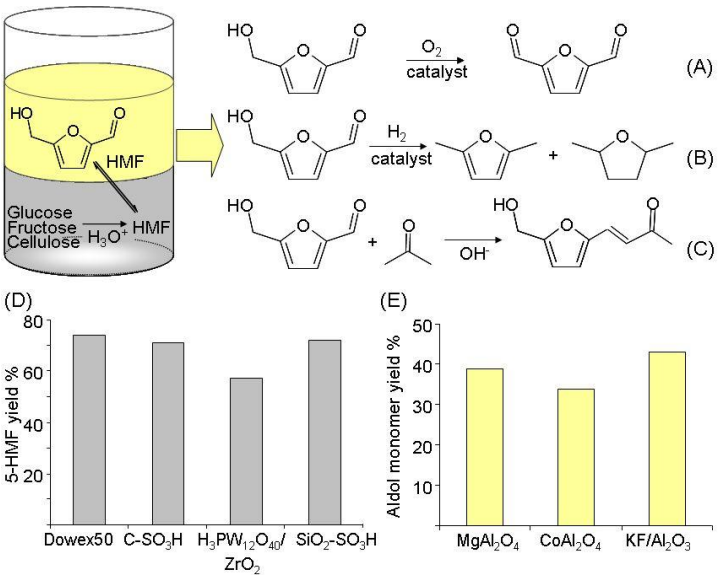


Fig. 1. (A-C) Possible two-phase systems combining dehydration of sugars to 5-HMF, extraction and subsequent conversion to products of lower polarity; (D) dehydration of fructose in aqueous phase in the presence of an extracting phase; (E) aldol condensation of 5-HMF with acetone.

dehydration and reactive extraction depend on a proper balance between extraction of 5-HMF and subsequent transformation. Consequently, extraction and reaction kinetics have to be investigated.

An alternative strategy relates to the direct transformation of cellulose via combined hydrolysis and hydrogenation in aqueous phase yielding sugar alcohols which are stable

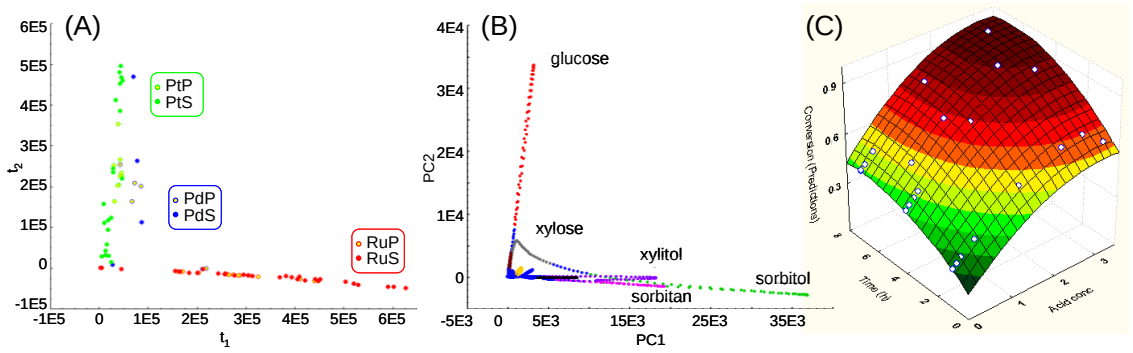


Fig. 2. (A) Score plots t_1/t_2 showing an overview of the 85 observation contained in the primary data set (catalysts choice is indicated with Pt, Pd, Ru and the used mineral acid with P or S, respectively. (B) Loading plot p_1/p_2 of the products formed in celullose hydrogenolysis. (C) Composition-activity model of the Ru/C – H_2SO_4 system (SVM plot) based on the dataset.

against further degradation. In a first approach, mineral acids (H_3PO_4 and H_2SO_4) and supported noble metals (Pd, Pt and Ru on activated carbon) were studied to develop a quantitative composition-activity relationship model (Figure 2). The noble metal had a strong impact on product selectivity, while acid strength and concentration determined the conversion, indicating a two-step process via hydrolysis of cellulose to yield glucose, which undergoes further hydrogenation and hydrogenolysis. Combining H_2SO_4 and Ru/C, 60% yield of sugar alcohols could be reached. Furthermore, optimization of the ruthenium catalysts with respect to particle size showed a strong effect and the influence of support material and particle size on product selectivity has to be investigated (Figure 3). Further investigation revealed that among various acids, heteropoly acids (HPA) in

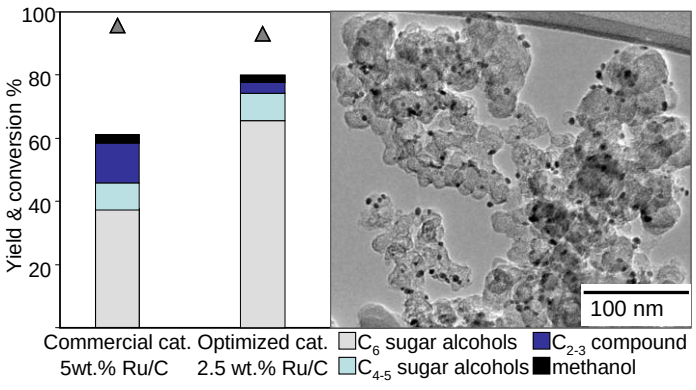


Fig. 3. Activity of commercial 5 wt.% and optimized 2.5 wt.% Ru/C catalysts (TEM) combined with 2.5 wt.% H_2SO_4 in the hydrogenolysis of cellulose (500 mg cellulose, 100 mg Ru/C, 10 ml H_2SO_4, 3 h, 160°C, 50 bar H_2 at 25°C).

combination with supported Ru catalysts (Ru/C) allow not only for excellent conversion of cellulose with > 80% yield of C_4 to C_6 sugar alcohols and 91% carbon efficiency at only 160°C, but may even be applied effectively in the transformation of spruce as real biomass feedstock (Figure 4). Crucial points refer to synthesis of suitable solid acids and bifunctional catalysts combining acid and hydrogenation function. Therein, factors influencing conversion and selectivity have to be identified. Based on ion exchanged HPAs and surface functionalized polymer or silica materials, first promising systems could be prepared. Future investigations will not only cover further catalyst development and optimization, but also concentrate on kinetic and mechanistic studies to gain insights into the complex reaction network and factors influencing selectivity to certain target products.

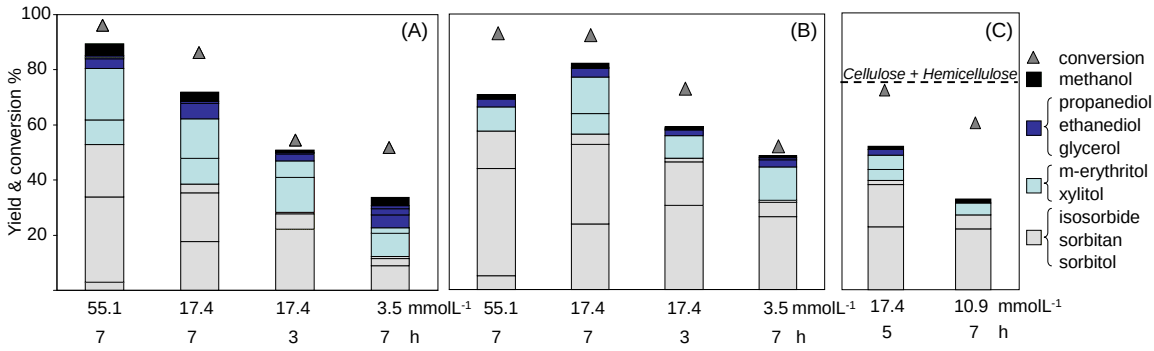


Fig. 4. Activity of (A) $H_4SiW_{12}O_{40}$ and (B) $H_3PW_{12}O_{40}$ combined with Ru/C in the conversion of cellulose to sugar alcohols and application of (C) $H_4SiW_{12}O_{40}$ and Ru/C in the transformation of spruce (10 ml H_2O, 100 mg Ru/C, 160°C, 50 bar H_2 at 25°C).

Publications resulting from this research area: 79, 97, 98, 99, 225, 368, 370, 371, 372, 391, 408

External funding: Cluster of Excellence “Tailor made fuels from biomass” RWTH Aachen; Robert-Bosch Foundation; Nano Energy Technology Center (NETZ); Fonds der Chemischen Industrie

Cooperations: J. Procelewska, R. Rinaldi, F. Schüth (Mülheim/Ruhr, DE); W. Leitner / N. Theyssen (Aachen / Mülheim/Ruhr, DE)

2.3.7 Research Area "Depolymerization of Cellulose in Ionic Liquids" (R. Rinaldi / F. Schüth)

Involved: N. Meine, J. vom Stein

Objective: Depolymerization of cellulose is desirable to produce cello-oligomers or glucose, which can be used as entry-point into biorefinery schemes for the production of chemicals and biofuels. Nevertheless, the recalcitrance of the biopolymer poses serious challenges to the chemical and biological processing of cellulose. The solubilization of cellulose in ionic liquids (ILs) completely disassembles the supramolecular structure of the cellulosic fibers. This markedly improves the reactivity of cellulose and enables the depolymerization of cellulose under mild conditions. In this group of projects, we are developing new strategies to circumvent the recalcitrance of cellulose using ILs.

Results: The addition of acid species into a solution of cellulose in 1-butyl-3-methylimidazolium chloride (BMIMCl) initiates a complex reaction chain. In the first step, cellulose undergoes depolymerization through hydrolysis of 1,4-*β*-glycosidic bonds. Either smaller 1,4-*β*-glucans (cello-oligomers) or glucose can be formed at this stage. In the presence of acidic species, glucose is likely to be dehydrated, producing a number of compounds, such as 5-hydroxymethyl-furfural (5-HMF), levulinic acid, formic acid, and several others. These products are prone to recombination with sugars or oligosaccharides via aldol condensation, resulting in polymers with undefined structures and stoichiometry called humins. In practice, stopping the process at the cellooligomer stage is crucial because they can be easily isolated from the ILs upon addition of water (cf. Figure 1), while the workup for the extraction of

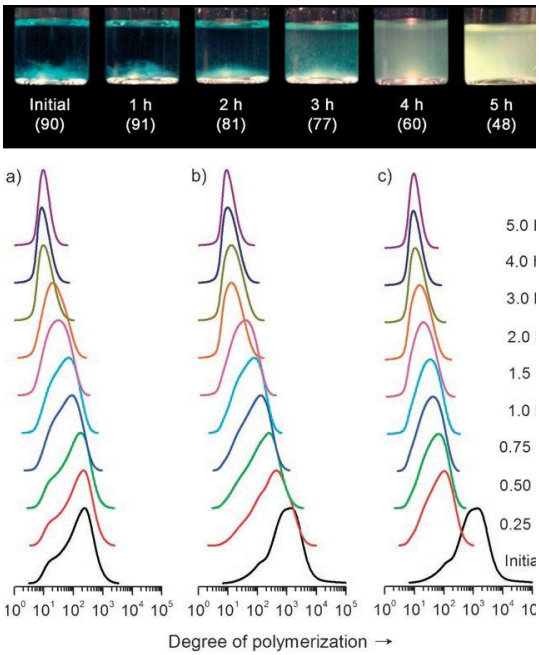


Fig. 1. (*top*) Hydrolysis of microcrystalline cellulose. Appearance of cellulose recovered from BMIMCl by addition of water after the reaction times indicated. The values between parentheses represent the percentage of isolated cellulose. (*bottom*) Distribution of apparent degree of polymerization of celluloses isolated from BMIMCl solution during the reaction: a) Microcrystalline cellulose (Amberlyst 15DRY). b) α-Cellulose (Amberlyst 15 DRY). c) α-Cellulose (*p*-TSA).

sugar and dehydration products is normally very difficult, or not even achievable, due to the high solubility of the products in both ILs and water.

A novel strategy for controlling the depolymerization of cellulose in ionic liquids has been the use of solid acids as source of H_3O^+ species for the reaction. Performing the acid-catalyzed depolymerization of cellulose using Amberlyst 15DRY enables the control of the reaction progress effectively. As a result, cello-oligomers with a tunable degree of polymerization can be conveniently produced (cf. Figure 1). The acidic resin releases H_3O^+ species into the solution, controlling the initial rate of depolymerization.
The preferential cleavage of large polymeric molecules occurs because of statistical reasons. The preference can be understood considering that cello-oligomers are produced upon cleaving the polymeric chain at any position, while formation of glucose requires specific cleavage at the ends of cellulose. In this manner, the formation of glucose is not favored at the beginning of the depolymerization process, because the reaction mixture contains large polymeric chains at this reaction stage. Therefore, the high selectivity for cello-oligomers is a feature linked to cellulose rather than to the acid catalyst used. A high degree of control of the depolymerization reaction can be achieved also in the case of molecular acids, if they are added slowly over time to the reaction batch, thus mimicking the slow ion exchange process occurring over the solid acids.

Almost quantitative conversion of cellulose into fermentable sugars is achieved when starting from the cello-oligomers. Figure 2 shows the performance of a commercial cellulase preparation (Celluclast®, *T. reseei*) in the enzymatic hydrolysis of several cellulosic materials. In contrast to untreated α-cellulose and to cellulose regenerated from ILs, which show substrate conversions of 46 and 79%, respectively, the cello-oligomers are nearly quantitatively hydrolyzed (94%) by cellulases within 4 h at 45°C. Furthermore, this reaction produces exclusively cellobiose and glucose, *i.e.* the enzymatic selectivity is maintained. The ratio between cellobiose and glucose, however, depends heavily on the pretreatment of cellulose and on the substrate conversion.

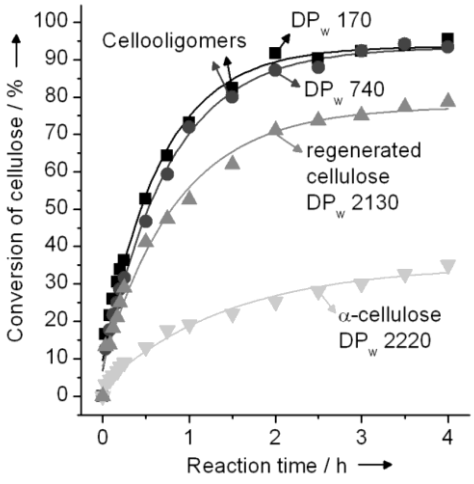


Fig. 2. Enzymatic hydrolysis of α-cellulose, cellulose regenerated from IL and cellooligomers. Conditions: substrate (eq. 1 g of dry cellulose), cellulase (Celluclast®, 350 U/g substrate), pH 4.5 (acetate buffer), 45°C.

Surprisingly, no marked effect of the degree of polymerization on the enzymatic performance is observed in the reactions carried out with cello-oligomers smaller than 800 anhydroglucose units (AGU). This finding has important implications for process development. Starting from native cellulose (DP 2,000 - 10,000 AGU), suitable cellooligomers for the enzymatic hydrolysis would be already produced after 3 to 16 scissions in the cellulosic chains, which is reached in less than 1 h through the acid-catalyzed depolymerization in IL. Owing to the preference for the production of cellooligomers over the formation of glucose in the earlier stages of acid-catalyzed depolymerization, losses of glucose, due to its dehydration, are completely suppressed. Consequently, the integration of acid- and enzyme-catalyzed conversion unites the advantages of both "worlds", bringing rapid and quantitative conversion of cellulose to fermentable sugars.

In summary, the findings presented here demonstrate that a fast, efficient and integrated process for the complete hydrolysis of cellulose to fermentable sugars is indeed feasible. On a laboratory scale, the acid-catalyzed depolymerization of cellulose achieved nearly quantitative yield of cellooligomers (95-100%) within 0.5 to 1 h. Likewise, commercial cellulase preparations hydrolyze the cellooligomers to a mixture of glucose (40%, 4 h) and cellobiose (54%, 4 h), reaching a conversion of 94% in 4 h. These results are remarkable, since the overall process is accelerated by about one order of magnitude at much higher yields of fermentable sugars. For the sake of comparison, for sugar yields exceeding 50%, pretreatment of cellulose by conventional means is required that then leads to reaction times of days in enzymatic hydrolysis. Finally, research on the further optimization of the cellulase "cocktail" is required to take full advantage of the high accessibility of cellulosic chains in the cellooligomer hydrogel. This is an important issue for future research, because cellulases account for ca. 40% of the cost of cellulosic ethanol.

Publications resulting from this research area: 97, 98, 99, 244, 245, 328, 359, 360, 390, 391

External funding: Cluster of excellence Tailor-made fuels from biomass (RWTH Aachen)

Cooperations: J. Büchs, A. Spiess (Aachen, DE); R. Palkovits, W. Thiel (Mülheim/Ruhr, DE); W. Leitner / N. Theyssen (Aachen / Mülheim/Ruhr, DE)

2.3.8 Research Area "Exploration of Nanoporous Solids" (W. Schmidt)

Involved: U. Wilczok, A. Cepak, C. C. Pavel, H. Bongard, J. Nitz, B. Spliethoff

Objective: Nanoporous solids possess pores with sizes equivalent to molecular dimensions and serve as molecular sieves and selective catalysts in various applications. Pore diameters as well as pore shapes and pore organization determine the interaction with molecules from fluid phases. Further crucial factors are crystallite sizes and morphologies. These parameters determine adsorptive and diffusional properties as well as catalytic activity of these solids. Tailoring of textural and/or surface properties of particles allows subtle modifications with respect to pore accessibility, diffusivity of guest molecules, and solid-fluid interaction. Preparation and detailed characterization of nanoporous solids is subject of this research area.

Results: MFI-type zeolites belong to a class of prominent nanoporous materials. Even though they are used as catalysts in various applications, many of their features are still not fully understood. An open question concerns the existence of particular aluminum sites in MFI structures. Recently, several theoretical investigations have indicated certain potentially preferred aluminum positions. However, experimental reports are rare and often inconsistent. Therefore, investigations have been performed with the aim of locating such sites experimentally. Aluminum is generally not evenly distributed over the MFI crystallites (zoning) if certain structure directing agents, such as tetrapropylammonium cations, are used in the synthesis. As a starting point, suitable MFI materials have been synthesized. Crystallographic identification of specific sites in such materials would thus be difficult, since diffraction methods result in averaged structure models. To avoid that problem, MFI crystals have been synthesized with a homogeneous aluminum distribution from template-free synthesis gels. Electron microprobe investigations verified the homogeneous aluminum distribution. Silicon and aluminum cannot be distinguished in XRD experiments and also neutron diffraction experiments did not allow direct identification of specific sites.

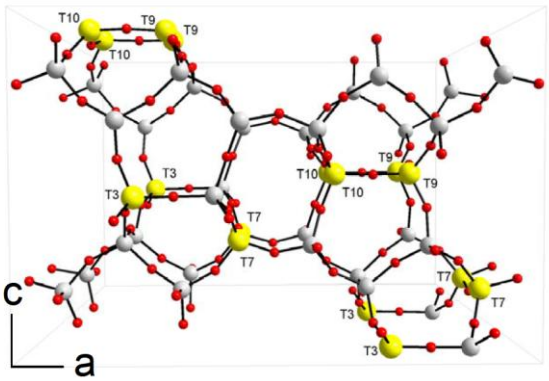


Fig. 1. Representation of the MFI structure. The yellow spheres indicate the sites T3, T7, T9, and T10 which are likely to be occupied by aluminium.

Thus, an indirect method has been chosen. MFI materials consisting of the same parent zeolite that have been exchanged with different cations were examined by X-ray and neutron diffraction. Localization of the extra-framework cations allowed inference on four sites (Figure 1) that have a high probability to be occupied by aluminum. The most probable sites T3, T7, and T9 are accessible in the straight and in the sinusoidal channels of the MFI structure and catalytic conversions would be possible in both channel systems.

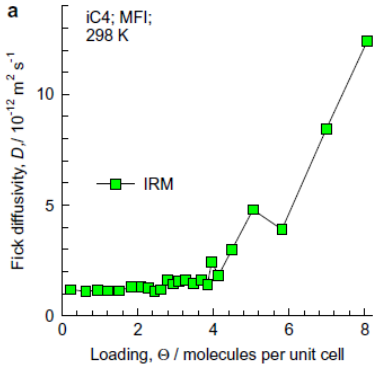


Fig. 2. Diffusivity of *iso*-butane in MFI zeolite at different loadings at 298 K.

Diffusion of molecules in these channels is another factor that determines the catalytic performance of the zeolite. Therefore, diffusion studies of molecules in MFI zeolites have been performed in collaboration with the groups of Kärger, Shah and Krishna. Large (150 µm) and uniform zeolite crystals have been synthesized and investigated. IR and theoretical studies on diffusion of branched alkanes, such as *iso*-butane in MFI, showed the existence of an inflection in the loading dependence of the diffusivity, D, of *iso*-butane. It appears at a loading of four molecules per unit cell, as illustrated in Figure 2. The branched molecules get adsorbed preferentially in the channel intersections (4 per unit cell) and the D is more or less constant for a loading of less than four molecules per unit cell. For higher loadings, inter-molecular repulsion provides the activation energy for a significantly enhanced diffusivity as been shown by KMC simulations.

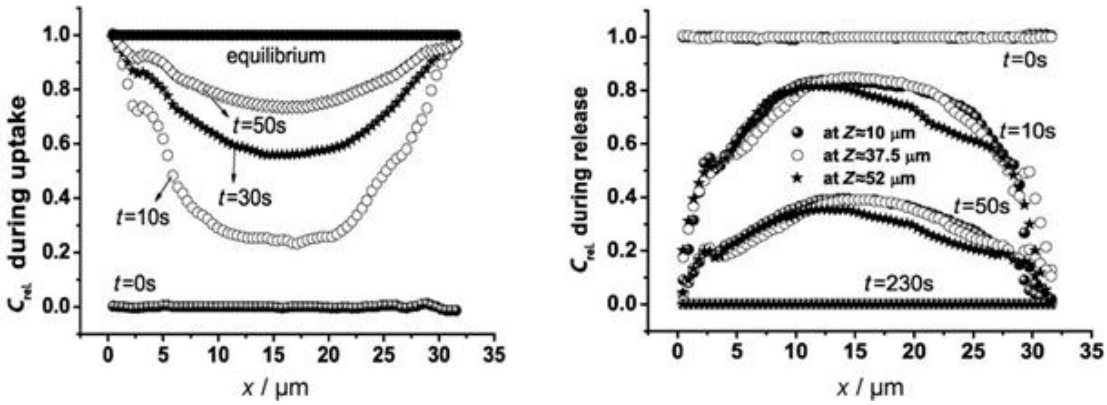


Fig. 3. Time-dependent concentration profiles of 2-methylpropane (isobutane) as a guest molecule in silicalite-1. Evolution of the guest concentration profile along the short x during uptake (left) and release at different z values (right); x being the short, z the long crystal axis.

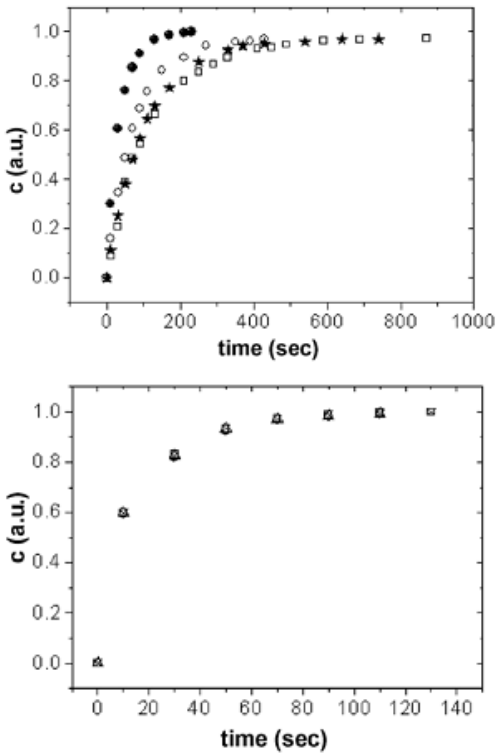


Fig. 4. *iso*-Butane uptake with time on silicalite-1 as observed in four subsequent cycles using iso-butane containing residual water (top) and water-free iso-butane (bottom).

Investigation of molecular diffusion with interference microscopy showed that neither surface barriers nor internal diffusion barriers necessarily exist for well crystallized large MFI crystals. As shown in Figure 3, saturation concentration is achieved close to the crystal surface immediately after exposition of the crystal to the vapor, a clear indication that no external diffusion barrier exists. This has been a rather unexpected discovery. Generally, it was accepted that diffusion barriers are always to be encountered on the surfaces of large MFI crystallites and that stacking faults cause frequent intracrystalline diffusion barriers. In contrast, we could show that for well-crystallized MFI zeolites such transport resistances are negligible if compared to the transport resistance exerted by the zeolite channel systems.

Interestingly, diffusion barriers can be created unwillingly in the course of diffusion experiments if the adsorptive contains residual amounts of water. In that case, successive adsorption of water molecules on the polar external surface of silicalite-1 (i.e., aluminum-free MFI) results in the formation of a surface barrier with increasing exposure time, as indicated in Figure 4 (top). This observation also was rather unexpected and

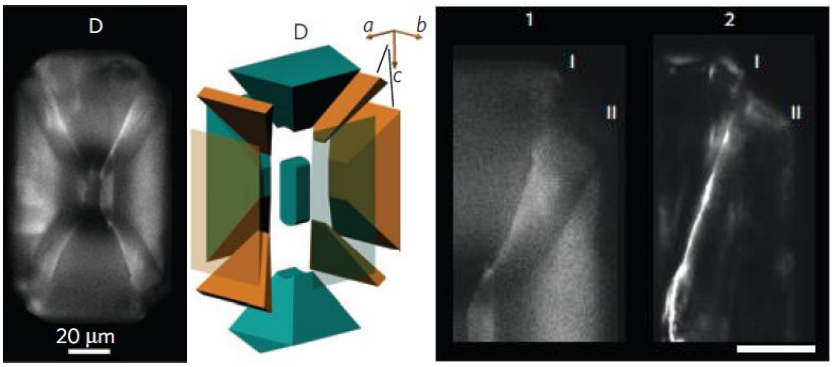


Fig. 5. Confocal fluorescent microscopy images of a twinned MFI-crystal (left) consisting of 5 different types of segments (middle). Fluorescence of stilbene molecules adsorbed at the interface between crystal segments.

showed that specific care has to be taken in the interpretation of diffusion phenomena. The formation of water films on the surface of the zeolite could be avoided using a water trap. As the result subsequent diffusion experiments result in identical uptake curves as illustrated in Figure 4 (bottom).

Different types of diffusion barriers have been observed on MFI crystallites with a rather complex twinning topology, as shown in Figure 5. In cooperation with the Weckhuysen group, rather ill-defined intracrystalline diffusion barriers, consisting of crack-like defects at the interfaces of individual crystal segments have been observed. The existence of rather thin wedge-shaped crystal segments running from the center to the crystal corners, as described in Figure 5 (middle), have been described for the very first time. Large fluorescent dye molecules (stilbene) were able to penetrate and accumulate along these cracks along the interfaces between these thin wedges and neighbor segments, as shown in Figure 5 (right). The defect is observed only on one side of the wedge, no accumulation of dye molecules is observed on the opposite side. Such crystal defects comprise a very specific type of diffusion barriers.

In a survey of NMR signal shapes of alkanes adsorbed on MFI zeolites, ^{1}H NMR signals have been found to be broadened in comparison to alkanes adsorbed on cubic zeolites. Deviations from cubic symmetry apparently does not allow that the dipolar interaction of guests molecules average to zero in MFI zeolites, a fact that is important for the interpretation of PFG NMR data, e.g. in diffusion studies.

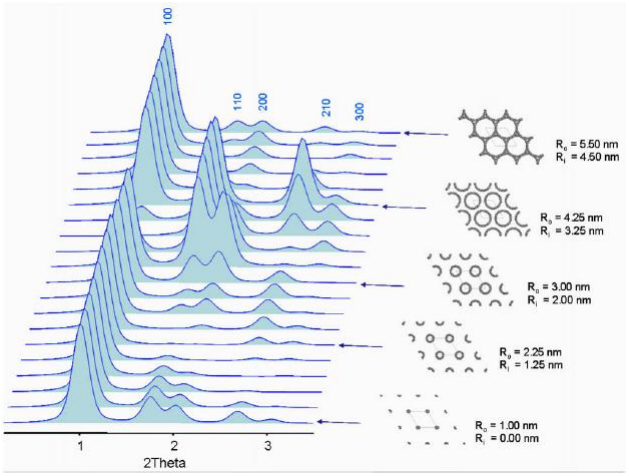


Fig. 6. XRD patterns as calculated from models of CMK-5 carbons.

In the groups of Grünert and Gies novel titanosilicate materials with hexagonally ordered mesopores have been synthesized from MFI-related reaction gels. The properties of these materials have been investigated in a joint collaboration. Even though the investigated materials were not microporous, they had surface properties comparable to those of titananosilicate TS-1 (MFI)

and an activity in the epoxidation of cyclohexene that was up to two orders of magnitude higher than that of the TS-1 or Ti-MCM-41 reference materials. The amorphous pore walls most probably consist of motifs comparable to sub-unit cell fragments of TS-1 but with the excessively high surface area of the mesoporous silica, the combination of which explains the high catalytic activity.

Replication of conventional hexagonally ordered mesoporous silica as carbon material results in rod-like CMK-3 or tubular CMK-5 type carbon. Cladding pore walls of SBA-15 with different amounts of carbon yielded carbons with strongly differing XRD patterns. Model building and calculation of theoretical XRD patterns allowed a detailed understanding of X-ray diffraction on such carbons. Minute changes of pore width and/or pore wall thickness of CMK-5 results in significantly different XRD patterns as illustrated in Figure 6. In turn, structural details of CMK-5 could be derived from stepwise optimization of the structure model and least squares optimization of calculated and measured XRD patterns.

An extension of such models in combination with calculation of electron density maps by inverse Fourier Transform methods allowed insight in the adsorption of vapors on CMK-5 carbon. Phase information was derived from structure models whereas structure factors were derived from diffraction intensities that were measured during in-situ XRD measurements during dichloromethane adsorption.

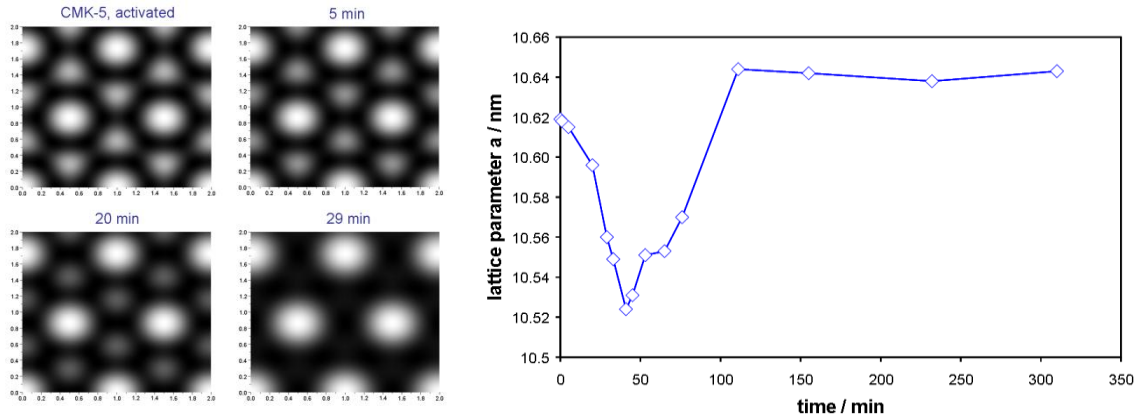


Fig. 7. Electron density maps at different stages of dichloromethane adsorption on CMK-5 (left) and change of lattice parameter during exposure to the vapor (right).

As shown in Figure 7, the adsorption of dichloromethane is a dynamic process. At low loadings it proceeds preferentially in the interstitial pores of CMK-5. During that process the array of carbon tubes contracts, probably as the result of very high capillary forces. After filling of the pores between the tubes, adsorption continues in the tubular pores, accompanied by an expansion of the CMK-5 structure. The distances between the

tubes are expanded to an extent that exceeds those that have been observed prior the vapor adsorption. Once all pores are filled, no further structural changes occur, further adsorption then proceeds only at the external surfaces of the carbon particles. The investigations revealed an unexpected flexibility of the CMK-5 pore system.

Publications resulting from this research area: 19, 79, 100, 131, 132, 192, 226, 254, 389, 394

External funding: Deutsche Forschungsgemeinschaft; Elettra Synchrotron Light Source (Trieste, IT)

Cooperations: J. Kärger, C. Chmelik, D. Tzoulaki, D. Freude (Leipzig, DE); H. Jobic (Lyon, FR); D. B. Shah (Cleveland, USA); R. Krishna (Amsterdam, NL); B. Weckhuysen (Utrecht, NL); V. Kahlenberg (Innsbruck, AT); H. Amenitsch (Graz, AT); F. Dreisbach, H. Gies, W. Grünert, A. Puls (Bochum, DE); A.-H. Lu (Dalian, CN); F. Schüth (Mülheim/Ruhr, DE)

2.3.9 Research Area "High-Throughput Multiplexing Chromatography" (O. Trapp)

Involved: S. K. Weber, S. Bauch, W. Hofstadt

Objective: Continuous real-time sampling in parallelized high-throughput assays is desirable to perform kinetic studies of catalysts or to detect activation and deactivation processes. However, this is often restricted to single-batch systems or has to be performed sequentially. Like in continuous wave spectroscopy the overall duty cycle of chromatographic systems is low and typically most of the acquisition time is spent for recording detector noise. Despite these limitations, performing kinetic studies on large catalyst libraries is a much sought-after objective to get conclusive insights into reaction mechanisms for future developments of advanced materials and catalysts. The major challenge is to increase the duty cycle of the separation system in order to maximize information and minimize analysis time. In this group of projects we continue developing a novel technique combining information technology and chemical analysis.

Results: Combination of information technology and separation sciences opens a new avenue to achieve high sample throughputs and therefore is of great interest to bypass bottle necks in catalyst screening of parallelized reactors or using multitier well plates in reaction optimization. Multiplexing gas chromatography utilizes pseudo-random injection sequences derived from Hadamard matrices to perform rapid sample injections which gives a convoluted chromatogram containing the information of a single sample or of several samples with similar analyte composition. The conventional chromatogram is obtained by application of the Hadamard transform using the known injection sequence or in case of several samples an averaged transformed chromatogram is obtained which can be used in a Gauss-Jordan deconvolution procedure to obtain all single chromatograms of the individual samples. The performance of such a system depends on the modulation precision and on the parameters, e.g. the sequence length and modulation interval. In continuation of our previous studies we could demonstrate the effects of the sequence length and modulation interval on the deconvoluted chromatogram, peak shapes and peak integration for sequences between 9-bit (511 elements) and 13-bit (8191 elements) and modulation intervals Δt between 5s and 500ms using a mixture of five components.

It could be demonstrated that even for high speed modulation at time intervals of 500 ms the chromatographic information is very well preserved and that the separation efficiency can be improved by very narrow sample injections. Furthermore we were able to show that the relative peak areas in multiplexed chromatograms do not deviate from conventionally recorded chromatograms.

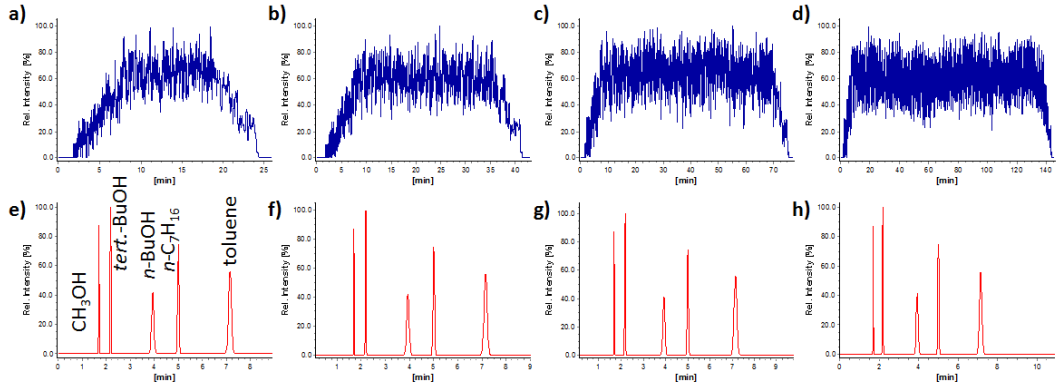


Fig. 1. Multiplexed gas chromatograms (a-d) and Hadamard transformed gas chromatograms (e-h) obtained by injection at a time interval of Δt = 1s and variation of the sequence length. a) 10-bit; b) 11-bit; c) 12-bit; d) 13-bit; e) corresponding transformed chromatogram of a); f) corresponding transformed chromatogram of b); g) corresponding transformed chromatogram of c); h) corresponding transformed chromatogram of d). 25 m fs-capillary (i.d. 250 µm), coated with 500 nm SE-30, isothermal conditions at 50°C, 80 kPa He as inert carrier gas.

Investigations were performed using sample mixture consisting of methanol, *tert*-butanol, *n*-butanol, *n*-heptane and toluene, which were injected into the GC according to *n*-bit binary pseudo-random sequences which are derived from (n+1) × (n+1) Hadamard matrices. With the newly developed and improved injection valve very well modulated gas chromatograms were obtained. The sequence length was systematically changed from 10-bit 1023 (elements) to 13-bit (8191 elements) and modulation intervals were set between 5s and 600ms. In the same study we also performed a detailed error analysis. Longer modulation sequences are of advantage over short sequences, because small injection fluctuations are compensated, have only a minor impact on the peak areas and the SNR is improved. In particular an average experimental improvement of the SNR of 1.2 for 10-bit sequences, 1.7 for 11-bit sequences, 2.4 for 12-bit sequences and 3.2 for 13-bit sequences compared to 9-bit sequences was observed.

Another highly interesting finding was that with increasing modulation speed (600 ms!) the encoded information in the chromatogram is still conserved.

Furthermore a 4-port multiplexing injector was designed and built for high-throughput screening of 96-well plates. Therefore a high-speed autosampler was built with two xyz axes, the electronics was extended and software to control this machine written.

Publications resulting from this research area: 123, 124

External funding: Deutsche Forschungsgemeinschaft (Emmy Noether Program); Fonds der Chemischen Industrie; Merck Research Laboratories

Cooperations: M. T. Reetz, F. Schüth (Mülheim/Ruhr, DE); R. N. Zare (Stanford, USA)

2.3.10 Research Area "High-Throughput Dynamic Chromatography and On-column Reaction Chromatography" (O. Trapp)

Involved: S. K. Weber, S. Bauch, H.-W. Hofstadt, B. Spliethoff

Objective: Integration of reactions and analysis at the same time opens a new avenue in detailed kinetic screening of catalytic reactions to gain insights into the reaction mechanism on a molecular level. In this group of projects we continue to explore our strategy, which truly unites synthesis and analysis by combining catalytic activity and separation selectivity in the polymeric stationary phase of a chromatographic separation capillary. This was made possible by the derivation of the unified equation which overcame expensive and very slow calculations of reaction rate constants. On-column reaction chromatography is investigated to develop a robust high-throughput system for kinetic and mechanistic investigations of catalytic processes. Several approaches are developed to dissolve or chemically anchor catalysts on polysiloxane matrices. Furthermore the stereodynamics of molecules is investigated in a high-throughput fashion with various separation techniques.

Results: The hydrogenation of 1-acetylcyclohexene, cyclohex-2-enone, nitrobenzene and trans-methylpent-3-enoate catalyzed by highly active palladium nanoparticles was studied by high-throughput on-column reaction gas chromatography. In these experiments catalysis and separation of substrates and products is integrated by the use of a catalytically active gas chromatographic stationary phase which allows to efficiently perform reaction rate measurements employing reactant libraries. Palladium nanoparticles embedded in a stabilizing polysiloxane matrix serve as catalyst and selective chromatographic stationary phase for these multiphase reactions (gas-liquid-solid) and are coated in fused-silica capillaries (i. d. 250 µm) as a thin film of 250 nm. The palladium nanoparticles were prepared by reduction of palladium acetate with hydridomethylsiloxane-dimethylsiloxane copolymer and self-catalyzed hydrosilylation with methylvinylsiloxane-dimethylsiloxane copolymer to obtain a stabilizing matrix. Diphenylsiloxane-dimethylsiloxane copolymer (GE SE 52) was added to improve film stability over a wide range of compositions.

We observed by TEM measurements that size and morphology of the Pd nanoparticles depend on the ratio of the stabilizing polymers, the activation conditions (under hydrogen atmosphere, temperature) as well as on the concentration of the Pd precursor. The obtained Pd nanoparticles stabilized by a 3:1 ratio of the two polysiloxanes

(HMPS:MVPS) are spherical and crystalline with a narrow size distribution of 3.2 ± 0.7 nm determined by TEM. After treatment with hydrogen at elevated temperatures (200°C) we found also amorphous nanoparticles with an increased size of 3.6 ± 1.6 nm, which can be attributed to the formation of Pd hydride and also agglomeration processes at these elevated temperatures. Surprisingly, the size is also controlled by the ratio of the two polysiloxanes. To study this effect systematically we prepared 40 Pd nanoparticles samples by variation of both the mixture of the two polysiloxanes as well as the Pd loadings.

The size distribution of the nanoparticles measured by TEM for five selected ratios of the two stabilizing polysiloxanes (HMPS:MVPS = 1:11, 1:2, 1:1, 2:1, 11:1) indicates that a 1:2 mixture of the two polysiloxanes leads to smaller Pd nanoparticles with a narrow size distribution.

Pd nanoparticles prepared with a polysiloxane ratio of HMPS:MVPS = 1:11 show an increased particle size and a broader size distribution. To study the effect of hydrogen on the size and morphology of the Pd nanoparticles, Cu grids for TEM analysis were coated with the viscous brownish-grey polysiloxanes and then treated with hydrogen at 200°C. It was found that high HMPS and low MVPS concentrations and vice versa as well as high Pd precursor concentrations lead to pronounced agglomeration of the particles with a broad size distribution (11.0 ± 6.2 nm) (cf. Table 1).

The dependency on particle size and distribution of the two polysiloxanes in the particle formation can be explained by kinetic effects. The reduction of Pd^{2+} to Pd^{0} is a fast process compared to the hydrosilylation leading to cross-linking and stabilization of the nanoparticles. It can be assumed that in a first step seeds of small Pd nanoparticles are formed which agglomerate to form the resulting nanoparticles. This process is controlled by diffusion. The here used MVPS is compared to HMPS less viscous which should allow easier diffusion of the nanoparticles resulting in the observed agglomeration to larger particles. Samples prepared with a high HMPS concentrations form quickly Pd nanoparticles which can be observed by darkening of the solution. The agglomeration itself is controlled by diffusion and by the rate of the cross-linking of the two polysiloxanes, which dynamically increases the viscosity and decreases diffusion of the particles.

To perform the kinetic investigations of the hydrogenation over the here prepared Pd nanoparticles, solutions of the polysiloxanes with the embedded Pd nanoparticles were

used to coat fused-silica capillaries (i. d. 250 µm, 250 nm film thickness) by the static method. For the activation of the Pd nanoparticles and to permanently bond the polysiloxanes to the fused-silica capillary by reaction of surface silanol groups with remaining hydridosiloxane groups the fused-silica capillaries were heated to 200°C at a temperature rate of 0.5 K/ min under slow hydrogen flow. It was found that polymers prepared with an excess of HMPS gave more stable films not leading to droplet formation, which indicates destruction of the polymer film. The on-column catalysis experiments were performed by coupling the Pd nanoparticle micro capillaries (length 2.02 cm, 2.90 cm, 3.84 cm, 5.10 cm, 6.15 cm) between a pre-separation capillary (1 m) and a separation column (25 m), which were installed in a gas chromatograph. The purpose of the pre-separation column was to thermally equilibrate the reactants and to spatially separate the substrates of the injected compound library, which enabled high-throughput kinetic investigations due to the absence of competing reactions. Hydrogen gas was used as reactive carrier gas. Reaction substrates and products were detected by flame ionization detection (FID) for quantification and identified by mass spectrometry (quadrupole ion trap MS). The reactant library consisting of four unsaturated and functionalized compounds (1-acetylcyclohexene, cyclohex-2-enone, nitrobenzene and *trans*-methylpent-3-enoate) was simultaneously injected onto this column configuration at different temperatures (60-100°C) and inlet pressures (60-100 kPa) to vary the reaction time and to obtain temperature dependent kinetic data.

By the use of reactant libraries and measuring reaction rate constants of the spatially separated compounds an extraordinary high throughput could be realized.
We also developed a theoretical model and equations for the efficient evaluation of such experiments.

Furthermore we investigated the stereodynamics of catalytically active metal complexes and diaziridines by enantioselective dynamic gas chromatography and electrophoresis.

Publications resulting from this research area: 121, 122, 125, 163, 411

External funding: Deutsche Forschungsgemeinschaft (Emmy Noether Program); Fonds der Chemischen Industrie; Merck Research Laboratories

Cooperations: F. Schüth (Mülheim/Ruhr, DE); N. H. H. Heegaard (Copenhagen, DK); C. Welch (Rahway, USA)

2.4 Department of Organometallic Chemistry

Director:

Alois Fürstner (born 1962)
Publications: 12, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 69, 115, 149, 155, 157, 158, 164, 176, 177, 178, 179,180, 181, 182, 210, 218, 220, 231, 258, 261, 286, 287, 288, 319, 320, 344, 362, 363, 398, 404, 409

Further group leaders:

Manuel Alcarazo (born 1978)
group leader since December 2008
Publications: 28, 29, 30, 149, 179, 285, 286, 287, 288, 298, 320, 326

Curriculum Vitae: Alois Fürstner

1962	Born in Bruck/Mur, Austria
1980-1987	Studies at the Technical University Graz, Austria; Ph.D. with Professor H. Weidmann
1990-1991	Postdoctoral Fellow, University of Geneva, Switzerland, with Professor 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 and affiliated as Professor ("apl. Prof.") with the University of Dortmund, Germany
2009-	Managing Director of the Max-Planck-Institut für Kohlenforschung

Awards and Honors

1994	Chemical Industries Prize ("Dozentenstipendium" des Fonds der Chemischen Industrie)
1998	Ruhrpreis for Arts and Sciences, Mülheim/Ruhr
1999	Leibniz Award of the Deutsche Forschungsgemeinschaft
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 of the American Chemical Society
2002	Member, Deutsche Akademie der Naturforscher Leopoldina
2002	Merck Academic Development Program Award
2004	Centenary Lecture, Royal Society of Chemistry
2004	Member, Nordrhein-Westfälische Akademie der Wissenschaften
2004	Corresponding Member, Österreichische Akademie der Wissenschaften
2004	Tetrahedron Chair
2005	Junior Award of the International Society of Heterocyclic Chemistry
2005	First Mukaiyama Award of the 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, Royal Society of Chemistry

Other Activities / Committees

2001-2007	Scientific Editor, *Chemical Communications*
2001-2006	Member, Board of Editors, *Organic Syntheses*
2002-2009	Member, Scientific Advisory Board, Leibniz Institut für Katalyse (LIKAT), Rostock
2002-2010	Member and since 2006 Chairman, Selection Committee of the Alexander von Humboldt Foundation (Feodor-Lynen-Program)
2004-	Member, Board of Governors, German Chemical Society
2007-	Member, Selection Committee, Otto-Hahn-Prize (GDCh)
2008	Member, Search Committee, Institute of Science and Technology Austria (ISTA)
2010-	Member, Selection Committee, Heinrich-Wieland-Prize

Member of the International Advisory Boards of:

1997-	*Topics in Organometallic Chemistry*
2000-	*Advanced Synthesis & Catalysis*
2002-2004	*Journal of Organic Chemistry*
2005-	*Progress in Heterocyclic Chemistry*
2006-	*ChemMedChem*
2007-	*Nachrichten aus der Chemie*
2009-	*Synthesis* and *Synlett*
2009-	*ChemCatChem*
2010-	*Israel Journal of Chemistry*

Organometallic Chemistry

The research in the Department of Organometallic Chemistry is focused on the development and understanding of organometallic catalysts, as well as on their application to advanced organic synthesis. Since Professor Fürstner was appointed Director in 1998, the Department has grown to its current size and has hosted several young scientists at the outset of their independent academic career (Professor Frank Glorius, 2001-2004; Professor Stefan Hecht, 2005-2006; Dr. Lisbet Kværnø, 2007-2008; Dr. Manuel Alcarazo, 2009-).

Dr. Lisbet Kværnø joined us in September 2007 as a "Max Planck Independent Research Group Leader" after she had finished her postdoc under the guidance of Professor D. A. Evans, Harvard University. For private reasons however, she decided not to pursue an academic career any further and left the Institute already in May 2008 to take up a position in industry. Her coworkers were integrated into the Fürstner group.

In December 2008, Dr. Manuel Alcarazo was appointed as a new junior research group leader. After a very successful postdoctoral stint with Professor Fürstner, with whom he had worked on the total synthesis of marine oxylipins as well as on the design of new ligands for homogeneous catalysis, Dr. Alcarazo won a prestigious "Ramon-y-Cajal" fellowship to start a research group in Spain. However, he accepted our offer to stay in Mülheim as an independent group leader. His research is currently focused on the coordination chemistry of main group elements in unusual oxidation states, the design of novel "frustrated Lewis pairs", and applications thereof to homogeneous catalysis and organic synthesis.

The major lines of Professor Fürstner's own research can be summarized as follows:

- The development of catalysts based on cheap, non-toxic, benign and readily available transition metals as substitutes for traditional noble metal complexes. Although not limited to, iron catalysis is prominently featured in this context. Particular attention is paid to the development of iron catalysts for cross coupling, cycloisomerization reactions, cycloadditions of unactivated substrates, and carbometalations of π-bonds. Considerable efforts are made to identify, isolate and characterize highly reactive organoiron intermediates to gain an understanding for the largely unknown mechanistic basis of such iron-catalyzed C-C bond-forming reactions.

- Catalysis based on the activation of π-systems with the aid of carbophilic Lewis acids such as Pt(2+) and Au(1+) has gained considerable momentum. Except for a few pioneering studies, this field was virtually inexistent until the late 1990's but is currently one of the most rapidly growing areas of homogeneous catalysis. As early as 1998, the Fürstner group proposed a unifying mechanism, which guided our investigations during the last decade. This hypothesis-driven approach led to the discovery of several new reactions, some of which have already been successfully applied to natural product synthesis. Moreover, we are dedicated to the characterization of pertinent reactive intermediates and the development of practical asymmetric variants.
- Significant efforts were made over the years to showcase the complementary logic of olefin metathesis and exploit its exceptional performance in advanced organic chemistry. We also wish to extend metathesis beyond its traditional scope. In this context, the group is committed to upgrade alkyne metathesis to a broadly applicable and user-friendly transformation, and to illustrate the remarkable scope of this reaction by applications to structurally complex and biologically relevant targets.
- The group is interested in developing concepts, which eventually allow one to replace notoriously stoichiometric reactions of proven versatility by catalytic processes (e.g. NHK reactions catalytic in chromium, carbonyl coupling catalytic in titanium etc.)
- An additional line of research implemented during the report period concerns the development of novel ligand architectures. Starting from conventional N-heterocyclic carbenes (NHC's), we proposed alternative design principles for (stable) singlet carbenes and also ventured into the coordination chemistry of formally zerovalent carbon. These investigations in the Fürstner laboratory are nicely complemented by the independent work of the Alcarazo group on nitrogen(+1)- or phosphorous(+1)-based ligands and novel frustrated Lewis pairs.

A significant part of our work is dedicated to the application of organometallic catalysis to the total synthesis of structurally complex natural products of biological significance; where indicated, we are also committed to prepare analogues by "diverted total synthesis" for further evaluation. From the chemical viewpoint, all projects intend to scrutinize the synthetic methods of interest to the Department. We wish to develop syntheses that are concise, convergent, productive and scalable; ideally, they should be largely catalysis-based and require a minimum of protecting group manipulations. With

regard to the targets, our choice is based on considerations of structural complexity, the biological activity, and the non-availability of meaningful amounts from the natural sources. Biological assessments of the compounds prepared in the laboratory are carried out in close collaboration with external academic and industrial partners. This includes contacts to the Chemical Genomics Center (CGC) of the MPG, of which Professor Fürstner is a founding member.

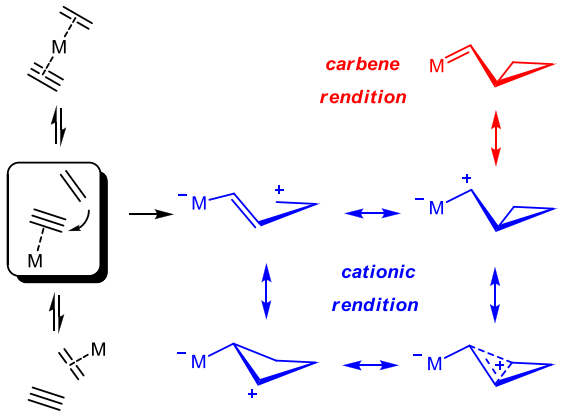
In many projects we enjoyed close collaborations with Professor Thiel and coworkers, who provided complementary insights into reactive intermediates, bonding modes and reaction mechanisms based on high-level computational methods. In certain cases, the Thiel group also helped with conformational analyses of complex macrocyclic target molecules. This mutually beneficial work has resulted in several joint publications during the reporting period.

Finally, it is emphasized that the research carried out in the Department would not be possible without the constant and excellent support by the analytical groups of the Institute. This invaluable input is reflected by the fact that various service group leaders and –members are coauthors of several published and forthcoming papers.

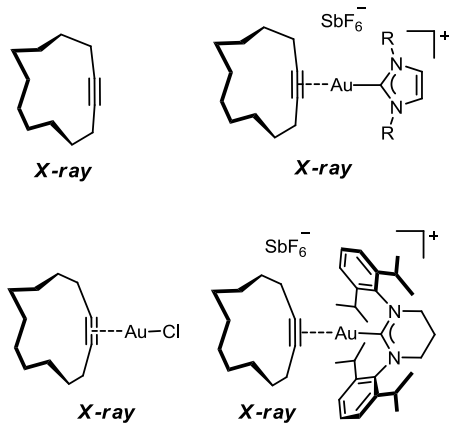
2.4.1 Research Area "π-Acid Catalysis" (A. Fürstner)

Involved: M. Alcarazo, S. Flügge, L. Morency, A. Schlecker, G. Seidel, T. Stork, H. Teller

Objective: During the last decade it became increasingly clear that the use of π-acids such as Pt(2+) or LAu(1+) provides tremendous opportunities for homogeneous catalysis and advanced organic synthesis. Guided by our own early mechanistic proposal, we continue to develop new Pt- or Au-catalyzed transformations and try to unravel the basis for the observed reactivity at the molecular level.

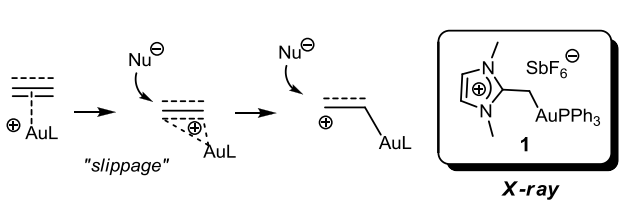


Results: In 1998, our group was the first to interpret skeletal rearrangements induced by carbophilic noble metal catalysts in terms of a unifying mechanism. It was proposed that activation of only one of the π-systems of the substrate(s) (here the alkyne) suffices to trigger the reaction, as the resulting complex is sufficiently deprived of electron density to experience attack by an appropriate nucleophile (here an alkene). The resulting net *trans*-addition product can formally be depicted as a non-classical cation in the coordination sphere of the metal or as an electrophilic metal carbenoid, if back-donation of electron density from the metal to the ligand plays a role. This proposal was speculative at the time but allowed many predictions to be made that could be experimentally probed. Although numerous calculations at different levels of theory published in the literature have addressed various aspects of this generic mechanism, the reactive intermediates themselves largely elapsed experimental characterization.

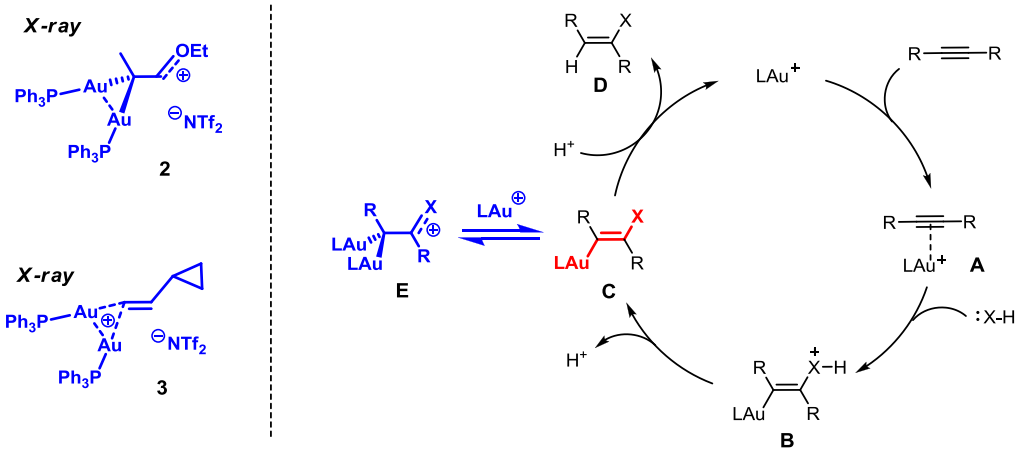


For example, only a very limited number of gold-alkyne complexes had been known at the outset of the project. During the report period, we managed to obtain a complete set of NMR- and crystallographic data for cyclododecyne as a prototype free ligand, the derived neutral [cyclododecyne·AuCl] complex, as well as for two

cationic [cyclododecyne·AuNHC]$^+$ complexes. These results allowed the changes to be studied in detail which different gold fragments impose onto the π-system. Comparisons with high-level DFT calculations carried out by the Thiel group led to valuable insights into the first step of a noble metal-catalyzed transformation.

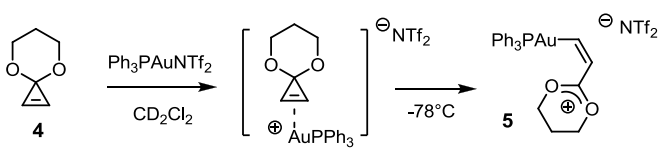


The second step of the generic mechanism consists of the attack of a nucleophile onto the π-complex. Literature reports had suggested that this process requires slippage of the metal along the ligand axis. We were able to provide experimental support for this notion; specifically, a series of gold complexes of diaminoalkenes was isolated, in which the reactivity of the nucleophile was trimmed down to that of a hardly coordinating counterion. X-ray crystallography revealed that the slippage process may even reach the extreme of an end-on coordination mode prior to reaction with the nucleophile. Although the heteroelement substituents in complex **1** are certainly non-innocent, this and related examples showed that the entire positive charge can be transferred from the catalyst to the π-system when functionalized substrates are used.

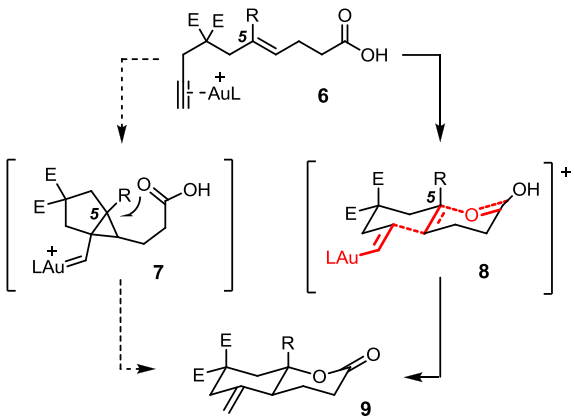


A remarkable result concerns the protodemetalation of the alkenylmetal species **B** formed upon net *trans*-addition of a protic nucleophile HX to an alkyne. It is generally assumed that simple loss of the proton followed by rapid protodeauration of **C** releases product **D** and regenerates the catalyst. By considering the isolobal relationship between H^+ and LAu^+ however, one may speculate that the catalyst itself could also (reversibly) incept **C** to give complexes of type **E**. Such a pathway might seriously compete with protodeauration given the affinity of the carbophilic transition metal to the π–bond. Although *gem*-diaurated species had previously been proposed in the literature, we were

the first to isolate and fully characterize two such complexes. At first sight, the structures of **2** and **3** in the solid state seem very similar; a closer inspection, however, revealed a surprisingly different bonding situation. In case of complex **2**, the C1-C2 bond is long whereas the C2-O bond is short, which implies net transfer of the charge from Au to the ligand; **2** is hence best described as consisting of an oxo-carbenium center flanked by a *gem*-diaurated site. In contrast, complex **3** contains a short olefinic C1-C2 bond and a regular C2-C3 single bond, suggesting that a non-classical three-center/two-electron bonding motif [Au_2C] must be present, which largely retains the positive charge. The ease with which complexes **2** and **3** could be made and their surprising stability insinuates that *gem*-diauration may play a much larger role in gold catalysis than previously recognized. We are currently investigating possible implications for catalyst optimization and asymmetric synthesis.

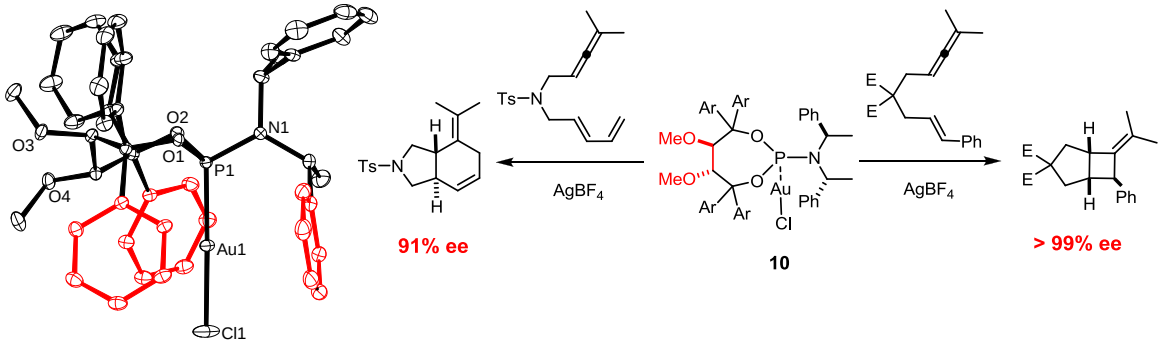


Our early mechanistic proposal had already pointed out that some reactive intermediates involved in platinum- or gold catalysis may be regarded as highly electrophilic metal "carbenoids" endowed with considerable "non classical" carbocation character. The argument was later simplified by others to the concept of "gold carbenes", which became invasive. Convinced that this description may not be fully adequate, experiments were devised to probe the character of the reactive intermediates in more detail. To this end, cyclopropenes such as **4** were reacted with LAu^+ fragments since the rearrangement of strained rings constitutes a well known entry into metal carbene complexes. In the case of gold, however, detailed NMR investigations showed that the resulting product **5** is a regular vinylgold species carrying the positive charge at a remote carbocationic site. In the ground state, the double bond character of the Au–C bond is marginal, with a rotational barrier as low as 30 $kJ \cdot mol^{-1}$ (which is less than the "double bond" character of the Ph–CHO bond in benzaldehyde and only one third of the double bond character of an amide bond). Although one may again argue that the substituents in **4** are not innocent, these data highlight the very strong bias for charge transfer from the metal to functionalized ligands.

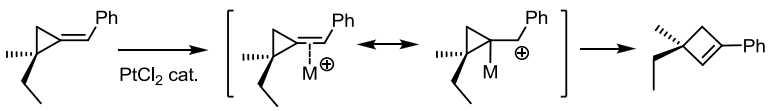


Additional information on the character of the reactive intermediates was deduced from reactivity data. Specifically, we could demonstrate that gold catalyzed

cycloisomerizations of enyne-carboxylic acid derivatives such as **6** are highly concerted processes, which follow the logic of the "Stork-Eschenmoser paradigm" of cationic polycyclizations. At least for substrates of this type, the outcome of the reaction is best explained by assuming highly delocalized charge density in the reactive intermediates (or transition states) rather than intervention of regular cyclopropyl gold carbenes.

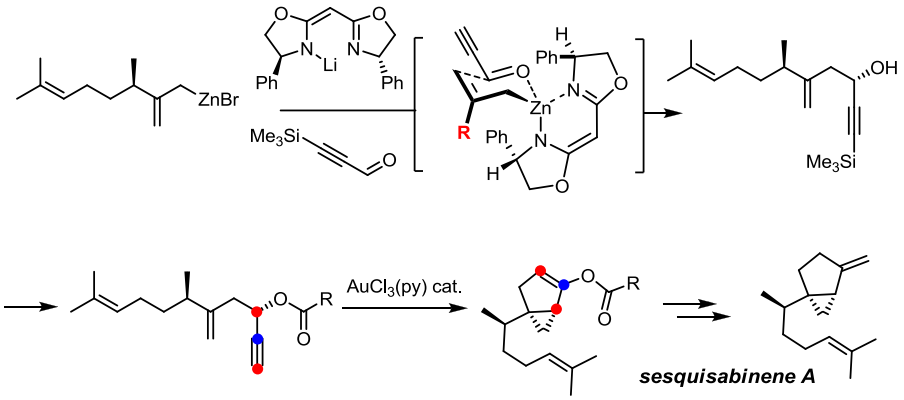


Asymmetric gold catalysis copes with the problem that the chiral ligand L* is located opposite to the substrate and is attached to the gold center via one-point binding. The rotational freedom of the L*–Au bond and the long distance render the effective transfer of stereochemical information highly challenging. Although several promising solutions were published in recent years using sophisticated ligands or chiral counterions, our group seeks to develop a less expensive alternative approach. It is based on the idea that free rotation about the L*–Au axis might be inconsequential if the crafted chiral environment is degenerate. In an attempt to reduce this design principle to practice, we developed a new type of TADDOL-based phosphoramidite with an open backbone. Despite an extensive literature, TADDOL's devoid of an acetal substructure have never been used in asymmetric catalysis before. X-ray diffraction studies showed that the derived phosphoramidites such as **10** craft a tight and highly C_3-symmetric chiral pocket about the coordinated gold center. Several applications to cycloaddition reactions led to high and, in part, unprecedented levels of chiral induction.



In parallel work, our group keeps exploring the preparative scope of noble metal catalysts. In collaboration with the group of Professor Marek at the Technion, Haifa, we were able to show that enantiomerically pure alkylidenecyclopropanes undergo ring expansion with retention of stereochemical integrity in the presence of catalytic $PtCl_2$. This method

allows cyclobutenes carrying quaternary chiral centers to be prepared in optically pure form, which are difficult to make otherwise.



We had previously proposed that propargyl esters, upon activation with π–acids, constitute stable synthetic equivalents of α–diazoketones. This notion was illustrated by a concise entry into cedrene, cedrol and no less than 10 terpenes of the sesquisabina- and sesquithuja families. Only the constitution of these latter compounds had been known at the outset; our stereochemically unambiguous synthesis allowed us to define the absolute and relative configurations of these olfactory natural products.
For additional studies on the control of gold catalyzed reactions with the aid of NHC ligands of different π–acceptor qualities, see Chapter 2.4.4.

Publications resulting from this research area: 29, 35, 36, 176, 178, 210, 258, 287, 398, 409

External funding: Fonds der Chemischen Industrie (stipends to S. Flügge and H. Teller); German-Israeli Project Cooperation (DIP); NSERC Canada (stipend to L. Morency); Spanish Ministerio de Educación y Ciencia (stipend to M. Alcarazo)

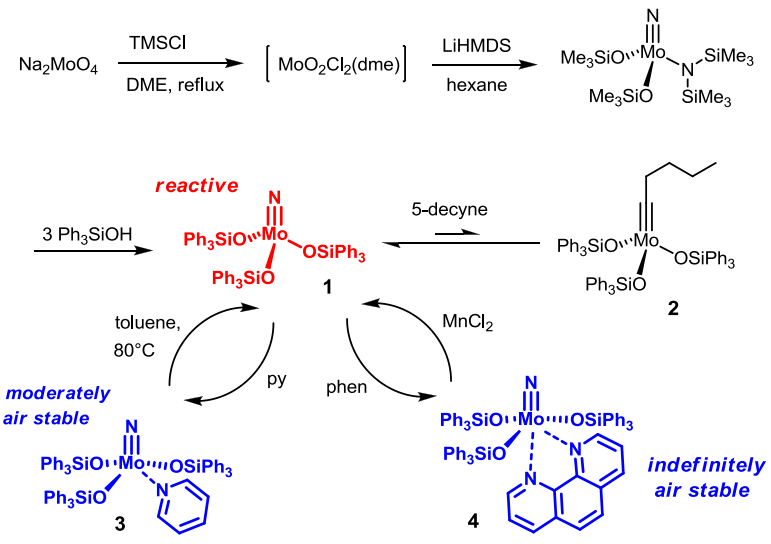
Cooperations: I. Marek (Haifa, IL); B. List, W. Thiel (Mülheim/Ruhr, DE)

2.4.2 Research Area "Metathesis" (A. Fürstner)

Involved: M. Alcarazo, M. Bindl, D. A. Clark, E. Heilmann, J. Heppekausen, V. Hickmann, A. Kondoh, K. Micoine, A. Picot, R. Stade

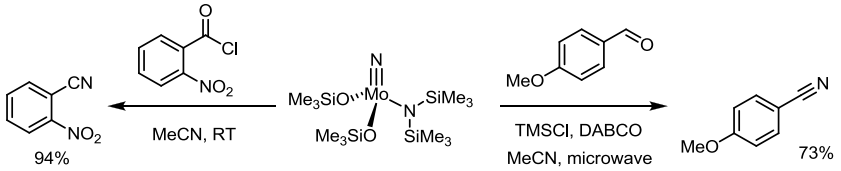
Objectives: Olefin metathesis has revolutionized organic synthesis during the last decade. While we continue to apply this transformation in our synthetic programs (see Chapter 2.4.5), our focus in metathesis research has shifted toward alkyne metathesis, for which we present user-friendly and exceptionally potent new catalysts.

Results: The first recorded examples of alkyne metathesis relied on the use of catalysts generated in situ from simple ingredients following empirically optimized recipes. Although these procedures are operationally simple, they require harsh conditions and are therefore of limited preparative value. It was only after the advent of defined high-valent metal alkylidyne complexes ("Schrock alkylidynes") that the full potential of this transformation could be exploited. Such complexes however, require careful handling under inert conditions; this may be one of the reasons why alkyne metathesis has not nearly become as popular as its alkene counterpart in the synthetic community. Our group is committed to change this situation by developing user-friendly catalysts and demonstrating their performance in synthesis.

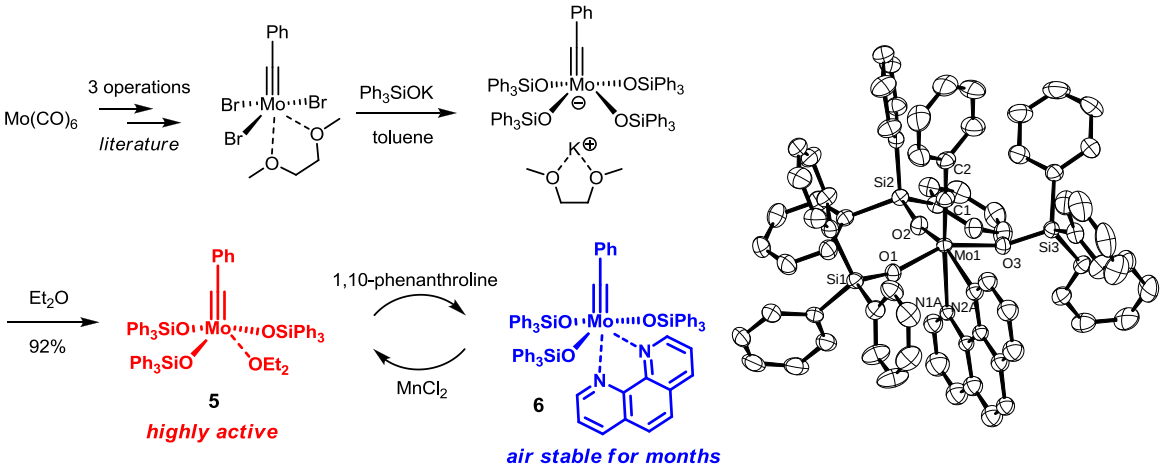


Inspiration was provided by a literature report, which showed that certain metal nitride complexes endowed with fluorinated alkoxide ligands, on treatment with sacrificial alkynes, equilibrate with the corresponding metal alkylidynes. However, the preparation of the required nitride precursor complexes was deemed unsatisfactory, not least because it involved potentially hazardous steps (azide chemistry). In a quest for more attractive alternatives, we were able to establish a much safer, quicker and scalable route to Mo-nitrides starting from inexpensive sodium molybdate. Moreover, we could show that triphenylsilanolate is a

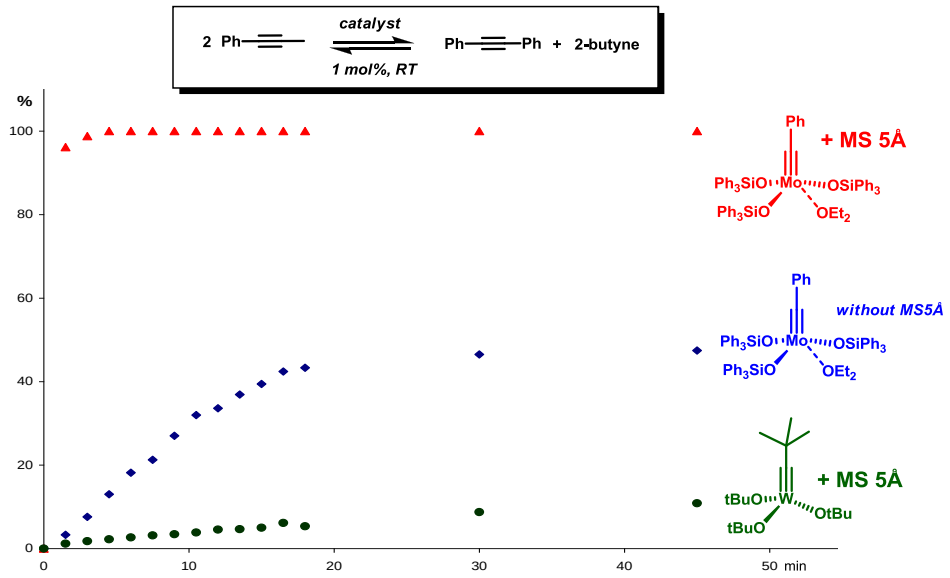
cheap and favorable substitute for the perfluorinated alkoxides previously used. The pyridine adduct **3** is sufficiently stable to be handled in air, yet reverts to the active species **1** at 80°C. The phenanthroline adduct **4** is indefinitely air stable. Although solutions of **4** themselves are inactive, addition of $MnCl_2$ engenders a ligand swap and thereby restores the catalytic performance. Mixtures of catalytic **4**/$MnCl_2$ (or other phenanthroline traps) gave excellent yields in alkyne metathesis reactions of all kinds and showed remarkable compatibility with a host of polar functional groups. So far, only acid chlorides and aldehydes were found to react with such molybdenum nitrides to give the corresponding nitriles (in the case of aldehydes by a mechanistically not yet fully understood redox process).



Despite the efficiency of **1** as precatalyst, the crucial equilibrium between **1** and the derived alkylidyne **2** clearly lies on the side of the nitride. This result suggested that the small amounts of **2** produced in situ must be superbly active. As a consequence, we prepared a series of previously unknown molybdenum alkylidynes of the general type $(Ph_3SiO)_3Mo{\equiv}CR$ (e.g. **5**) in pure form by adaptation of well established literature routes. These complexes were found to combine truly outstanding reactivity with a remarkable chemoselectivity profile; they clearly outperform all other alkyne metathesis catalysts previously tested in this laboratory. Equally rewarding is the fact that addition of 1,10-phenanthroline leads to an adduct of largely improved stability. Complex **6** can be stored in air for weeks without any signs of hydrolysis or degradation. Although solutions of **6** themselves do not induce metathesis, the highly active **5** is regenerated with $MnCl_2$ as a cheap, non-hygroscopic, hardly Lewis-acidic and benign additive.



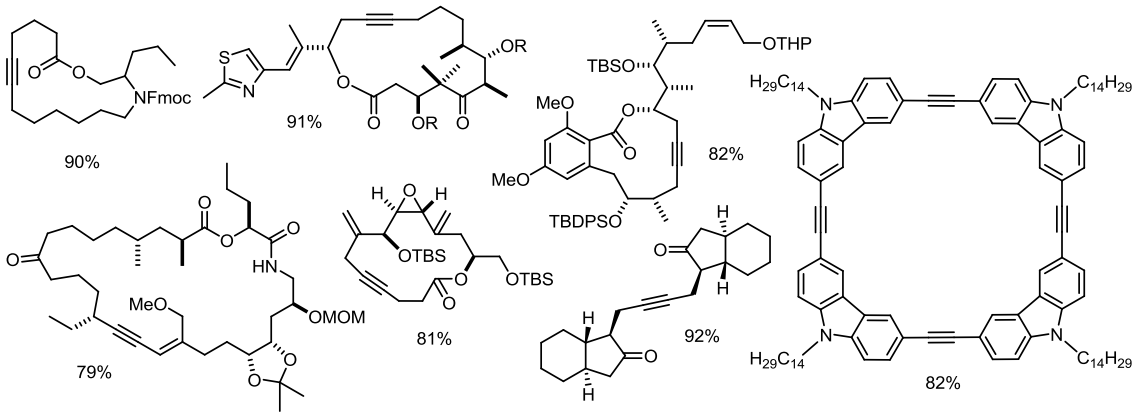
The distorted structure of **6** in the solid state explains the ease with which the phenanthroline ligand can be pulled off the Mo(6+) center. Likewise, the available data suggest that pending of the Mo–O–Si angles is facile. The resulting "flexible bulk" ensures the necessary space for substrate binding but protects the complex against bimolecular decomposition pathways. The only weakly donating Ph_3SiO-ligands impart a well-balanced level of Lewis acidity onto the d^0-molybdenum center, which ensures high activity and tolerance to polar substituents alike.



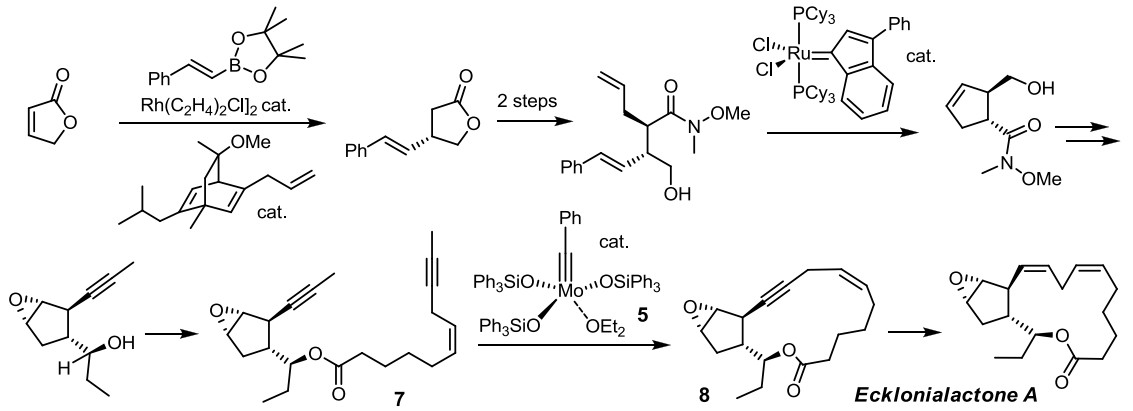
A priori, alkyne metathesis reactions of non-terminal alkynes lead to an equilibrium, which is traditionally shifted toward the products by driving the 2-butyne by-product out of the mixture at higher temperatures. Since complex **5**, however, effects the reaction at ambient temperature or even below, it was necessary to find another way to render the reaction productive in preparative terms. The addition of powdered MS 5 Å to the mixtures constitutes a simple and effective solution. In the presence of this additive, which traps the released butyne in its pores, alkyne metathesis reactions proceed with unprecedented rates under notably mild conditions. Although not yet fully optimized, 0.1 mol% of **5** were shown to ensure quantitative conversions at ambient temperature within short periods of time.

The compatibility of the new (pre)catalysts **3**, **4**, **5** or **6** with various functional groups is outstanding. Esters, ethers, various silyl ethers, thioethers, sulfonates, amides, carbamates, ketones, acetals, epoxides, nitro- and trifluoromethyl groups as well as various types of aromatic heterocycles (pyridine, thiophene, thiazole, carbazole) are well tolerated; nitriles are at least kinetically stable. Chiral centers next to an enolizable carbonyl group were not racemized, and elimination-prone primary tosylates as well as

acid- and base-sensitive aldol substructures remained intact. Although the orthogonal character of alkene- and alkyne metathesis had already previously been recognized, the rigorous distinction between the π-systems of alkynes and olefins is noteworthy: olefins are inert, independent of whether they are mono-, di- or trisubstuted, terminal, internal, or conjugated to a carbonyl group. A few representative products formed with the aid of these catalysts by inter- or intramolecular alkyne metatheses are shown below.

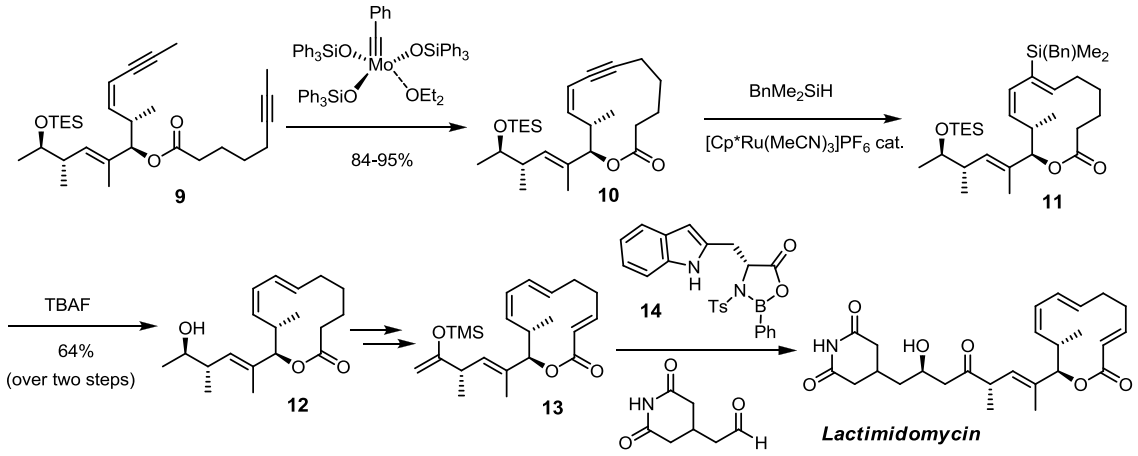


Our synthetic programs have already benefitted from these novel tools. Specifically, we developed a protecting group-free and catalysis-based total synthesis of the marine oxylipins of the **ecklonialactone** family. However, the projected RCAM of diyne **7** containing an unusually sensitive oxirane ring was unsuccessful when the traditional alkyne metathesis catalysts were used. Only complex **5** gave the desired cycloalkyne **8** in well reproducible 80% yield. This favorable outcome is ascribed to the tempered Lewis acidity of the catalyst as well as to the poor nucleophilicity of the peripheral silanolates. Semi-reduction of **8** then completed the total synthesis of ecklonialactone A.



A recent total synthesis of the potent cell migration inhibitor **lactimidomycin** features the stereocomplementary approach to *E*-alkenes via an alkyne metathesis/semi-

reduction sequence. The highly strained 12-membered 1,3-enyne **10** could be formed in excellent yield on a multigram scale with complex **5**. A subsequent ruthenium-catalyzed *trans*-hydrosilylation followed by protodesilylation of the resulting alkenylsilane **11** gave the 1,3-diene **12**. Its further elaboration to the target involved an oxidative enoate formation and a highly diastereoselective Mukaiyama aldol reaction as the key steps. Since lactimidomycin effectively reduces the motility of cancer cells, this compound holds considerable promise as a lead for the development of anti-metastatic drugs.



Other projects based on the use of alkyne metathesis completed during the report period concerned the preparation of all stereomers of the cytotoxic marine macrolide **amphidinolide V** as well as the total synthesis of the exceptionally potent F-ATPase inhibitor **cruentarin A** and a small collection of designer analogues. In both cases, the synthetic work was complemented by biological and biochemical evaluations of these natural products.

Publications resulting from this research area: 157, 158, 181, 319, 320, 362

External funding: Alexander von Humboldt Foundation (stipend to D. A. Clark)

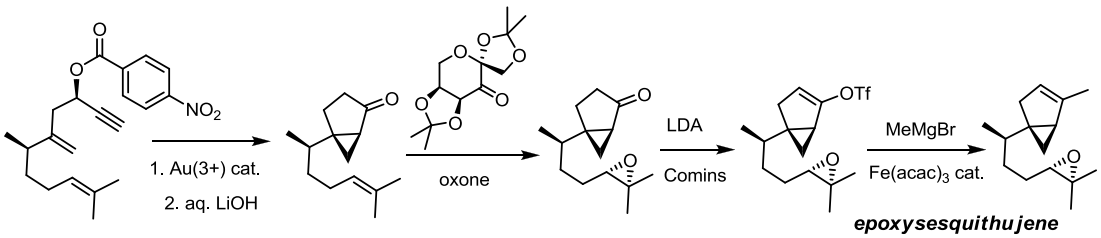
Cooperations: none

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

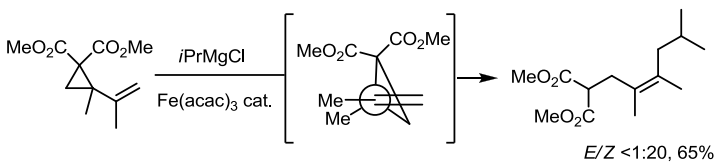
Involved: H. Krause, D. Laurich, A. Moyeux, A. Schlecker, B. D. Sherry, M. Sircoglou

Objective: The noble metals dominate a significant part of contemporary catalysis research despite of the high price, the need for expensive ligands, toxicity issues and environmental concerns. We are interested in emulating "noble" behavior by non-noble metals in a quest for more affordable and sustainable methodology.

Results: Inspired by pioneering studies of Kochi et al. published in the 1970's, our group has explored the preparative scope of iron catalyzed cross coupling reactions in some detail. Specifically, we showed that iron salts allow various types of (challenging) substrates to be activated under notably mild conditions (aryl chlorides, aryl tosylates, alkyl halides, alkynyl epoxides, enol triflates and –phosphates, acid chlorides, thiolesters etc.), yet is compatible with many functional groups. Such transformations are compliant with scale-up and have already been used with considerable success in other academic and industrial laboratories. An Account describing the current status of the field was published in the reporting period.

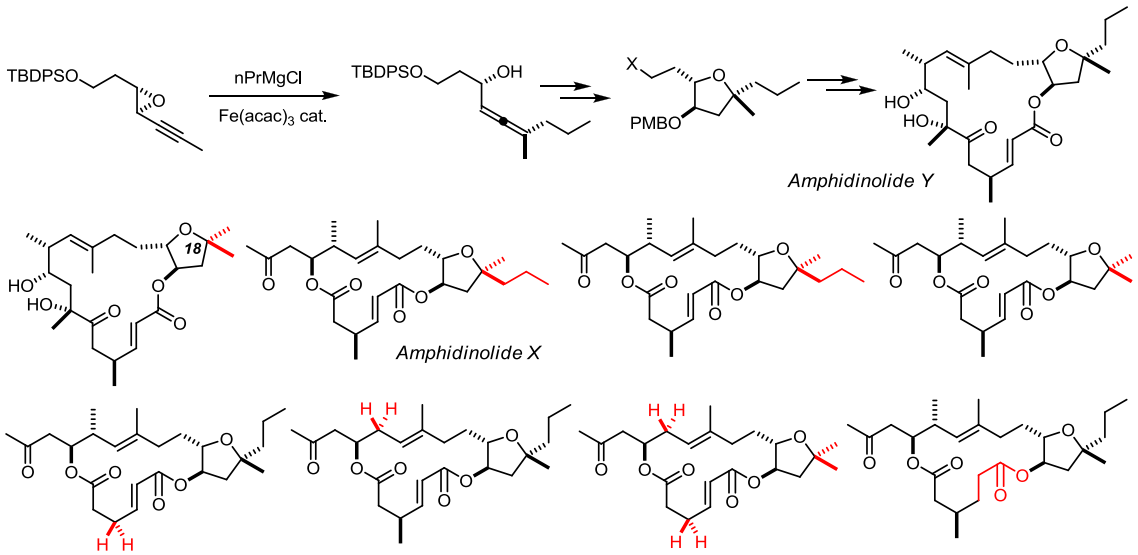


An illustrative example comes from our recent total synthesis of epoxysesquithujene, an ingredient of the essential oil of Asian *Valeriana* species. This application showed that the iron catalyzed coupling of an enol triflate leaves an adjacent cyclopropyl group as well as a reactive epoxide untouched. Based on this favorable outcome, all possible diastereomers could be formed without undue effort, which allowed us to assign the previously unknown stereostructure of this natural product as shown in the Scheme.



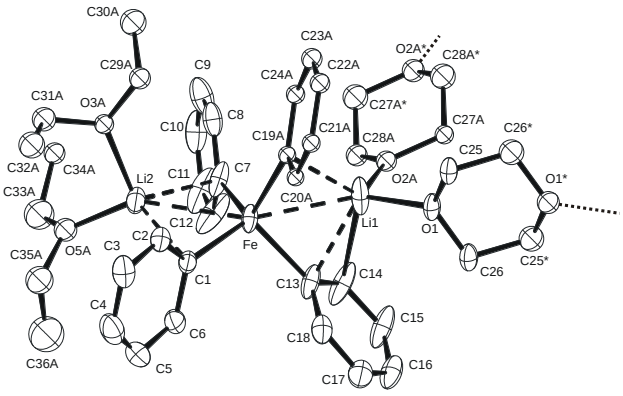
An unprecedented iron catalyzed transformation was found in the highly regioselective addition of

branched primary, secondary or even tertiary Grignard reagents to activated alkenylcyclopropanes. Compelling evidence for a direct addition mechanism as opposed to a single electron transfer- or an iron-allyl based process was obtained.



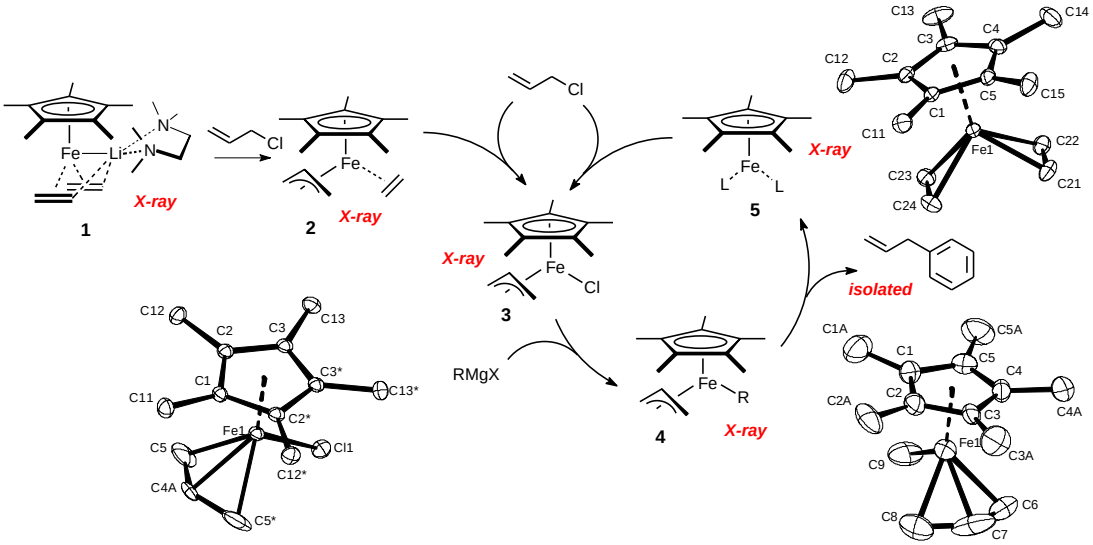
The iron catalyzed ring opening of propargyl epoxides with formation of allenes had previously served as a key step in our total synthesis of amphidinolide X and Y. In view of the promising cytotoxic activity of these extremely scarce macrolides, we now prepared a focused “library” of analogues for biological investigations, which were carried out in collaboration with a partner specialized in oncology. Ongoing projects intend to further illustrate the advantages of iron catalysis by practical and saleable syntheses of economically relevant compounds and by the preparation of structurally complex polycyclic natural products from the bis(bibenzyl) series.

In contrast to the mechanisms of traditional cross coupling reactions using palladium- or nickel catalysts, which have been extensively studied over the years, the understanding for iron catalysis is in its infancy. Therefore, our investigations into this largely void area of organometallic chemistry were extended during the report period. It becomes increasingly clear that iron catalyzed cross coupling reactions can follow at least two distinctly different mechanisms:

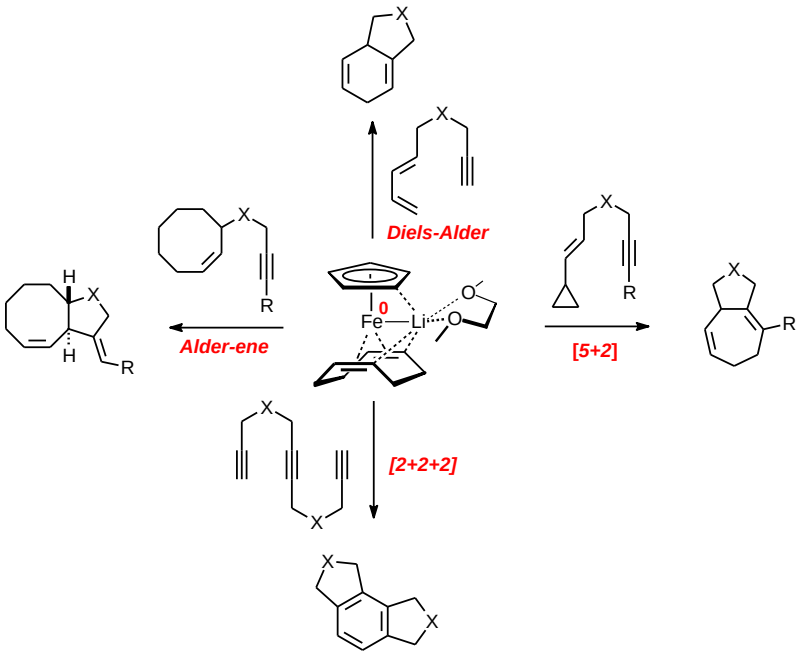


Iron catalyzed reactions of nucleophiles, which are unable to undergo β-hydride elimination,

most likely involve organoferrate complexes as the pertinent reactive intermediates. This notion had previously been supported by the isolation of the exceptionally sensitive and structurally unique "super ate" complex $[(Me_4Fe)(MeLi)][Li(OEt_2)]_2$. During the report period, we were able to gain further experimental evidence for the ferrate manifold by full characterization of $[Ph_4Fe][Li(Et_2O)_2][Li(1,4\text{-dioxane})]$, an equally pyrophoric species formed from $FeCl_2$ and PhLi. These structurally defined ate-complexes react with activated electrophiles such as acid chlorides, enol triflates or alkyl halides, but are unable to engage with aromatic substrates.



Iron catalyzed reactions of aryl chlorides and related electrophiles proceed via redox cycles. Since the active iron catalysts produced in situ from $Fe(acac)_3$ and RMgX themselves are ill defined and hardly amenable to mechanistic study, we used formally low-valent but well characterized iron complexes such as **1** for our mechanistic investigations. Control experiments made sure that **1** and related species themselves are catalytically competent. They react with prototype substrates such as chlorobenzene or allyl halides to give the regular insertion products. Surprisingly, however, excess substrate engenders a subsequent single electron oxidation (**2** → **3**); the resulting Fe(3+) species are amenable to transmetalation to give diorganoiron intermediates of type **4**, which, upon reductive elimination, release the product together with formally monovalent Fe-complexes such as **5**. As **5** is able to insert into the substrate, a basic catalytic cycle is closed. Despite their very high sensitivity, all intermediates of this scenario were unequivocally characterized by X-ray crystallography. Moreover, we started collaboration with Professor Wieghardt in an attempt to gain further insights by Mössbauer and/or EPR spectroscopy.



Our investigations into iron catalyzed cycloaddition and cycloisomerization reactions have also flourished during the report period. A host of preparative results showed that such transformations rival their noble metal catalyzed ancestors in terms of efficiency; the scope and the functional group tolerance are remarkable. Compelling evidence for the formation of metallacyclic intermediates was obtained by deuterium labeling studies as well as by the isolation and full characterization of pertinent organoiron intermediates. These studies are actively pursued since recent X-ray data indicate a very unusual bonding situation in 1,3-diene complexes of low valent iron.

Publications resulting from this research area: 33, 34, 36, 115, 177, 182, 261

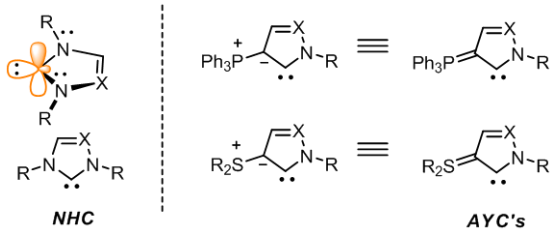
External funding: Fonds der Chemischen Industrie; Merck Research Council

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

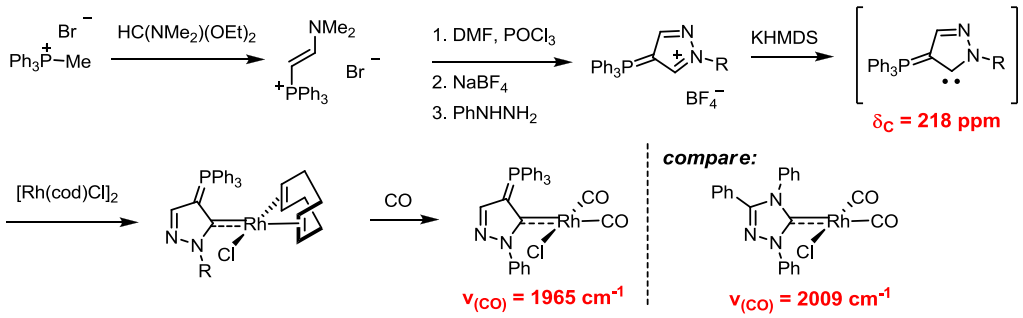
2.4.4 Research Area "Novel Donor Ligands" (A. Fürstner)

Involved: M. Alcarazo, K. Radkowski, T. Stork, R. M. Suárez

Objective: The tremendous success of NHC's as ancillary ligands for homogeneous catalysis has overshadowed the fact that alternative design may also lead to stable or metastable singlet carbenes. Likewise, carbon(0) compounds seem to promise interesting coordination chemistry.

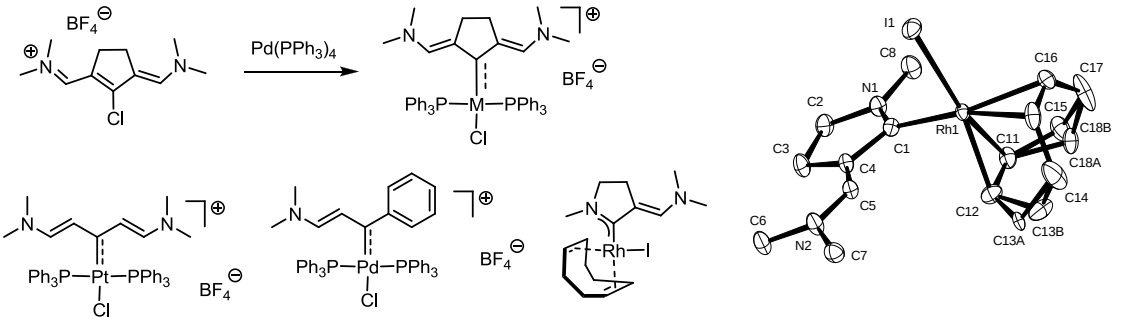


Results: All diaminocarbenes, including the classical N-heterocyclic carbenes (NHC's), largely owe their stability to the overlap of the lone pairs of the N-atoms with the empty p-orbital at the singlet carbene site; this interaction is much more important than steric shielding of the reactive center. Under this premise, it should be possible to obtain other types of (stable) singlet carbenes by formally replacing the N-atoms by other structural elements containing an electron pair in an orbital of appropriate symmetry.

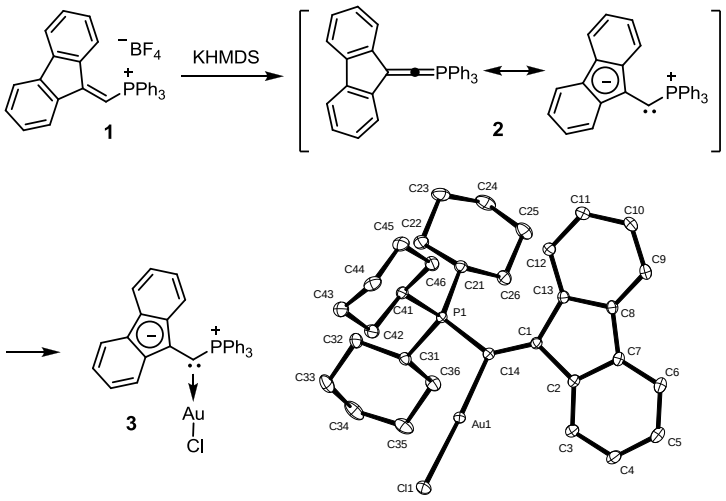


The polarized π-bond of a phosphorus-, sulfur-, or nitrogen ylide may represent an adequate structural element. Formal exchange of an endocyclic N-atom for an ylide leads to constructs termed "amino-ylide carbenes" (AYC's), which gain stability from the neighborhood of two very reactive sites. As the π-donating capacity of an ylide arguably exceeds that of an endocyclic N-atom whereas the inductive effect should be smaller, one might expect that AYCs exhibit pronounced electron releasing capacities. The required precursor salts are available in large quantities and in many structural variants by following well established synthesis routes. Deprotonation with a non-nucleophilic base generates the corresponding carbenes, which were trapped with appropriate metal salts to give air stable complexes of Rh(1+), Pd(2+) or Au(1+).

Along similar lines, the π-system of an enamine might qualify as a substitute for the N-atoms of traditional NHC's. We could demonstrate that stable metal complexes bearing singlet carbene ligands stabilized by lateral enamine moieties (vinylogous NHC's) are easily accessible by oxidative insertion of metals into chloro vinamidinium salts. Since the latter can be formed in great diversity and the resulting metal complexes are stable and rich in electrons, applications to homogeneous catalysis seem promising. The carbene character of the ligands is evident from spectroscopic and crystallographic data.

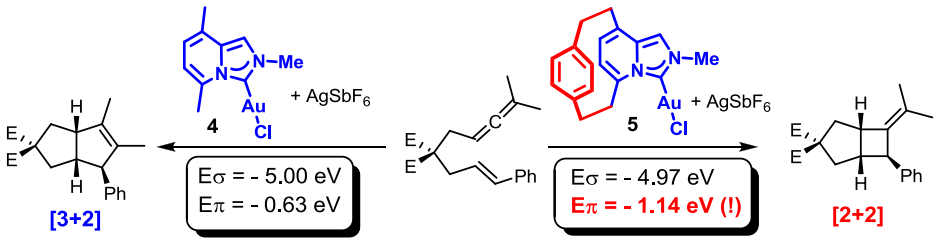


Yet another class of singlet carbene can be formed by deprotonation of alkenyl phosphonium salts such as **1**. The resulting product **2** can either be interpreted as a push-pull cumulene or as a singlet carbene. Whereas the observed ^{13}C NMR shift of the central C-atom at 198.8 ppm does not allow these resonance extremes to be distinguished, the exclusive binding of metals to the central position proves the availability of a lone pair at this site. Because of the excellent donor qualities of these new carbenes, the resulting complexes are rich in electron at the metal center yet air stable in many cases.

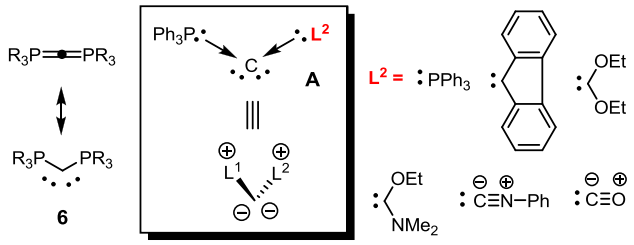


Whereas the σ-donor qualities of NHC's are undisputed and extensively used as an enabling feature for homogeneous catalysis, their π-acceptor properties are often considered weak or even negligible. In contrast to this perception, a study from this laboratory showed that the acceptor properties of NHCs can be up-regulated to the extent that they start dictating the observed reactivity. The comparison of the known imidazopyridin-ylidene ligand in **4** with its cyclophanic analogue contained in complex

5 is an instructive example. DFT calculations indicate that the σ-donor capacity of both NHCs (E_σ) is virtually identical, whereas the energies of their π-acceptor orbitals (E_π) are greatly different. This feature translates into the reaction behavior: exposure of an ene-allene to catalytic amounts of **4** triggered a [3+2]-cycloaddition, whereas complex **5** engendered exclusive formation of the corresponding [2+2] cycloadduct. The course of two additional, mechanistically unrelated transformations could similarly be affected by altering the π-acceptor property of the ancillary NHC, which is also considerably upregulated in triazol-ylidenes and the novel AYC's prepared in this laboratory. As it seems easier to tune the π-acidity of an NHC than to change the σ-donor properties, the general perception of this important class of ligands needs to be revised.

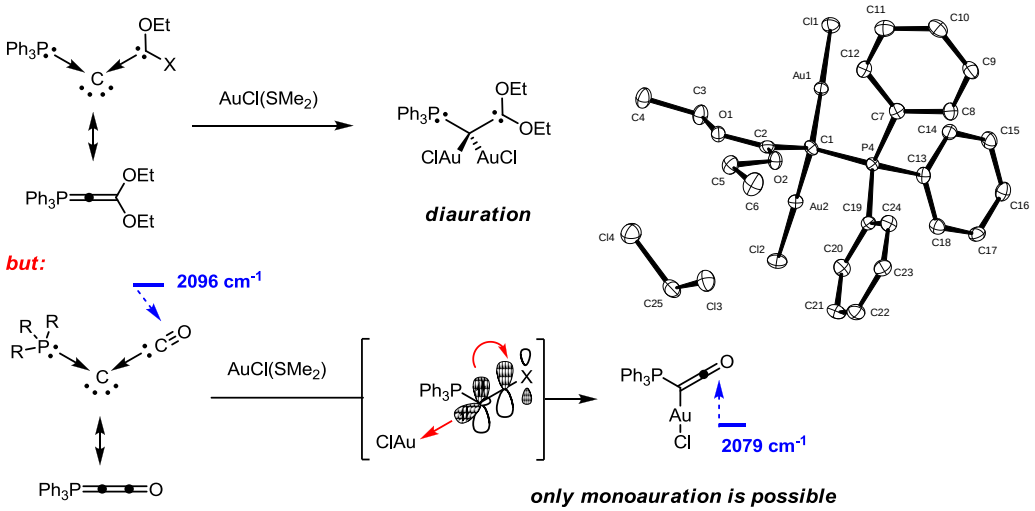


Organic compounds are commonly understood as substances based on carbon atoms which involve all four valence electrons in bonding. If two electrons form a lone-pair, as is the case in carbon monoxide, isonitriles or singlet-carbenes, one crosses the traditional borders to coordination chemistry and/or enters the realm of reactive intermediates. Compounds, wherein a carbon atom configures all four valence electrons in form of *two* lone-pairs may seem elusive at first sight. Following insightful early reports in the literature, however, recent computational studies led Frenking et al. propose that carbodiphosphoranes such as **6** actually consist of two phosphine "ligands" coordinated to a central, formally "zerovalent" carbon atom with two orthogonal lone pairs at disposition; one of them resides in an orbital of σ-symmetry (HOMO–1), whereas the other one occupies an orbital with largely π-character (HOMO).



We became interested in proving or disproving this provocative concept by experimental data. Moreover, we want to see if other (hetero)cumulenes endowed with electron releasing substituents should also be described as *complexes* of the general type $L^1 \rightarrow C \leftarrow L^2$ (**A**). Traditionally, capto-dative bonding modes are invoked only upon complexation of carbogenic compounds to a metal center, whereby the organic moiety always serves as

the "ligand". If the description $L^1 \rightarrow C \leftarrow L^2$ is physically meaningful, however, it implies that carbon itself can act as the "central atom" of a coordination compound, which differs fundamentally from the common understanding of organic chemistry.



To this end, we prepared a series of compounds of the conceived type $L^1 \rightarrow C \leftarrow L^2$, in which $L^1 = PPh_3$ was kept constant, whereas the donor capacity of the second internal "ligand" L^2 was gradually altered. By studying their coordination behavior, we could show that C(0)-compounds are present only if L^1 and L^2 are both strongly donating and, at the same time, meet rigorous geometrical requirements to prevent "back donation" of electron density from the central C-atom to the internal donor ligands L. This topological condition had not been recognized before; it explains why compounds with L^2 = CO, isonitriles or even certain carbenes cannot make two lone pairs available at the central C-atom they bind to. While our study has hence provided strong experimental support for the concept of carbon(0) as such, it also showed that C(0)-compounds are not as abundant as previously suggested solely on the basis of computations. The use of CO, isonitriles, or fluorenylidene as "ligands" L does not impart carbon(0) character onto a central C-atom, even though the resulting compounds are still best described in terms of σ-donation and π-back donation between neighboring carbon atoms. Therefore we conclude that the concept of "coordination chemistry *at* carbon" is by no means limited to seemingly exotic oxidation states but is much more general than previously anticipated. These investigations were carried out in close collaboration with Professor Thiel to back the experimental data up with high level computational results.

Publications resulting from this research area: 28, 29, 30, 149, 179, 286, 288

External funding: Fonds der Chemischen Industrie; Spanish Ministerio de Educación y Ciencia (stipend to M. Alcarazo)

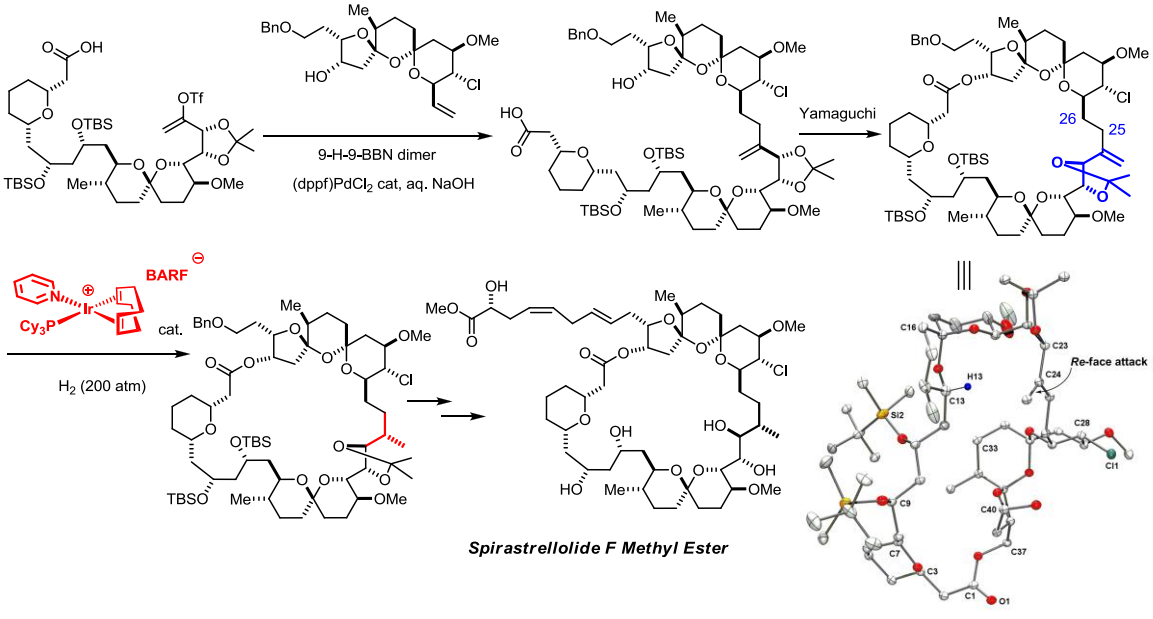
Cooperations: W. Thiel (Mülheim/Ruhr, DE)

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

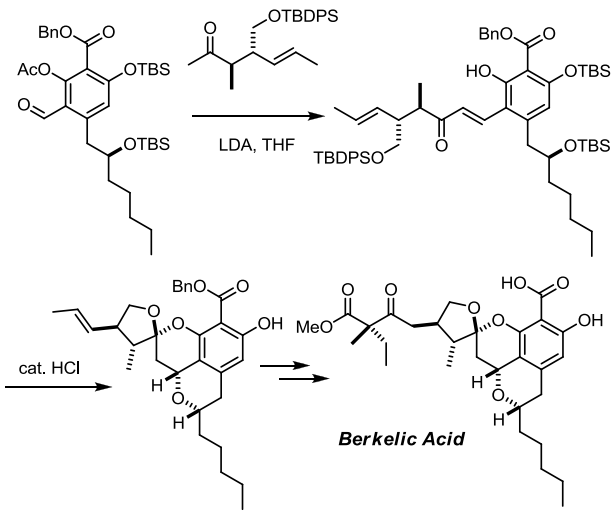
Involved: J. Ackerstaff, S. Benson, M. Bindl, L. C. Bouchez, P. Buchgraber, J. Ceccon, G. Chollet, M.-P. Collin, B. Fasching, J. Gagnepain, V. Hickmann, L. Jean, D. Laurich, K. Micoine, L. Morency, E. Moulin, G. O'Neil, J. Pospíšil, S. Schulthoff, T. N. Snaddon, M. Tamiya

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.

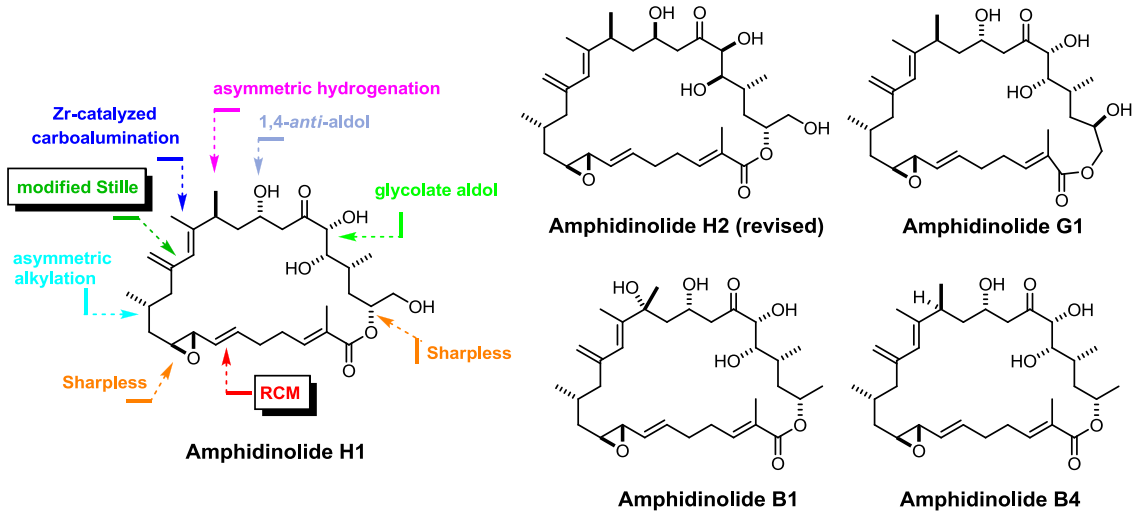
Results: The total synthesis of **spirastrellolide F**, a potent phosphatase inhibitor of marine origin, was successfully completed during the report period. At the outset of this project, neither the absolute nor the relative stereochemistry of this target containing no less than 21 chiral centers had been rigorously established. This situation forced us to devise particularly concise approaches to the required building blocks as well as a highly effective assembly process. After a first attempt to close the macrocyclic edifice by RCM at the non-stereogenic C25-C26 bond had failed (even a "relay strategy" was unsuccessful), we implemented an effective Suzuki reaction/macrolactonization strategy. This approach allowed the sensitive northern hemisphere to be combined with an elaborate enol triflate bearing a free carboxylic acid terminus.



The course of the subsequent reduction of the *exo*-methylene group was rigorously controlled by imposing conformational constraints onto the macrocylic scaffold. To this end, an isopropylidene acetal on the adjacent diol unit was used to orient the olefin such that the *Si*-face was shielded by the BC-ring spiroacetal whereas the *Re*-face was open. Because of considerable transannular strain, however, only the use of a modified Crabtree catalyst escorted by a strictly non-coordinating BARF counterion was able to effect the hydrogenation. Since the reaction was exquisitely selective in our favor, a sound basis for the completion of the total synthesis was reached. A valuable spin-off of the project was the development of a new route to substituted pyrans via an alkyl-Suzuki-reaction/Michael addition cascade.

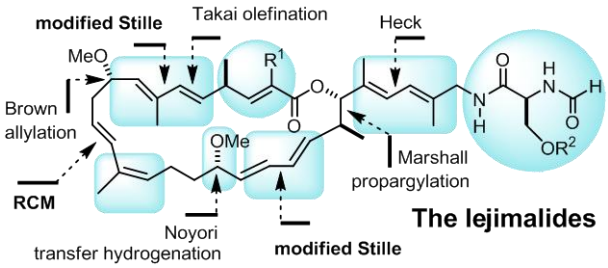


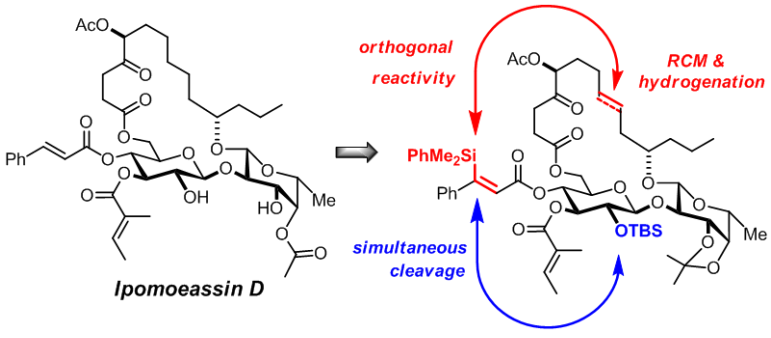
Another challenging project concerned the total synthesis of **berkelic acid**. Although less complex than the spirastrellolides, we noticed that the structure of this matrix metalloproteinase inhibitor derived from an extremophilic fungus had been misassigned by the isolation team. A newly devised one-pot triple-deprotection / 1,4-addition / spiroacetalization cascade brought all possible diastereomers into reach. The resulting comprehensive data set allowed us to determine the correct structure of the natural product.



The lability of more than one substructure embedded into the skeleton of **amphidinolide** H1 rendered the first total synthesis of this potently cytotoxic macrolide (IC_{50} in the picomolar range) exceptionally demanding. Key to success was the development of a modified Stille-Migita reaction protocol for the formation of the non-thermodynamic 1,3-diene unit of the target. This new protocol relies on the combined use of Pd(0), copper thiophene-2-carboxylate and tetrabutylammonium diphenyl-phosphinate as the promoter of choice and allowed this and a variety of other exigent cross coupling reactions to be performed under strictly neutral and fluoride-free conditions. The total synthesis of amphidinolide H1 also featured a ring closing metathesis reaction of a sensitive alkenyl epoxide derivative, which had hardly any precedent prior to this work. Once the route had been worked out and the fragment syntheses were optimized, the sister compounds amphidinolide B1, B4, G1 could also be obtained. In the case of amphidinolide H2, we noticed that the structure originally assigned to this product must be incorrect; a revision has been proposed.

The modified Stille-Migita protocol is also instrumental for our still ongoing **iejimalide** project. To meet the demands of a serious preclinical evaluation of these promising cytotoxic agents, the total synthesis of iejimalide B has now been fully optimized to deliver one gram of this natural product in 16 steps (longest linear sequence, ca. 42 steps overall). In addition, more than 20 fully synthetic analogues were prepared and their antitumor properties evaluated by a company specialized in oncology using cell-based as well as tumor colony-based assays; in vivo studies are underway. Moreover, we prepared a hybrid structure, which combined the core of iejimalide with the tail region of the archazolids, a structurally related class of potent ATPase inhibitors.

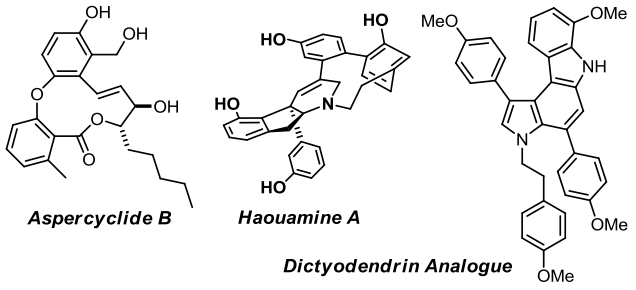




Another promising class of anticancer agents are the **ipomoeassins**, a family of glycolipids isolated from a tropical morning glory plant. Our group completed the first total synthesis of all

members of this series, which required the development of a novel protecting group strategy (*C*-silylated cinnamate) to allow for the selective hydrogenation of the macrocycle formed by RCM without destroying the unsaturation in the esters attached to the carbohydrate rim. The acquired biological data show a striking correlation between the peripheral acylation pattern of the compounds and their cytotoxicity, which can be increased by two orders of magnitude by manipulation of a single acetyl group.

Another successful project concerned the **aspercyclides**, which posed considerable challenges due to the strain of their 11-membered ring containing seven sp^2-hybridized C-atoms. Only a Nozaki-Hiyama-Kishi reaction furnished the necessary thermodynamic driving force for the closure of this demanding ring system. Likewise, our synthesis of **haouamine A** is largely based on organometallic reactions and catalysts; the chosen approach intercepted a known intermediate of a previous total synthesis of this polycyclic alkaloid. Finally, a small collection of analogues modeled around the **dictyodendrin** alkaloids was prepared using a titanium-induced reductive coupling reaction previously developed by the group. This project revealed the peculiar reactivity of these highly electron rich heteroaromatic compounds, which were shown in our laboratory to efficiently cleave double stranded DNA in the presence of copper salts.



Publications resulting from this research area: 12, 27, 31, 32, 36, 37, 69, 155, 157, 164, 180, 181, 182, 218, 220, 231, 319, 344, 362, 363, 404

External funding: Chemical Genomics Center (MPG); Alexander von Humboldt Foundation (stipends to G. O'Neil and E. Moulin); Association pour la Recerche sur le Cancer, France (stipend to E. Moulin); Fonds der Chemischen Industrie (stipend to S. Benson); Natural Sciences and Engineering Research Council of Canada (stipend to L. Morency); Japan Society for the Promotion of Science (stipend to M. Tamiya); F. Hoffmann-La Roche

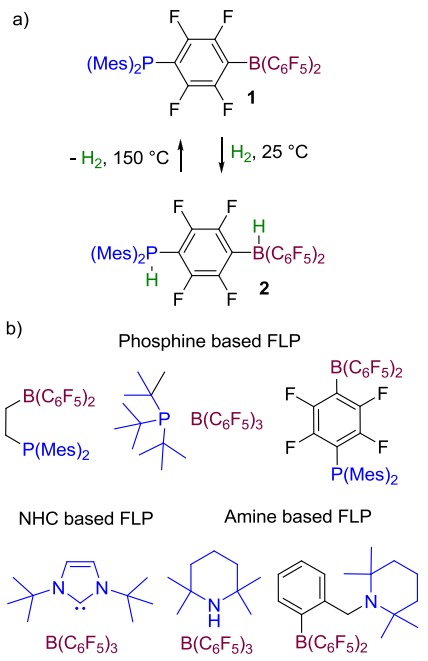
Cooperations: Chemical Genomics Center (Dortmund, DE); Oncotest GmbH (Freiburg, DE); R. Müller (Saarbrücken, DE); C. Nevado (Zurich, CH)

2.4.6 Research Area "Design, Synthesis and Applications of Organic Frustrated Lewis Pairs" (M. Alcarazo)

Involved: H. Bruns, S. Holle, B. Inés, D. Palomas

Objective: With the aim of overcoming the current limitations of frustrated Lewis pairs (FLP) as catalysts for the reduction of C=C and C=X functionalities, we started a program oriented to broaden the range of bases and acids that can be used in FLP chemistry. The activities in this field during the report period mainly concerned the use of carbodiphosphoranes as carbon-based Lewis bases and electron poor allenes as surrogates of perfluorinated boranes.

Results: In 1923 G. N. Lewis classified molecules into those that behave as electron pair donors (bases), and inversely, those that are able to accept an electron pair (acids). Since then, this notion of Lewis acids and bases has proven to be extremely useful and it is a very powerful tool to explain and rationalize, from a molecular-orbital-based point of view, the reactivity of many main-group and transition metal complexes. When a Lewis acid is combined with a Lewis base a neutralization reaction takes place. However occasionally, some systems that deviate from this general principle have been found. For example, as early as in 1942, Brown discovered that 2,6-dimethylpyridine does not react with trimethylborane to form the pyridine-borane adduct. Based on molecular models, he assumed that the steric interactions between the methyl groups from the borane and those on the *ortho* position of the pyridine were responsible for this lack of reactivity.

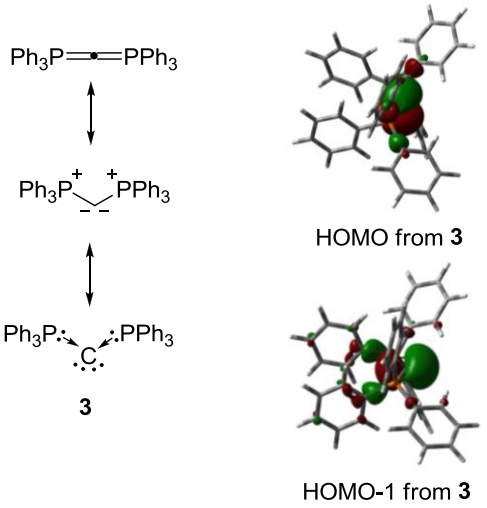


Scheme 1. a) Reversible activation of H_2 by **1**. b) Other combinations of Lewis acids and based that form FLPs.

More than sixty years later the group of Stephan synthesized compound **1** in an attempt to study the reactivity of systems in which Lewis acid and base functions were incorporated into the same molecule but sterically protected in order to preclude self quenching, (Scheme 1a). Addition to H_2 to a solution of **1** generated the zwitterionic species **2** that upon heating at 150°C regenerated **1** and H_2. This reactivity represents the first example of a non-transition-metal system that is able to activate

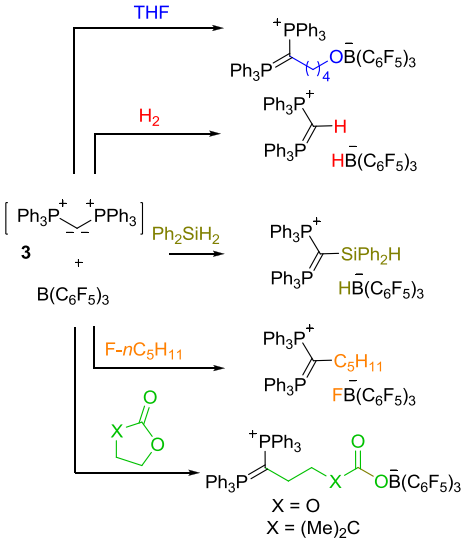
dihidrogen in a reversible manner. As compound **1** is a monomer in which steric demand precludes classical adduct formation, the term "frustrated Lewis pairs" (FLPs) was coined.

Since then many other combinations of Lewis bases and acids have also proven to form FLPs and share similar reactivity towards dihidrogen (Scheme 1b). Even more remarkable, Stephan and Erker were able to apply some of them on the metal free hydrogenation of imines using directly H_2 instead of any surrogate such as Hantzsch esters. Despite of the tremendous synthetic interest of this transformation the substrate scope is still extremely narrow. Only very sterically demanding imines can be reduced as they are the only ones that do not directly react with the borane used as Lewis acid partner for the FLP system.



Scheme 2. a) Electronic structure of **3**.

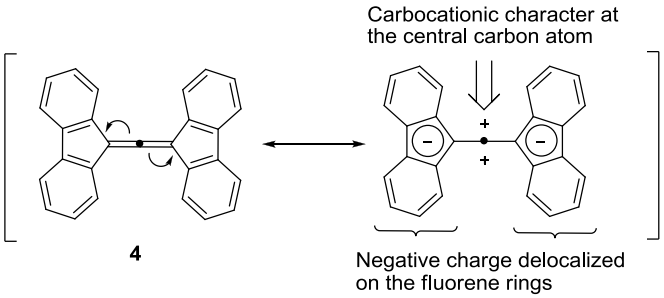
With the aim of overcoming these important limitations, we have started a program oriented to broaden the range of bases that can be used in FLP chemistry. In this regard we were inspired by the computational investigations of Tonner and Frenking on the nature of carbodiphosphoranes. They propose that these compounds should be considered as comprising two phosphine ligands coordinated to a central zerovalent carbon atom that retains its four valence electrons. This view has been subsequently confirmed experimentally by the work of Bertrand, Fürstner, and others (Scheme 2). The available information suggests that C(0) compounds must be exceptionally good nucleophiles. In fact, the calculated proton affinity for carbodiphosphoranes surpasses the values reported for amines, phosphines and even N-heterocyclic carbenes. It was envisaged therefore that, if sufficiently sterically hindered, C(0) compounds should qualify as bases in the framework of frustrated Lewis pair chemistry. In an



Scheme 3. Reactivity of the pair $C(PPh_3)_2$ / $B(C_3F_5)_3$.

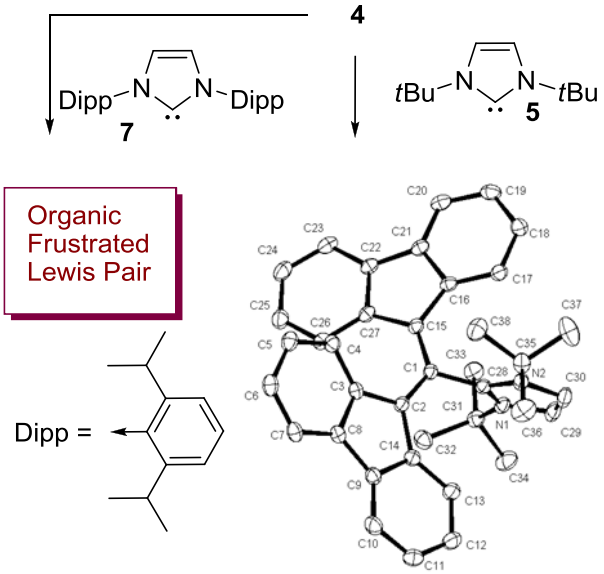
attempt to address this issue, we studied the reactivity of the pair hexaphenylcarbodiphosphorane **3**/B(C_6F_5)$_3$ towards several small molecules. The reactivity observed is summarized in Scheme 3. The system is not only able to achieve the already classical H-H, C-O and C-H bond cleavages, but also the activation of Si-H bonds and even alkyl fluorides. Moreover the peculiar electronic situation of the C(0) base makes the system unique: after the first protonation or alkylation, some degree of frustration persists, allowing for a second consecutive activation.

Additionally and with the same objective, we have also very recently studied the possibility of employing carbon-based Lewis acids instead of polyfluorinated boranes. Especifically, we realized that allene **4** can be envisaged as neutral trityl cation surrogate, and thus as a promising alternative to B(C_6F_5)$_3$. The intrinsic polarization/charge separation in this molecule, which is the result of the tendency of fluorene to accept a pair of electrons on the π system in order to gain aromatization, generates a partial carbocationic character on the allene central carbon. Likewise, the delocalized negative charge at both molecular extremes should prevent any undesired nucleophilic attack from the basic partner onto the periphery (Scheme 4).



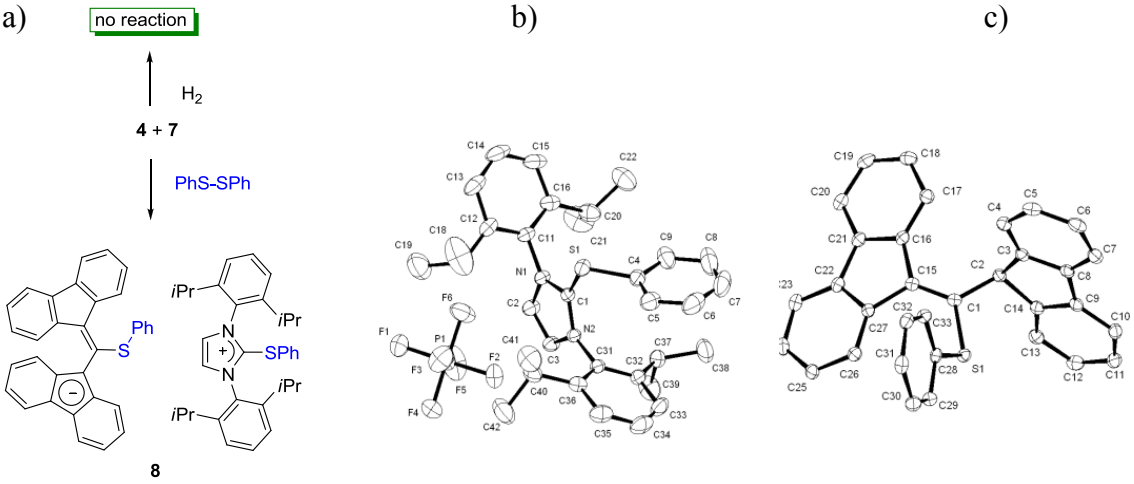
Scheme 4. Electronic situation on allene **4**.

In early attempts, the combination of 1,3-di-*tert*-butylimidazol-2-ylidene (I*t*Bu) **5** with allene **4** was investigated as a possible FLP. However, that mixture generated deep blue solutions from which the classical Lewis adduct **6** was isolated (Scheme 5). In contrast, when **1** was mixed with 1,3-bis(2',6'-diisopropylphenyl)-imidazol-2-ylidene (IDipp) **7**, NMR spectroscopy indicated no interaction between the partners, denoting the formation of a frustrated Lewis pair (Scheme 5). At that point the Lewis acidity of allene **6** was quantified by the Childs



Scheme 5. Formation of adduct 6 between allene 4 and 1,3-di(tbutyl)imidazol-2-ylidene and generation of an organic FLP with 1,3-bis(2',6'-diisopropylpheny)imidazol-2-ylidene.

method using crotonaldehyde as the reference base. The obtained Δδ values rank the acidity of **4** as clearly weaker than polyfluorinated boranes but still of the order of $B(OPh)_3$. Due to this limited Lewis acidity of **4**, dihydrogen cleavage was neither expected nor has it been experimentally realized. However, a weaker non-polar covalent bond such as that of S-S in disulfides could be heterolytically cleaved, thus demonstrating the potential of these systems (Scheme 6).



Scheme 6. a) Activation of disulfides by the organic pair **4**/**7**. b) Crystal structure of the cationic part of **8**. c) Crystal structure of the anionic part **8.**

Publications resulting from this area: 285, 326

External funding: Regional Government of the Basque Country, Spain (fellowship to B. Inés); Fonds der Chemischen Industrie

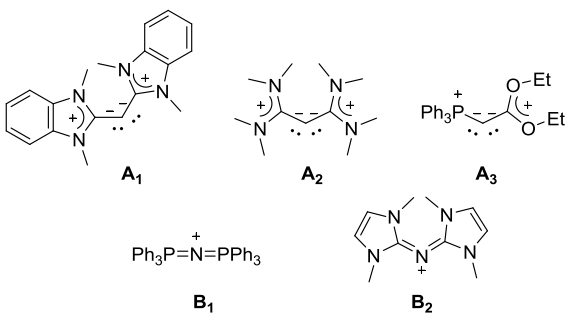
Cooperations: W. Thiel (Mülheim/Ruhr, DE)

2.4.7 Research Area "Design and Synthesis of Unconventional Ligands" (M. Alcarazo)

Involved: H. Bruns, J. Carreras, S. Holle, J. Petuškova, A. Vázquez

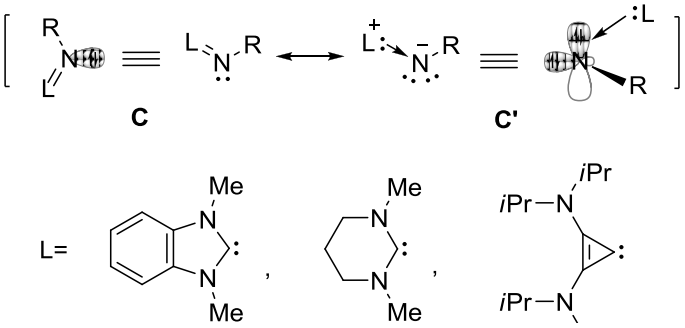
Objective: Synthesis and study of the coordination properties of ligands based on N(I)

Results: In most organic compounds nitrogen uses three of its five valence electrons to form bonds with surrounding atoms while keeping the other two as a lone pair, having therefore a formal oxidation state of +3. Analogously with the exception of CO, carbenes and isonitriles, carbon is normally tetravalent in organic molecules. However, following seminal work from Ramírez and inspiring theoretical studies from Tonner and Frenking, Bertrand and Fürstner have synthesized and evaluated the coordination behavior of carbodicarbenes **A_1-A_2** and carbophosphinocarbenes **A_3** (Scheme 1). These compounds may be considered as consisting of two carbene ligands, or a carbene and a phosphine, coordinated to a central zerovalent carbon atom. This bonding situation can, in principle, be extrapolated to **B_1** and **B_2**, compounds where the central carbon in carbodiphosphoranes or carbodicarbenes has been formally replaced by an isoelectronic N^+ fragment. However, the positive charge introduced in the systems by such a formal substitution precludes interaction with metal centers. In fact bis(phosphine)iminium ions have been extensively used as non-interfering cations for the isolation and structural characterization of -ate species. A further structural change, directed to keep charge neutrality, is therefore essential.



Scheme 1. Representative structures of carbodocarbenes **A_1** and **A_2**, cabophosphinocarbenes **A_3**, bis(phosphine)iminiun cations **B_1** and bis(carbene)iminium cations **B_2**.

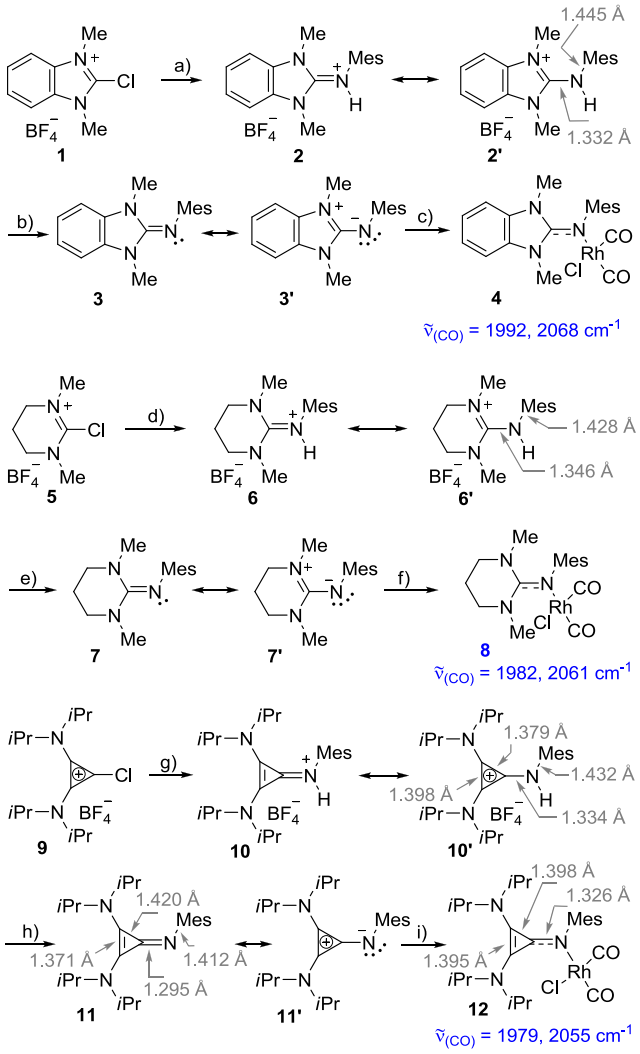
Replacement of one of the carbene moieties in **B_2** by anionic R^- or Ar^- groups eliminates the global positive charge, yet keeps the system isoelectronic with carbodicarbenes. To favor the particular electronic configuration



Scheme 2. Conceivable resonance extremes of **C**-type imines.

in which the nitrogen atom is able to donate four electrons, over the one typical of imines, an adequate selection of the ligand L is crucial. It must be a strong σ donor and at the same time a very poor π acceptor to minimize back donation from the central nitrogen to the carbene moiety.

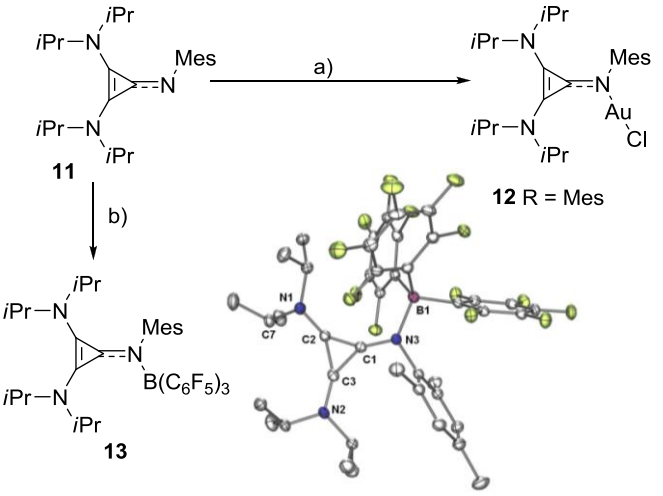
This extreme situation, represented by resonance structure **C'**, is better characterized as a coordination complex in which a carbene donates two electrons into the empty orbital of a nitrene (Scheme 2). The preparation of these compounds starts with the condensation of readily available chloroiminium or chlorocyclopropenium salts and mesitylamine, followed by deprotonation with KH or KHMDS.



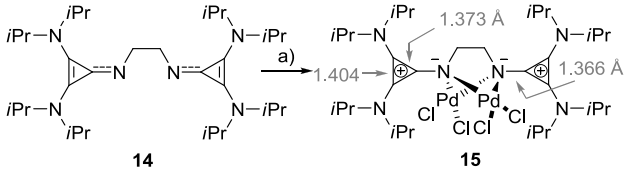
Scheme 3. Reagents and conditions: a) $MesNH_2$, MeCN, 160°C (microwaves), 1 h, 48%. b) KH, THF, 45°C, overnight, 56%. c) $[RhCl(CO)_2]_2$, THF, 20 min, 88%. d) $MesNH_2$, *n*BuLi, THF, reflux, 12 h, 78%. e) KHMDS, toluene, -20°C, RT, 96%. f) $[RhCl(CO)_2]_2$, THF, 20 min, 61%. g) $MesNH_2$, THF, reflux, 24 h, 93%. h) KH, THF, 60°C, overnight, 91%. i) $[RhCl(CO)_2]_2$, THF, 20 min, 72%.

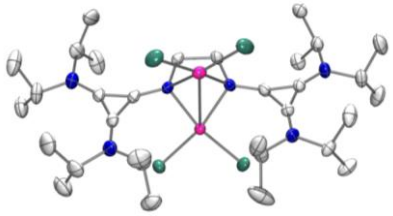
The donor ability of these ligands was evaluated by analysis of the CO stretching frequencies in complexes of type $[RhCl(CO)_2\mathbf{C}]$. The corresponding data suggest that **3** has a donor capability similar to iminophosphoranes. Compound **7** surpasses the strongest electron releasing N-heterocyclic carbenes while **11** clearly rivals (amino)(ylide) carbenes and carbodicarbenes. These exceptional donor properties are highlighted by comparison with other nitrogen based ligands such as pyridines or imines. As an indicative example, the unsymmetrical stretching mode of the CO ligands in complex **12** appears at a frequency 36 cm^{-1} lower than in the analogous pyridine complex.

Once the bis(diisopropylamino) cyclopropenyl-ylidene was identified as the most appropriate carbene to produce extremely electron rich **C'**-type structures, the reactivity and coordination properties of these new compounds were studied. Compound **11** smoothly reacts with soft Lewis acids like [AuCl(Me_2S)] affording the desired metal complex **12** in good yield (Scheme 3). A hard Lewis acid like $B(C_6F_5)_3$ also reacts cleanly with **11** to form the corresponding adduct **13** as colorless crystals. A conclusive evidence of whether the central nitrogen atom in these species is a N(I) is the isolation of compounds where they formally donate two electron pairs. That has been achieved by reaction of the dimeric structure **14** with two equivalents of [$PdCl_2(CH_3CN)_2$]. Complex **15** thus obtained shows an unprecedented coordination mode for neutral imine-type ligands where the central nitrogen atoms donate four electrons each, one pair to each palladium centre (Scheme 4).



Scheme 3. Reagents and conditions. a) AuCl(Me_2S), THF, RT, 76%. b) $B(C_6F_5)_3$, toluene, RT, 72%.





Scheme 4. Reagents and conditions: a) $PdCl_2(MeCN)_2$ (2 eq), THF, 21%.

Publications resulting from this area: 298

External funding: Spanish Ministerio de Educación y Ciencia, Spain (short stay fellowship to J. Carreras and A. Vázquez); Fonds der Chemischen Industrie

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

2.5 Department of Theory

Director:

Walter Thiel (born 1949)
Publications: 2, 8, 20, 22, 23, 24, 39, 61, 63, 64, 65, 70, 71, 72, 106, 116, 130, 134, 141, 142, 143, 149, 150, 151, 153, 170, 176, 185, 190, 193, 200, 201, 207, 213, 214, 222, 247, 248, 249, 259, 260, 267, 268, 271, 273, 279, 280, 281, 287, 289, 290, 294, 298, 303, 323, 337, 343, 361, 374, 393, 400, 401, 402, 403, 405, 420, 421, 422

Further group leaders:

Mario Barbatti (born 1971)
joined the Institute in April 2010
Publications: 291, 292, 304, 365, 366, 392, 406

Other publications: 62, 156, 174, 318, 356, 378, 417

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 of the Verband der Chemischen Industrie
1982	Heisenberg Fellowship of the Deutsche Forschungsgemeinschaft
1988	Förderpreis of the Alfried-Krupp Stiftung
1991	Member of the European Academy of Sciences and Arts
2002	Schrödinger Medal of the World Association of Theoretical Chemists
2007	Member of Deutsche Akademie der Naturforscher Leopoldina
2007	Member of International Academy of Quantum Molecular Sciences
2008	Member of Nordrhein-Westfälische Akademie der Wissenschaften
2009	Festschrift, Journal of Physical Chemistry A 2009, 113 (43), 11455-12044

Other Activities / Committees

1986-1992	Member of the Board, Institut für Angewandte Informatik, Wuppertal
1990-1992	Speaker of the "DFG-Forschergruppe: Reaktive Moleküle"
1997-	Member of the Editorial Board, *Theoretical Chemistry Accounts* and *Journal of Computational Chemistry*
1999-	Editor, *Encyclopedia of Computational Chemistry*
2000-2006	Member of the Board (Lenkungsausschuss) of the Bavarian Supercomputer Center (Höchstleistungsrechenzentrum Bayern)

2000-2008	Reviewer (Fachkollegiat) of the Deutsche Forschungsgemeinschaft
2001-2005	Chairman of “Arbeitsgemeinschaft Theoretische Chemie”
2004-2007	Member of “Ständiger Ausschuss der Bunsengesellschaft”
2004-	Member of the Beirat of the “Lise Meitner Minerva Center for Quantum Chemistry”, Jerusalem/Haifa, Israel
2006-2008	Managing Director of the Max-Planck-Institut für Kohlenforschung
2006-	Chairman of the BAR Committee of the Max Planck Society
2006-	Member of the Kuratorium, *Angewandte Chemie*
2008-	Associate Editor, WIRES: Computational Molecular Sciences
2009-	Member of the International Advisory Board of the State Key Laboratory of Physical Chemistry (PCOSS), Xiamen, China
2010	Chairman of the Gordon Conference on Computational Chemistry

Research in the Department of Theory

The Department of Theory comprises the research groups of Professor W. Thiel and PD Dr. M. Barbatti, the successor of PD Dr. M. Bühl, who has become Full Professor at the University of St. Andrews (UK) in 2008.

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 Professor 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
(a) ab initio methods (e.g., coupled cluster approaches, CCSD(T)),
(b) density functional theory (DFT),
(c) semiempirical methods (MNDO model and beyond),
(d) combined quantum mechanical/molecular mechanical methods (QM/MM).

Recent applications in these four areas focus on
(a) vibration-rotation and electronic spectroscopy of small molecules,
(b) catalytic reactions of transition metal compounds,
(c) electronically excited states in large molecules,
(d) reaction mechanisms in enzymes.

The group of Dr. Barbatti carries out independent research in theoretical chemistry, using ab initio and density functional methods to study nonadiabatic processes that occur after molecular photoexcitation. Recent work has focused on excited-state dynamics simulations of ultrafast photoinduced processes in biologically relevant molecules.

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 the mechanism of Rh-catalyzed asymmetric hydrogenation and

of the Baeyer-Villiger oxidation reaction in cyclohexanone monooxygenase (Reetz) and on the electronic structure of reactive species in gold catalysis and of carbon(0) complexes (Fürstner). In addition, there are a number of ongoing joint projects that employ quantum-chemical calculations to unravel the mechanisms of catalytic reactions studied by the experimental groups in the Institute (Fürstner, Alcarazo, List, Maulide, Rinaldi).

More detailed information on the research areas of the Department is available in the following five individual reports and in the scientific papers published in 2008-2010. It should be noted that, for the sake of brevity, some of these papers have not been discussed in the reports on the research areas of the Department, and should therefore be consulted directly, if necessary.

The overall direction of research in the Department has remained unchanged during the reporting period, with a notable trend to put more emphasis on the study of electronically excited states. This has been initiated by our participation in a collaborative research program (SFB 663) and is also reflected in the appointment of Dr. Barbatti. Projects that have started or intensified over the past three years include advances in variational treatments of ab initio vibration-rotation spectroscopy, the development of QM/MM techniques with improved accuracy and sampling, multi-scale modeling with the use of boundary potentials, and the study of dynamic events both in the ground state and in excited states. Interactions with the local experimental groups have also triggered new application-oriented projects in various fields of catalysis. For the future, we anticipate that the focus on large complex systems will remain prominent in the research of the Department, both with regard to methodological developments and chemical applications.

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

Involved: J. Breidung, M. Schreiber, M. R. Silva-Junior, A. Yachmenev

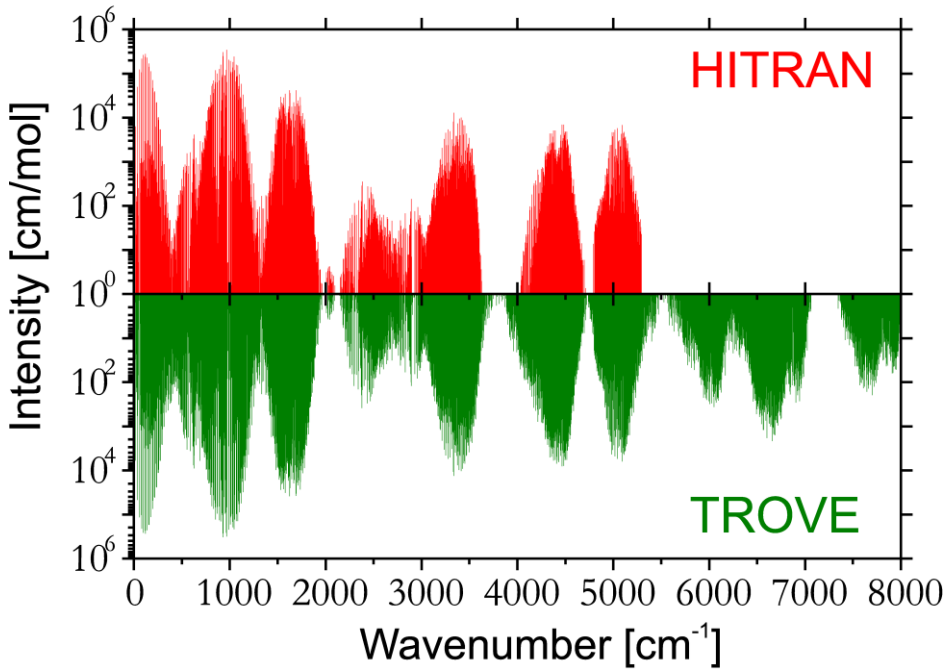
Objective: Vibration-rotation and electronic spectra of small molecules are computed with high accuracy using high-level ab initio calculations with large basis sets. This includes the further development of a general variational treatment of nuclear motion that allows the prediction of rovibrational energies and intensities not only for semirigid molecules, but also for molecules with large amplitude motions. Highly correlated ab initio methods are used to provide theoretical benchmark data for the electronically excited states of representative organic chromophores.

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 large basis sets (e.g., CCSD(T)/aug-cc-pVQZ in standard notation), possibly with complete basis set (CBS) 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) which was published in 2007.

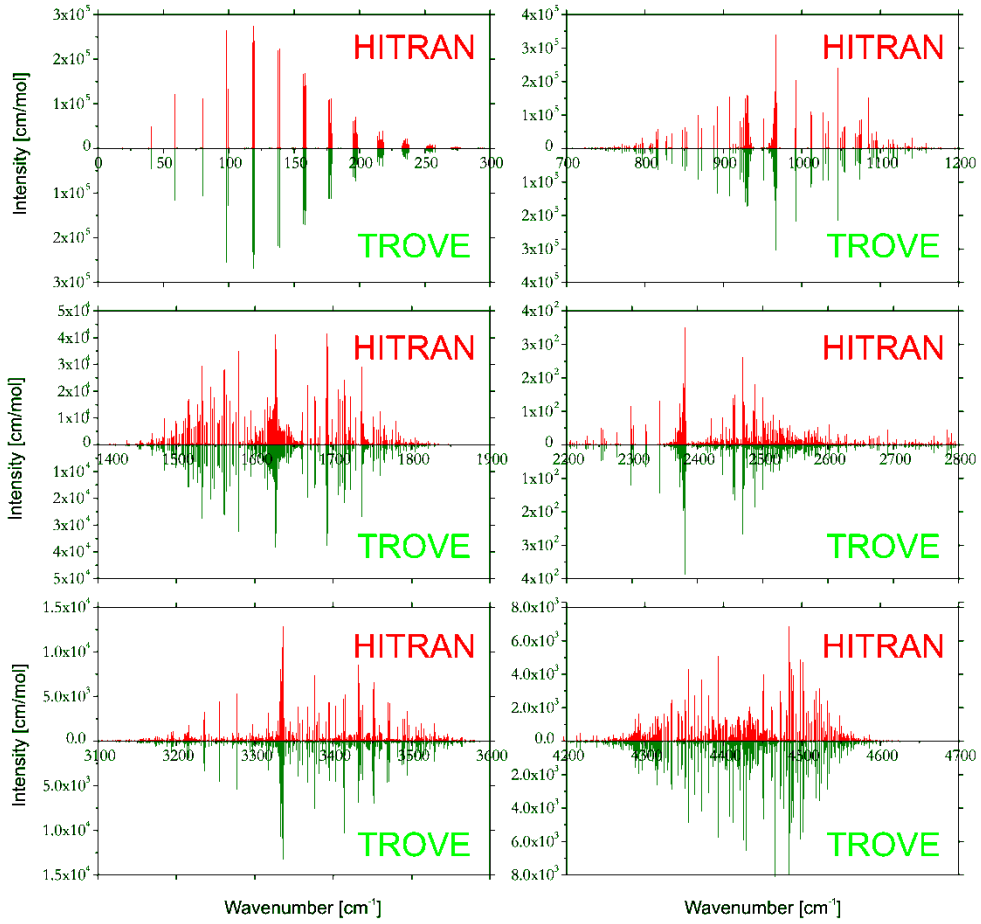
Over the past three years, TROVE has been extended in several ways. The convergence of the calculated vibrational energies with increasing vibrational basis set was improved by introducing an extrapolation scheme analogous to the CBS schemes used in electronic structure theory [72]. A reaction path Hamiltonian (RPH) approach was implemented to enable the adiabatic separation of large amplitude motion in TROVE calculations; this procedure converges quickly and is much faster than full calculations [70]. In the course of a comprehensive study of ammonia (see below), several algorithmic improvements were introduced into TROVE to speed up the evaluation of the rovibrational matrix elements and the line strengths [279]. The code was extended to allow for thermal averaging of molecular properties using a novel matrix exponential technique that is more efficient than the standard matrix diagonalization approach; this technique can also be applied to compute the rovibrational partition function [421]. Finally, the DVR (discrete variable representation) technique was implemented as an alternative method for solving the nuclear-motion Schrödinger equation.

The TROVE program has been applied to study NH_3 [279,421], NH_3^+ [142], PH_3 [71,72], SbH_3 [422], XH_2D and XHD_2 (X=Bi, P, Sb) [280] as well as HSOH [70,281,420]. The most extensive project was the calculation of a line list for ammonia ($^{14}NH_3$) covering all rovibrational transitions that involve states up to 12000 cm^{-1} and rotational quantum number J = 20 (3.25 million transitions between 184400 energy levels) [279]. The TROVE computations were based on a six-dimensional potential energy surface determined at the CCSD(T)/CBS level with corrections for core-valence correlation and relativistic effects, with a subsequent very slight adjustment of selected potential parameters against experimental data, and on a corresponding CCSD(T)/aug-cc-pVQZ dipole moment surface. The rovibrational spectra calculated at T = 300 K agree very well with the available experimental results from the HITRAN database, as illustrated by the comparisons for overview spectra and for several selected low-lying band systems (see figures) [279]. It should be emphasized that the HITRAN database does not provide experimental data for ammonia in some high-energy parts of the spectrum where the theoretical results thus serve as predictions. This is of particular interest for astrophysical research which requires complete line lists at various temperatures for identification purposes. We are currently calculating a high-temperature line list for ammonia at T=1500 K.

In the case of NH_3^+ [142], PH_3 [71,72], and SbH_3 [422], improved ab initio potential energy surfaces were computed and partly refined against spectroscopic data. They were used in combination with new ab initio dipole moment surfaces [142,422] and polarizability surfaces [142] to generate accurate theoretical rovibrational spectra using variational TROVE calculations. The intensity predictions for PH_3 and SbH_3 were shown to be in accordance with local mode theory [72,422]. For the deuterated species XH_2D and XHD_2 (X = Bi, P, Sb), the formation of rotational energy clusters was observed in the vibrational ground state at high rotational excitation (up to J = 70); in the case of XHD_2, the centrifugal-force-induced dynamic symmetry breaking at high J leads to predominant rotation in the cluster states around one of the X-D bonds [280].



Overview of the simulated absorption (T = 300 K) spectrum (TROVE) of NH_3 compared to experiment (HITRAN), with logarithmic intensity scale.



Comparison of the simulated (TROVE) and observed (HITRAN) spectra of NH_3 at T = 300 K for several low-lying band systems.

Our ab initio work on HSOH [70,281,420] was motivated by the challenge to understand the spectroscopic consequences of the large amplitude torsional motion, in particular for the rotation-torsion transitions. High-level ab initio potential energy and dipole moment surfaces were generated and served as input for variational TROVE calculations. Using the RPH approach, the observed torsional splittings could be reproduced within 0.002 cm^{-1} (up to J =40, K_a = 4), and their irregular variation with K_a could be explained in terms of a simple model of rotation-torsion motion [70]. Full-dimensional variational studies of HSOH gave unambiguous assignments of the high-resolution spectra and allowed us to rationalize the extensive perturbations in the fundamental S-H stretch region [281] and the intensity anomalies caused by the large amplitude torsional motion [420].

Further investigations in this area addressed the thermal averaging of the computed nuclear spin-spin coupling constants of NH_3 (focusing on the influence of the inversion motion) [421] and the spectroscopic refinement of the best available ab initio potential energy surface of HDO (leading to excellent agreement with experiment, root-mean-square deviation of 0.035 cm^{-1} for 4495 experimental levels) [143]. In unpublished work, we have computed a CCSD(T)/aug-cc-pVQZ potential surface for formaldehyde H_2CO and refined it against spectroscopic data (rms deviation of 0.05 cm^{-1} for 599 rovibrational levels up to J = 5). In thioformaldehyde H_2CS, such a refinement is not possible because of the lack of sufficient high-resolution experimental data (partly due to assignment problems caused by severe resonances); to guide the experimental analysis of the spectra, we have computed a highly accurate, purely ab initio potential energy surface that is based on CCSD(T)/CBS energies (derived from an explicitly correlated F12 treatment) and incorporates various smaller corrections (due to higher-order coupled cluster, core-valence correlation, relativistic, and non-diagonal Born-Oppenheimer effects).

In addition to the ab initio studies on vibration-rotation spectroscopy, we also use ab initio methods in other projects for reference purposes. In the area of spectroscopy, we have performed extensive benchmarking on electronically excited states [106,116,249,401,402,403]. For a set of 28 medium-size reference molecules that cover all typical organic chromophores (213 singlet and triplet excited states), systematic ab initio calculations were carried out using multi-configuration perturbation theory (CASPT2) and coupled cluster theory (CC2, CCSD, CC3), and best estimates were derived for the vertical excitation energies of 104 singlet and 63 triplet excited states [106]. The resulting reference database has subsequently been used by us [116,403] and

by several other groups for the assessment and validation of lower-level theoretical methods. On the ab initio side, we have explored various improvements to the original benchmark [106]. A comparison of noniterative and iterative triples corrections in coupled cluster treatments [CCSDR(3) vs. CC3] showed that the former are essentially as accurate as the latter, so that CCSDR(3) can be applied when CC3 is computationally not feasible [249]. Basis set extension from TZVP to aug-cc-pVTZ had in most cases relatively minor effects on the vertical excitation energies from coupled cluster [401] and CASPT2 [402] calculations, but the changes were still considered large enough to warrant an update of the recommended best estimates for the vertical excitation energies [402].

Publications resulting from this research area: 70, 71, 72, 106, 142, 143, 249, 279, 280, 281, 290, 401, 402, 420, 421, 422

External funding: European Research Training Network QUASAAR (MRTN-CT-2004-512202); Deutsche Forschungsgemeinschaft (SFB 663, project C4)

Cooperations: J.-M. Flaud (Paris, FR); T. F. Giesen (Köln, DE); P. Jensen (Wuppertal, DE); S. P. A. Sauer (Copenhagen, DK); J. Tennyson (London, UK); S. N. Yurchenko (Dresden, DE); other QUASAAR partners include A. Campargue (Grenoble, FR), L. Halonen (Helsinki, FI), M. Herman (Brussels, BE), T. Rizzo (Lausanne, CH)

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

Involved: A. Anoop, J. Gonthier, B. Heggen, M. Patil, T. Tuttle, D. Wang

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.

Results: Many of our applications of density functional theory (DFT) focus on transition metal compounds. Based on previous extensive validation our standard DFT approach normally employs the Becke-Perdew functional with an effective core potential at the metal and with medium-sized polarized basis sets. In the case of organic compounds, we normally use the B3LYP hybrid functional.

In joint work with the Fürstner and Alcarazo groups, we have studied a number of ligands and transition metal complexes that are relevant for their experimental work on homogeneous catalysis [149,176,287,298]. The computed structures were generally found to be in good agreement with the available crystal structures, and the computed metal-ligand binding energies generally reflected the experimentally observed trends. The computed molecular orbitals and natural bond order (NBO) analysis were used to characterize the electronic structure of these compounds. To be more specific, neutral and cationic 14-electron gold alkyne complexes were investigated to gain insight into the first elementary step common to many gold-catalyzed transformations; in the complexes with cyclododecyne, $\pi \rightarrow \sigma^*$ donation clearly dominates over $d(Au) \rightarrow \pi^*$ backdonation, thus explaining the highly electrophilic character of the alkyne within the coordination sphere of any chosen Au(I) fragment [176]. The π-acceptor properties of N-heterocyclic carbenes (NHCs), commonly used as ligands in gold catalysis, were studied for cyclophanic and triazo analogues of imidazopyridine-2-ylidene derivatives; it was established that the π-acceptor strength can easily be tuned in these ligands to control the course of three mechanistically distinct gold-catalyzed processes [287]. The captodative binding in carbon(0) coordination compounds was probed experimentally by auration, i.e., by the reaction between $AuCl(SMe_2)$ and $(PPh_3)CL^2$ with a variety of ligands L^2; in line with the experimental findings, the computed complexation energies predicted diauration to be possible only for two specific ligands L^2 (monoauration always), and population analysis indicated that the central carbon atom carries a

substantial negative charge not only in the free ligand, but also in the monoaurated and diaurated complexes – a counterintuitive behavior typical of carbon(0) coordination compounds [149]. A subsequent investigation of highly electron-rich imines, in particular cyclopropenylylidenimines, showed that they can be classified analogously as nitrogen(I) compounds with two lone pairs at nitrogen that are prone to interact with Lewis acids, so that they may be valuable as ligands in homogeneous catalysis [298].

Experimental work in the Reetz group has shown some time ago that rhodium catalysts with chiral monodentate phosphorous ligands can achieve asymmetric hydrogenation with high efficiency and enantioselectivity, and may thus serve as an economic alternative to the classical catalysts with bidentate ligands. Unlike the latter, the new catalysts follow the "lock-and-key" principle, i.e., the major enantiomer of the product is formed from the more stable diastereomeric prochiral catalyst-substrate complex. We have continued a detailed DFT study of the enantioselective hydrogenation of itaconic acid using a chiral Rh(phosponite)$_2$ catalyst and calculated the previously missing parts of the catalytic cycle (i.e., reactions with solvent molecules in the initial and final phase of the cycle), to set the stage for kinetic Monte Carlo simulations aimed at understanding the origin of the observed enantioselectivity. Since such simulations depend critically on the adopted relative energies and barriers, we have checked the accuracy of the applied DFT methods in a related case [290], i.e., the asymmetric hydrogenation of two prochiral enamides using a rhodium catalyst with a bidentate phosphorus ligand, [(*R*,*R*)-MeDuPHOS]$^+$. Since this system is smaller than the Reetz system, it could be treated by accurate local pair natural orbital coupled cluster theory with single and double excitations (LPNO-CCSD). The DFT(B3LYP) results were found to be in reasonable agreement with the single-point LPNO-CCSD results, although some small deviations exist that are not entirely systematic in the minor and major reaction branches [290].

Several DFT studies have been carried out without involvement of experimental groups from the Institute [141,271,337]. In continuation of an external cooperation with an industrial partner, we have computed the mechanism of olefin hydrosilylation catalyzed by dichloro(*p*-cymene)ruthenium(II) and some related complexes; as in previous cases, it was found that the reaction involves an initial exchange of one of the σ-donor ligands for a hydride ligand in the induction step [271]. A combined experimental and theoretical study addressed the electronic structure of a series of iron-corrole complexes with strongly electron-deficient corrole ligands; the combination of Mössbauer data with DFT calculations provided convincing evidence for an intermediate-spin iron(III)

ion antiferromagnetically coupled to a dianionic π-radical corrole yielding an overall triplet ground state [141]. Ongoing unpublished work concerns the mechanism and the origin of selectivity in Pd-catalyzed allylic alkylation reactions.

In our benchmarks of DFT-based methods for electronically excited states, the DFT/MRCI approach (DFT combined with multi-reference configuration interaction) reproduced the ab initio reference data for vertical excitation energies best and clearly outperformed standard time-dependent DFT approaches [116]. We have applied DFT/MRCI to study the photophysics of phenalenone, a widely used singlet oxygen sensitizer, and indeed found a very high intersystem crossing rate, much larger than the fluorescence and phosphorescence rates, which rationalizes the experimentally observed behavior of phenalenone [170].

Publications resulting from this research area: 116, 141, 149, 170, 176, 271, 287, 298, 337

External funding: German-Israeli Project Cooperation (DIP-F.6.2)

Cooperations: M. Alcarazo, A. Fürstner, B. List, N. Maulide, M. T. Reetz (Mülheim/Ruhr, DE); M. Braun (Düsseldorf, DE); B. Ganguly (Gujarat, IN); Z. Gross (Haifa, IL); F. Neese (Bonn, DE)

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

Involved: J. Breidung, E. Fabiano, T. Keal, A. Koslowski, Z. Lan, Y. Lu, M. R. Silva-Junior, T. Tuttle, O. Weingart, X. Wu

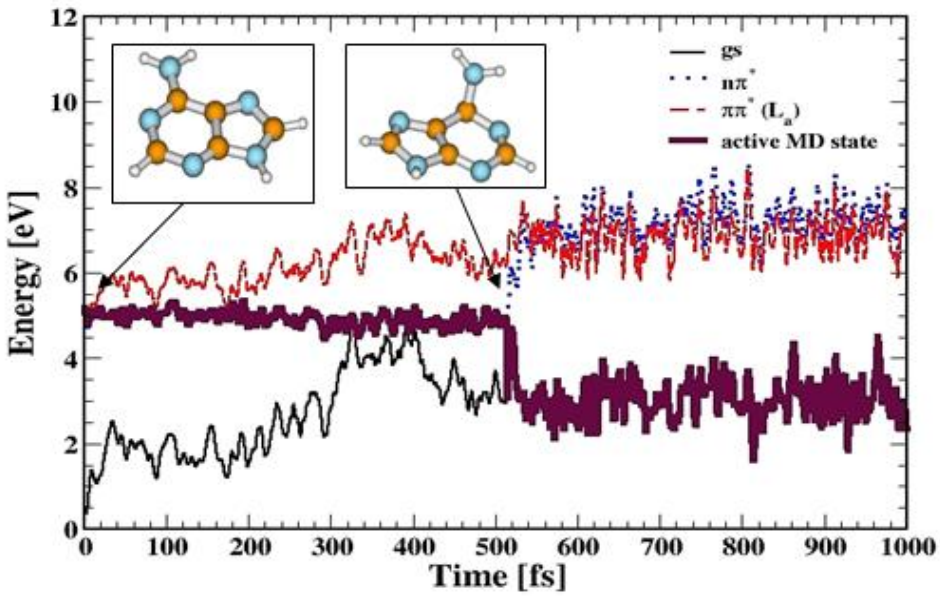
Objective: This long-term project aims at the development of improved semiempirical quantum-chemical methods that can be employed to study ever larger molecules with useful accuracy. This includes the development of more efficient algorithms and computer programs. Our current focus in this area is on 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 labeled OM1, OM2 and OM3 (orthogonalization models 1-3) which offer significant improvements over established MNDO-type methods in several areas, including conformational properties, hydrogen bonds, reaction barriers, and electronically excited states.

During the reporting period, we have concentrated on semiempirical excited-state dynamics. In our MNDO software, we had previously implemented the GUGACI method in a semiempirical in-core version that handles general CI expansions (up to full CI) efficiently for small active spaces. The software had already included an analytic GUGACI gradient code which has now been extended to the analytic computation of the full nonadiabatic coupling matrix elements. Building on these ingredients, we have implemented [23] the surface hopping method with the fewest switches algorithm (Tully). Our code offers different integration schemes as well as different options for treating the nonadiabatic coupling and ensures proper orbital and state tracking. In an initial validation with three case studies (ethylene, methaniminium ion, and methanimine), the OM2-CI approach yielded decay times and dynamics paths similar to high-level ab initio results [23]. Subsequently more approximate switching algorithms were tested that adopt simpler models for the hopping probability; it was found that one popular variant based on a local diabatic representation shows qualitative failures and overestimates the decay times severely (compared with the standard fewest switches algorithm) [22]. In unpublished work, several decoherence corrections were implemented and tested to establish a proper default procedure.

The semiempirical surface hopping module was used to study the gas-phase excited-state dynamics of adenine [24], guanine [200], uracil, thymine, and cytosine [201] at the

OM2/MRCI level. For all these nucleobases, the OM2/MRCI energies and geometries of the relevant species (including conical intersections) showed good agreement with the available ab initio reference data. The OM2/MRCI surface hopping trajectory calculations gave sub-ps relaxation via different pathways, and the experimental decay times from time-resolved fs photoelectron spectroscopy were well reproduced in all cases. The excited-state dynamics of adenine involves excitation into the bright second excited state (L_a, ππ*, S_2) and then proceeds mostly (90%) by an ultrafast relaxation to the nπ* state (S_1) followed by sub-ps decay to the ground state (see the figure for a typical trajectory); the minor decay channel (10%) leads directly to the ground state (gs) via a L_a/gs conical intersection [24]. In the other nucleobases, the dynamics also involves the lowest two excited states, but the nonadiabatic decay paths differ in their relative importance and need to be assessed separately for each molecule (e.g., because of differences in the energy level schemes) [200,201].



State energies for a typical trajectory following the (nπ*/gs)CI decay path in adenine.

We have also implemented our surface hopping code in the ChemShell QM/MM framework and applied it to study the nonadiabatic dynamics of nucleobases in aqueous solution (adenine, guanine) and in model DNA strands (adenine). Going from the gas phase to aqueous solution causes rather small changes in the optimum geometries (e.g., of conical intersections). The relaxation paths via the various conical intersections remain qualitatively similar, but there are changes in their relative importance because of the solvent-induced shifts in the energetics. Overall, the decay times in solution are even slightly lower than those in the gas phase, in qualitative agreement with

experiment. By contrast, the S_1 lifetime of adenine in a solvated B-type DNA oligomer model $(dA)_{10}$ is computed to be about ten times larger (ca. 5 ps) than in the gas phase, again in accordance with experiment. This is at least partly due to the higher rigidity of the DNA strand: the two relevant conical interactions are both characterized by strong out-of-plane deformations that are more difficult to reach in the DNA environment. In our DNA double strand model, solvated $(dA)_{10}\cdot(dT)_{10}$, one of these two decay paths is suppressed because the out-of-plane motion of the amino group is impeded by inter-strand hydrogen bonding (unpublished).

We are currently investigating the photoinduced dynamics of several other systems using OM2/MRCI surface hopping simulations. These include azobenzenes in the gas phase and in a condensed-phase environment, the chromophore in selected red fluorescent proteins, Feringa-type fluorene-based molecular motors, and a prototypical charge transfer molecule (4-*N*,*N*-dimethylamino-benzylidene malononitrile). Already published is an OM2/MRCI investigation on the photoisomerization of a protonated Schiff base that serves as a retinal model [193].

To assess the accuracy that can generally be expected in semiempirical studies of excited states, we have evaluated the performance of several popular semiempirical methods for vertical excitation energies, oscillator strengths, and excited-state dipole moments [403] using our standard ab initio benchmark set [106]. The OMx/MRCI methods were found to be much better than standard MNDO-type ground-state methods (as expected), and surprisingly also slightly better than the INDO/S excited-state method. In fact, the mean absolute deviations of the OMx/MRCI results were only somewhat higher than those obtained for standard time-dependent DFT results.

Turning to the electronic ground states, we have incorporated empirical dispersion corrections into the OMx approaches, in analogy to corresponding work by others at the DFT level; this led to significant improvements for non-covalent interactions, with mean absolute errors of 1.3-1.4 kcal/mol in the OMx-D binding energies of the complexes in the standard JSCH-2005 data base [130]. These advances support the use of dispersion-corrected OMx-D methods in studies of biomolecules, as demonstrated for the example of antibody-hapten binding [130].

Ground-state molecular dynamics (MD) simulations of large systems can be computationally very demanding even at the QM/MM level and often become practical only with semiempirical QM components. We have adopted this approach in OM3/MM

MD simulations of a QM water solute in liquid MM water to assess the merits of a polarizable water force field [39] and partly also in a systematic study of finite-temperature effects in enzymatic reactions by QM/MM free-energy calculations [259]. To further enhance the efficiency of such simulations, we have implemented a generalized solvent boundary potential (GSBP) for hybrid QM/MM MD simulations with semiempirical MNDO-type QM methods [8].

Finally, in a combined experimental and theoretical study [207], we used semiempirical methods to investigate fluorophores as optical sensors for local forces. In the case of OPV5, an oligoparaphenylene vinylene derivative with twisted backbone, correlations were observed experimentally between the external mechanical force (applied to the fluorophore embedded in a foil) and the changes in the fluorescence properties. Both the blue-shift of fluorescence and the reduced lifetime of OPV5 under tensile stress were consistent with the results of the semiempirical calculations [207].

Publications resulting from this research area: 8, 22, 23, 24, 39, 130, 193, 200, 201, 207, 259, 393, 403

External funding: Fonds der Chemischen Industrie; Deutsche Forschungsgemeinschaft (SFB 663, project C4)

Cooperations: M. Filatov (Groningen, NL); B. Hartke (Kiel, DE); G. Groenhof (Göttingen, DE); C. M. Seidel (Düsseldorf, DE)

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

Involved: M. Altarsha, A. Altun, T. Benighaus, M. Bocola, M. Doerr, E. Fabiano, Y. Hsiao, J. Kästner, T. Keal, D. Kumar, Z. Lan, Y. Lu, S. Metz, N. Otte, M. Parac, I. Polyak, E. Sanchez-Garcia, H. M. Senn, M. R. Silva-Junior, S. Thiel, T. Tuttle, D. Wang, O. Weingart, J. 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 address biocatalysis and aim at a better understanding of enzymatic reactions including the role of the protein environment.

Results: Combined quantum mechanical/molecular mechanical (QM/MM) methods have become a popular tool for studying reactions in complex systems such as enzymes. Typical applications make use of density functional theory (DFT) or semiempirical methods as QM component and a standard biomolecular force field (e.g., CHARMM or GROMOS) as MM component. The accuracy of QM/MM calculations can be improved by going beyond these standard methods both in the QM and MM part.

For this purpose, we have explored the use of correlated ab initio methods in two QM/MM case studies on *p*-hydroxybenzoate hydroxylase (PHBH) and aldehyde oxidoreductase (AOR), in collaboration with the Werner group [61,303]. This involved DFT(B3LYP)/MM optimizations of reaction paths and stationary points followed by single-point ab initio QM/MM energy evaluations using local correlation methods up to the LCCSD(T0) coupled cluster level. In both cases, the qualitative conclusions from the preceding DFT(B3LYP)/MM studies were confirmed, but there were non-negligible changes in the computed relative energies and barriers. Careful validation of the applied local correlation methods with regard to all computational parameters indicated convergence of the QM contribution to the barriers to within 1 kcal/mol in PHBH [61] and 2 kcal/mol in AOR [303].

In a similar vein, we have carried out a multi-reference ab initio QM(MRCI)/MM study of three intermediates in the catalytic cycle of cytochrome P450cam [2]. The calculated spin state energies are generally quite similar to those obtained at the simpler DFT(B3LYP)/MM level, despite the fact that two of these intermediates are multiconfigurational in character. This provides further justification for the use of DFT(B3LYP) in this area.

The accuracy of the MM treatment can be enhanced, in principle, by moving from standard force fields with fixed MM charges to polarizable force fields. In a cooperation with the van Gunsteren group, we had previously implemented a particular variant of polarizable force fields, the charge-on-spring model, into our ChemShell QM/MM software; this had been done through a special interface to the GROMOS MM code. Following the modular ChemShell philosophy, we have now carried out a general implementation that can be coupled with any MM code since the polarizable terms are handled in a generic ChemShell module. On the application side, we have shown that semiempirical OM3/MM MD simulations of a QM water solute in liquid MM water benefit from the use of a polarized MM model for water [39].

In QM/MM work, geometry optimization techniques are commonly employed to determine reaction paths and the relevant minima and transition states. We have extended the range of optimizers available in the DL-FIND library that is used in ChemShell, the most notable additions being the nudged elastic band method for path optimization, the dimer method for transition state searches, and three algorithms for finding conical intersections [190].

For the calculation of free energies that govern reaction rates, several methods are available in ChemShell (including thermodynamic integration, umbrella sampling, and free energy perturbation theory). These methods employ MD simulations along pre-computed reaction paths for conformational sampling. We have used these techniques to study finite-temperature effects in enzymatic reactions by QM/MM free energy simulations [259], covering reactions catalyzed by chorismate mutase (CM), fluorinase, PHBH, and cytochrome P450cam. The entropic contribution to the barrier was generally found to be rather small (mostly less than 1 kcal/mol). This suggests that barriers from QM/MM geometry optimization may often be close to free energy barriers for enzymatic reactions that involve only localized small-scale geometry changes within the active site [259].

In further methodological work, we have 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. This offers two major advantages: conceptually, the long-range electrostatic interactions in a solvated enzyme are well described in this manner, and technically, the computational effort is reduced significantly by the strong reduction of the number of explicitly treated MM atoms (typically 2000 compared with around 30000 in standard QM/MM work). Initially, we adopted the generalized solvent boundary potential (GSBP) proposed by Roux for MM-MD simulations, and implemented it in a semiempirical QM/MM framework [8]. This required a new ChemShell module for performing Poisson-Boltzmann calculations that was thoroughly optimized for performance. Because of the associated overhead, the semiempirical QM/MM/GSBP approach is faster than the standard QM/MM treatment only for system sizes beyond 12500 atoms (e.g., by a factor of about 3 for 30000 atoms); it is thus an efficient tool for large-scale QM/MM MD simulations [8]. In a second step, we developed a new boundary potential (SMBP, solvated macromolecule boundary potential) that is conceptually similar to GSBP, but can be used with any QM method and is also efficient for geometry optimization [153]. Its generality derives from the use of virtual point charges on a sphere surrounding the explicitly modeled inner region, which represent the boundary potential arising from the outer region and the bulk solvent in the sense that they generate essentially the same electrostatic potential in the QM region. These virtual point charges and the QM wavefunction are determined in a self-consistent reaction field procedure. QM/MM/SMBP geometry optimizations on enzymes reproduce the standard QM/MM results very well, and it is therefore possible to calculate free energy profiles and barriers along QM/MM/SMBP optimized reaction paths, which reduces computation times typically by one order of magnitude without significant loss of accuracy [153]. In an initial application of these techniques, we studied the influence of long-range electrostatic interactions on the enzymatic reactions in CM and PHBH. The corresponding energetic effects were found to be non-negligible (several kcal/mol) for the hydroxylation reaction in PHBH during which there is a formal transfer of one negative charge from the substrate to the cofactor. The QM/MM/SMBP approach allows a separate analysis of the effects due to the outer MM region and the bulk solvent [294].

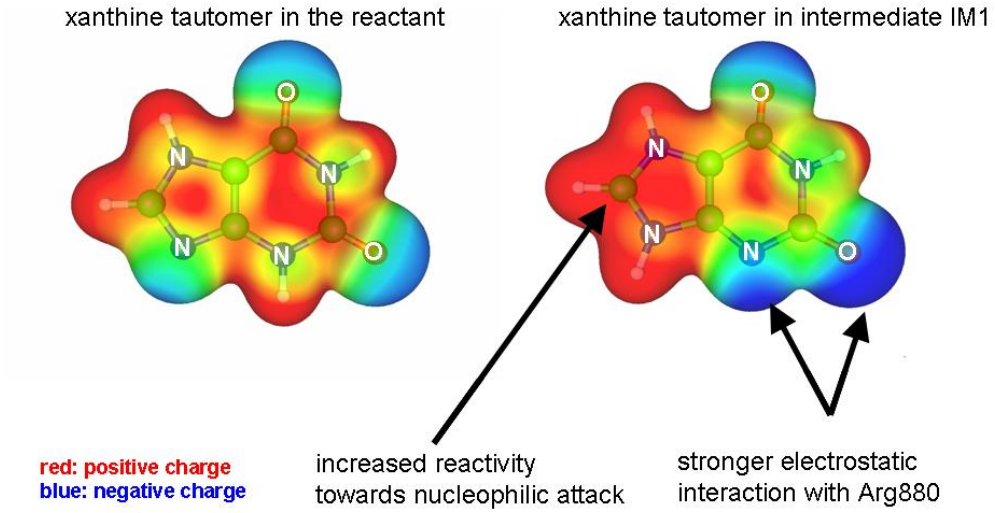
A final methodological advance concerns the implementation of quantum refinement into ChemShell [323]. The traditional procedure for solving protein crystal structures is to supplement the X-ray diffraction data with restraints from simple MM force fields during the refinement. These restraints are taken from QM/MM energies in quantum

refinement which should thus be more reliable especially in regions that are not well described by the available MM force fields (e.g., metal centers, inhibitors, substrates, and chromophores). Our implementation goes beyond the original proposal (Ryde) in several aspects, most notably by also allowing for an electrostatic QM/MM embedding (instead of a simple mechanical embedding). As a first application, we have used quantum refinement to derive an improved structure for the DsRed.M1 fluorescent protein, especially in the chromophore region [323]. A similar improvement was achieved for the pB_2 intermediate of the photoactive yellow protein (submitted).

Turning to QM/MM applications on enzymatic reaction mechanisms, we have continued our studies on the catalytic cycle of cytochrome P450cam, mostly at the DFT(B3LYP)/CHARMM level (partly in collaboration with the Shaik group). In the reporting period, we characterized the ferrous dioxygen and ferric peroxo complexes of P450cam [273] and compared the electronic structure of the reactive species (Cpd I) in several different heme thiolate enzymes [20]. As indicated above, ab initio QM(MRCI)/MM calculations were performed for a detailed analysis of the electronic structure of Cpd I, the ferric hydroxo complex (Cpd 0), and the hydroxo complex formed during camphor hydroxylation [2]. In addition, we have investigated several key reactions, in particular the proton transfers that generate Cpd 0 [134] and Cpd I [150,151,289] in wild-type P450cam and in several mutants. Protonation of the distal oxygen atom in Cpd 0 leads to the formation of Cpd I and water (coupling reaction), whereas protonation of the proximal oxygen atom yields the ferric resting state and hydrogen peroxide (uncoupling). In agreement with experiment, the DFT(B3LYP)/CHARMM calculations predict exclusive coupling in wild-type P450cam and exclusive uncoupling in the Thr252X (X = alanine, glycine) mutants, because in the latter case an extra water molecule can enter the hydrogen bonding network in the proton transfer path for uncoupling and thus favor this channel over coupling [150]. Detailed mechanistic insight was also gained in analogous QM/MM studies on the D251N mutant [151] and the methoxy-threonine mutant [289]. The role of single water molecules as biocatalysts in P450cam chemistry was analyzed in general terms [343]. Finally, a comprehensive review was written together with Sason Shaik to summarize the available QM/MM work on the structure, reactivity, and selectivity of P450 enzymes [400].

Concerning molybdenum enzymes, we have studied the reaction mechanism of the oxidation of acetaldehyde to acetic acid catalyzed by aldehyde oxidoreductase (AOR) and the conversion of xanthine to uric acid by xanthine oxidase (XO). In both cases, a

number of different pathways were explored to elucidate the productive binding mode of the substrate and the catalytic effect of active-site residues. The DFT(B3LYP)/CHARMM calculations on AOR favored a Lewis base catalyzed mechanism with initial deprotonation of the cofactor by Glu869 over the alternative one-step and two-step mechanisms that had been considered previously in DFT model studies; the reaction then proceeds by an attack of the activated cofactor at the substrate and a subsequent formal hydride transfer [213]. This mechanism was confirmed by high-level ab initio and free energy QM/MM calculations on AOR which did not change the mechanistic preferences and provided best estimates for the free energy barriers that differ by up to 3 kcal/mol from the DFT(B3LYP)/CHARMM barriers [303]. In the case of XO, the situation is more complicated since the xanthine substrate can adopt different orientations in the binding pocket (upside vs. upside-down) and convert between different tautomer and protonation states. Systematic DFT(B3LYP)/CHARMM calculations on XO gave a clear preference for one particular pathway: three initial proton transfers (involving Glu1261) activate both the cofactor and the substrate such that the subsequent nucleophilic and hydride transfer become more facile, through electrostatic stabilization of the rate-limiting transition state by Arg880 [214]. This is illustrated in the figure by showing the two relevant xanthine tautomers, i.e., the most stable form in the gas phase and the reactive form in the enzyme. Additional QM/MM studies on XO addressed the effects of variations in the cofactor, the substrate, and the active-site Glu802 residue; the computational results were fully consistent with the corresponding experimental findings, thus providing further support for our calculated mechanism [361].



Electrostatic potentials of the most stable (left) and the reactive (right) tautomer of xanthine.

In collaboration with the Bühl group, we have assessed QM/MM models of the peroxo forms of vanadium-containing haloperoxidases (VHPOs) in terms of active-site geometries, hydrogen bonds within the active site, isotropic and anisotropic ^{51}V NMR chemical shifts, and TD-DFT excitation energies [185]. The models showed appreciable differences between the anisotropic chemical shifts of the different protonation states. The most likely candidates for the peroxo forms of VHPO enzymes were identified on the basis of QM/MM modeling in combination with X-ray, ^{51}V NMR, and UV-Vis data [185].

In collaboration with the Engels group, we have performed QM/MM studies on cysteine proteases to gain insight into the structure and stability of the resting state and the mechanisms of inhibition. The DFT/CHARMM calculations favored the zwitterionic resting state over the neutral form by about 8-9 kcal/mol due to a complex hydrogen bonding network involving several active-site residues and water molecules that stabilizes the zwitterionic form [64]. These studies also clarified the regiospecifity and inhibition potency of epoxide- and aziridine-based inhibitors [65] as well as the stereoselectivity of epoxide-based inhibitors [63]; such insights are expected to be helpful for rational drug design.

In an ongoing collaboration with the Reetz group that is motivated by their experimental work on directed evolution, we examine the mechanism of the Baeyer-Villiger oxidation reaction in cyclohexanone monooxygenase (CHMO). The currently available QM/MM results from reaction path calculations and from the optimization of the Criegee intermediate and the subsequent transition state already allow us to at least partially explain the high regioselectivity of CHMO towards certain cyclohexanone derivatives, but further work is needed to arrive at a more complete picture.

Turning to QM/MM applications on electronically excited states, we have already mentioned the semiempirical QM(OM2/MRCI)/MM surface hopping studies of nucleobases in water and in DNA strands. We have also performed QM/MM calculations of electronic absorption spectra in the condensed phase, mostly using DFT/MRCI as QM component. The corresponding protocols were established and discussed in much detail in an investigation of solvent effects on the absorption spectrum of guanine [374]. Concerning proteins, the properties and the electronic spectra of the chromophores in the red fluorescent proteins DsRed.M1 [248,393] and HcRed [405] were computed, and the influence of the LOV domain of the blue-light photosensor YtvA of *Bacillus subtilis* on the low-lying electronic states of the flavin

mononucleotide chromophore was analyzed and contrasted with the solvent shifts in water [247].

The ChemShell software that has been used in all these applications is available under a license agreement (see www.chemshell.org). The QM/MM methodology and QM/MM applications to biological systems have been reviewed [260,267].

Publications resulting from this research area: 2, 8, 20, 39, 61, 63, 64, 65, 134, 150, 151, 153, 185, 190, 213, 214, 222, 247, 248, 259, 260, 267, 273, 289, 294, 303, 323, 343, 361, 374, 393, 400, 405

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Cooperations: M. Bühl (St. Andrews, UK); B. Engels (Würzburg, DE); E. Keinan (Haifa, IL); C. M. Marian (Düsseldorf, DE); F. Neese (Bonn, DE); M. T. Reetz (Mülheim/Ruhr, DE); S. Shaik (Jerusalem, IL); P. Sherwood (Daresbury, UK); S. C. Smith (Brisbane, AU); W. F. van Gunsteren (Zurich, CH); H.-J. Werner (Stuttgart, DE)

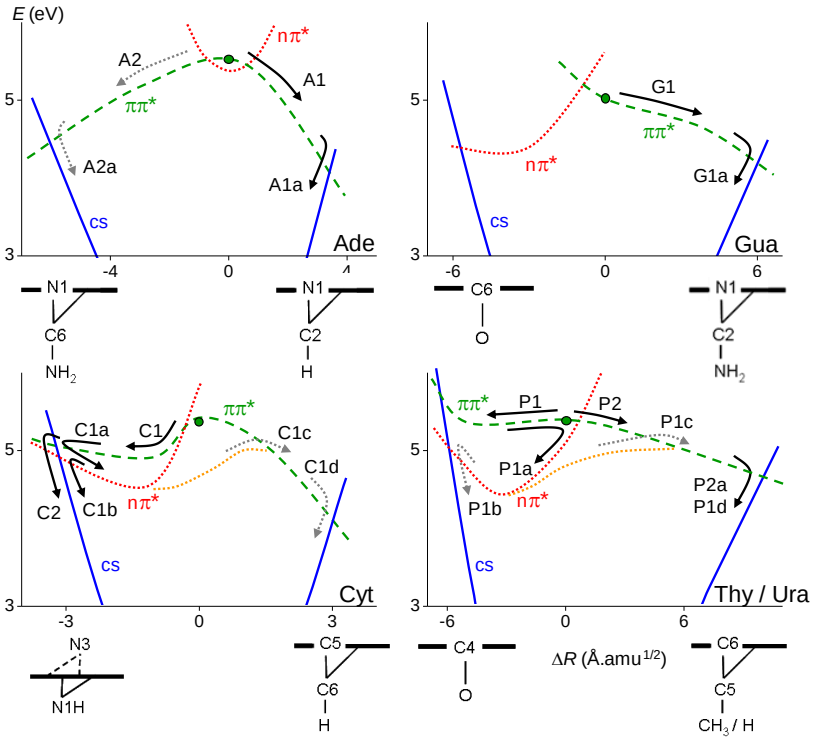
2.5.5 Research Area "Simulations of Photoexcited Molecules and Dynamical Processes" (M. Barbatti)

Involved: R. Crespo-Otero

Objective: Determination of steady and time-dependent properties of UV/vis excited molecules by means of semi-classical simulations based on ab initio quantum chemical methods.

Results:

1. Photodynamics of nucleobases and nucleobase models: We have performed excited-state dynamics simulations for all five naturally occurring DNA/RNA bases after UV-excitation. This research, carried out with our collaborators in Prague and Vienna, has allowed us to propose a very complete scenario for the mechanisms driving the internal conversion of the nucleobases. These mechanisms are schematically illustrated in the figure below.



Deactivation mechanisms in UV-excited nucleobases as determined by dynamics simulations. Purine bases (ade, gua) follow homogenous pathways along the ππ* state. Pyrimidine bases (cyt, thy, ura) follow inhomogeneous pathways composed by several steps.

Besides the nucleobases themselves, we have also investigated the nonadiabatic dynamics of the nucleobase models aminopyrimidine and diaminopyrimidine. The investigation of such models aims at determining the role of specific site restrictions to the internal conversion. First, we have systematically changed the substitutions in aminopyrimidine so as to understand how the imidazole group affects the out-of-plane modes of the pyrimidine ring in adenine during the dynamics. Moreover, we

investigated how the out-of-plane modes responsible for the internal conversion are affected by the stacking interactions in DNA strand geometry.

2. Simulations of UV spectra of organic molecules: We have recently developed a Monte-Carlo semi-classical method for simulation of UV/vis spectra. The quality of the method has been accessed by direct comparison to full quantum chemical approaches in simulations of azomethane. We have shown that the semi-classical approach predicts band shapes and intensities, including those resulting from weak vibronic couplings, of quality similar to the full quantum chemical approach if vibrational progressions are neglected.

3. Methods for photodynamics simulations: In the last years, we have developed the NEWTON-X program (www.newtonx.org) for excited-state semi-classical dynamics simulations. Giving continuity to the program development, we have implemented routines for excited-state QM/MM simulations, which have been tested with dynamics of UV-excited formamide in Ar matrix. We have also implemented routines to compute time-dependent non-adiabatic coupling vectors at the time-dependent DFT level. Dynamics of pyrrole was studied as a test case.

A central problem in dynamics simulations based on the complete active space self-consistent field (CASSCF) method is to determine how the results depend on the active space. Taking aminopyrimidine as a test case, we have systematically investigated the influence of the active space in the simulations. The results shed light on how different active spaces affect the results and how one should proceed to select adequate spaces.

Publications resulting from this research area: 291, 292, 304, 365, 366, 392, 406

External funding: none

Cooperations: V. Bonacic-Koutecký (Berlin, DE); M. Eckert-Maksic (Zagreb, HR); H. Lischka (Vienna, AT); D. Nachtigallová, J. Pittner (Prague, CZ); P. G. Szalay (Budapest, HU)

CHAPTER 3

Scientific Service Units

3 Scientific Service Units

The Institute's Scientific Service Units are integral parts of the research efforts of the individual scientific groups. 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"), of analytical methods (Chromatography, Mass Spectrometry, Nuclear Magnetic Resonance, Chemical Crystallography, Electron Microscopy), and of 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). With the implementation of an electronic laboratory notebook (ELN, in progress), secure data storage and retrieval will be put on a uniform basis and will be taken care of by the IT group as described in more detail in Chapter 3.7.

3.1 Technical Laboratories (N. Theyssen)

Involved: A. Brinkmann, I. Sahm, L. Winkel

The "Technikum" of the Max-Planck-Institut für Kohlenforschung is a dedicated technical laboratory space consisting of a large central high pressure laboratory, several solvent purification and drying distillation apparatuses (turnover ~ 13.000 L per year), large scale synthesis facilities, the infrastructure for receiving and sorting the different types of waste chemicals (about 21 tons per year), two research laboratories (please see chapter 2.1.7 for further details) and office space. One chemical engineer (A. Brinkmann) and one chemical technician (L. Winkel) are mainly concerned with providing service for the scientific departments. Since 2009, the Technikum also houses the office of a new health and safety officer (I. Sahm) after the duties relating to work safety and accident prevention were assigned to N. Theyssen in 2008.

The high pressure laboratory provides the necessary infrastructure, equipment and support for all groups of the institute to carry out chemical reactions under elevated pressure. It comprises 27 especially designed high pressure boxes and an automatic and self-regulating ring line system for hydrogen, carbon monoxide and ethylene. High pressure stainless steel reactors of various designs are available from 36 to 5000 mL volumes for exploratory studies and batch-wise synthesis. The demand of this central facility was high in the reporting period as the operation rate was 100% for the larger and medium size boxes and between 90 and 100% for the small ones.

The delivery and exhaust air supply of the high pressure laboratory was extensively rebuilt in the reporting period. This measure included the installation of local exhaust devices for all drying apparatus of technical scale, which guarantee compliance with occupational exposure limits. Furthermore, the low-voltage supply installation in the high pressure laboratory was largely replaced in 2009. This included the installation of ground fault circuit interrupters and emergency stop switches to ensure a uniform security level in the entire building.

During the reporting period the small- and medium-sized high-pressure boxes were equipped with new automatic control engineering. This system allows the routine acquisition of pressure and temperature curves as well as the continuous monitoring of the maximum pressure and temperature operating parameters. Importantly, the program controllers of each box can be fully operated from outside. Their displays show the

actual, the set point and the inner temperature as well as the reactor pressure for two autoclaves. An additional on-off switch allows a cut-off for heating energy in case of emergency. Each controller is connected via a bus line to a central computer for data storage and alerting. The electric lines of the different sensors and the individual reactor heatings are connected to the controllers via separated junction boxes, which also contain semi-conductor relays for heating control and temperature limiters. These units were built in-house by our electronic technician (R. Thomas) and are installed inside the high-pressure boxes. In addition, 30 new reactor heatings of different sizes were built by co-worker from our fine mechanics workshop (D. Ullner and K. Gräfenstein). In combination with the highly sophisticated autotuning procedures of the program controller (self-optimization of the regulator circuit), a much better temperature control with sufficient small hysteresis has been established, which is of particular importance for kinetic investigations.

In 2008 an additional rectification plant was installed for the removal of plasticizers from the used hexane isomer mixture. Likewise, the measuring and control technology of the existing rectification plant for ethyl acetate was also renewed. This led to a substantial improvement in plant safety, which allows a safe overnight operation and consequently a higher productivity. At the moment, a third rectification plant is being built, in which *tert*-butyl methyl ether **(**MTBE) will be purified. We hope that this measure will foster the substitution of diethyl ether (turnover ~ 1.000 L per year) as a problematic peroxide precursor.

Currently, the coolers for the drying distillation apparatus of technical scale are being replaced by stainless steel coolers. Moreover, new automatic control engineering as well as a new low-voltage supply were installed in this area, classified as one of the rare zones with a potentially explosive atmosphere.

Publications resulting from this research area: 410

3.2 Chromatography and Separation Science (P. Schulze)

As a central facility the department provides scientific services such as isolation and analysis of compounds in chemical mixtures. A variety of modern chromatographic and electrophoretic separation methods as well as hyphenated techniques are available. Since September 2010 the group is headed by P. Schulze.

Gas chromatography (U. Häusig)

The gas chromatography laboratory provides the equipment for modern gas chromatographic techniques such as high temperature GC, GC x GC and GC-MS. Recently, a dynamic head space system has been installed enabling the pre-concentration of volatile samples. This is advantageous if complex matrices are present and small sample concentrations have to be analyzed. The MLS-GC enabled the preparative isolation of volatile compounds present in very complex mixtures. The distillation laboratory purified solvents and various substrates.

Beside routine analysis, low-cost gas bags for the analysis of gas samples have been developed (Figure 1). They were used for kinetic GC determinations of autoclave reaction gases. In contrast to commercial Tedlar® bags, the septum-tightened sample device is reusable and only the bag itself has to be replaced (€ 0.25 each). The inertness of the polymer material is somewhat lower than of commercial bags.

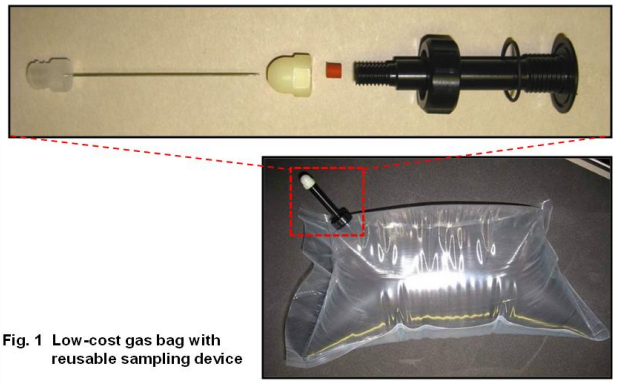


Fig. 1 Low-cost gas bag with reusable sampling device

Liquid chromatography and electrophoresis (A. Deege)

The liquid chromatography and electrophoresis laboratory applies liquid phase separations e.g. high pressure liquid chromatography and (capillary) electrophoresis. In 2008-2010 the liquid chromatography group focused on the increase of separation efficiency and the shortening of analysis time. For this reason, ultra-high-pressure systems (≥ 60 MPa) with achiral sub-2µm- and chiral 3µm-columns have been installed, resulting in higher plate numbers and significantly faster LC runs. Furthermore, a hyphenated UHPLC/MS-IT-TOF system was installed enabling the identification of unknown products or the characterization of sample contaminants. For fast chiral

determinations a standard HPLC system was upgraded to chiral supercritical fluid chromatography. The LC group was involved in the following projects:

- fast chiral separation of e.g. 150 racemic mixtures of organometallic catalysts and natural materials
- optimization of the efficiency of semi-preparative separations of synthetic materials for NMR and MS
- screening issues, for example ~ 64.500 conversion- and *ee*-determinations of epoxide hydrolases and ~ 25.500 analyses of hydroxylated steroids (Figure 2)

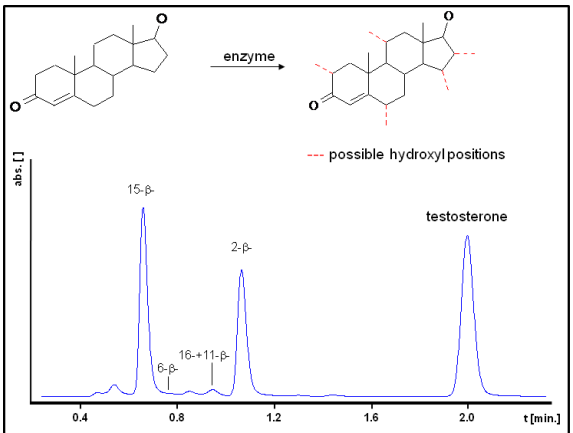


Fig. 2 Separation of hydroxylated stereoids

Two HPLC systems were equipped with valves for column switching. One is a combination of achiral 2µm columns and chiral 3µm columns enabling the separation of complex mixtures with subsequent chiral analysis of selected signals ("heart cut"). This supersedes purification steps of reaction mixtures with thin layer chromatography or solid phase extraction. The second system was utilized for simultaneous determination of saccharides and their reduction products with an improvement in analysis time by a factor of 3.

In (semi-) preparative HPLC covalently bounded stationary phases as well as chiral anion exchangers were introduced. The latter were used for separation of e.g. chiral phosphoric acids, chiral sulphonic acids and their imides.

Recently, the capillary electrophoresis section was modernized with an instrument utilizing very sensitive photodiode array detection. It was used for chiral electrophoresis of enantiomers and also for the separation of ionic liquids (Figure 3).

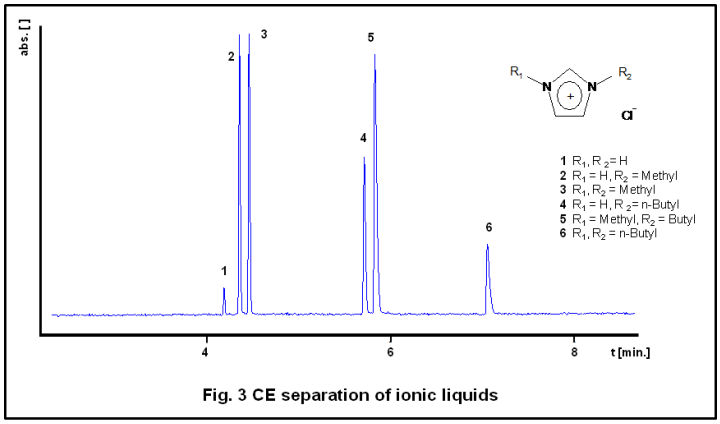


Fig. 3 CE separation of ionic liquids

Publications resulting from this research area: 411

Cooperations: O. Trapp (Heidelberg, DE)

3.3 Mass Spectrometry (W. Schrader)

The mass spectrometry group is responsible for providing a thorough and state-of-the-art service for both institutes (Kohlenforschung and Bioanorganische Chemie). This means that modern analytical methodologies need to be present in order to solve the problems in the synthetic laboratories. This is being done by providing full support in identifying unknown and new components using all ionization methods available and interpreting the obtained data. Rapid completion is a strong priority that allows the synthetic chemists to obtain the results and implement them into their work. The institutes own data base and software package (MassLib) was modernized and the emerging analytical methods such as Electrospray and high resolution data have found a greater emphasis here. Additional ionization methods, including atmospheric pressure laser ionization (APLI), a method that was published in the literature but was not available from MS manufacturer, were implemented in the lab. Therefore, we have constructed a laboratory-built APLI-source and employed it in our work.

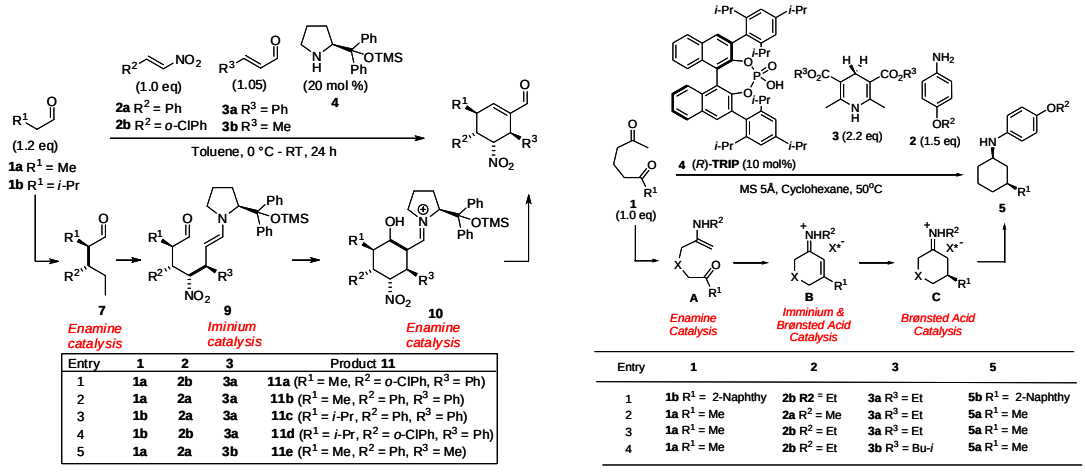
The major task is the service work for the groups of both institutes (Kohlenforschung and Bioanorganische Chemie) on the campus. The number of analyses measured varies between 7000-9000 samples annually, resulting in more than 12000 identified compounds.

Standard MS: The standard program includes direct evaporation of new volatile and solid synthetic compounds. Pure liquid compounds are analyzed by direct injection and GC/MS.

Special measurements: High resolution mass spectrometry has become an important tool for characterization of newly synthesized compounds. FT-ICR MS is a very accurate and high resolving MS technique that allows for the investigation of a much broader spectrum of samples. It is especially useful for the investigation of reaction mechanisms, where intermediates are being observed in order to study how chemical reactions proceed. In 2010 a new high-resolution MS/MS instrument was acquired that is being put into operation. High-resolution MS/MS data can provide accurate structural information about unknown compounds due to fragmentation and is an important tool for the investigation of chemical reactions.

The **research interests** are focusing on the investigation of complex and unusual reactions to gain information about mechanisms or formation pathways. Very often such reactions cannot be observed because potential intermediates are low in intensity or are available only for a short life-time. Other methods that could provide structural information do work in other analysis time segments or are not sensitive enough to gain

the desired information. Here, mass spectrometry can offer both sensitivity and the ability to gain structural information by using MS/MS techniques in a very fast time frame. It is even possible to observe important catalytic reactions in dependence of the reaction time by coupling a reactor in front of the mass spectrometer. This concept has been realized in two cooperations with the Schüth group and the List group on very different reactions. The work with the Schüth group continuous on a project investigating silicates in regard to their nucleation behavior in solution.



Entry	1	2	3	Product 11
1	1a	2b	3a	11a (R^1 = Me, R^2 = *o*-ClPh, R^3 = Ph)
2	1a	2a	3a	11b (R^1 = Me, R^2 = Ph, R^3 = Ph)
3	1b	2a	3a	11c (R^1 = *i*-Pr, R^2 = Ph, R^3 = Ph)
4	1b	2b	3a	11d (R^1 = *i*-Pr, R^2 = *o*-ClPh, R^3 = Ph)
5	1a	2a	3b	11e (R^1 = Me, R^2 = Ph, R^3 = Me)

Entry	1	2	3	5
1	1b R^1 = 2-Naphthy	2b R^2 = Et	3a R^3 = Et	5b R^1 = 2-Naphthy
2	1a R^1 = Me	2a R^2 = Me	3a R^3 = Et	5a R^1 = Me
3	1a R^1 = Me	2b R^2 = Et	3a R^3 = Et	5a R^1 = Me
4	1a R^1 = Me	2b R^2 = Et	3b R^3 = Bu-*i*	5a R^1 = Me

Fig. 1. Complex cascade reactions investigated with MS and MS/MS techniques; left: a triple cascade reaction to form *tetra*-substituted cyclohexene carbaldehydes (in cooperation with D Enders) and a highly enantioselective cascade reaction to form 3-substituted cyclohexylamines from 2,6-diketones (in cooperation with B. List).

The second project is the investigation of organocatalytic reactions with mass spectrometry to gain mechanistic information. Two cooperations (within the DFG Priority Program Organocatalysis) were carried out successfully, investigating complex cascade reactions (with D. Enders and with B. List). It was possible to study such complex catalytic multi-step, one-pot reactions as described in Figure 1. During the investigation of the cascade reaction leading to cyclohexylamines (right), it was possible to not only detect all critical cationic iminium ions and ammonium ions, but also to detect a key intermediate ion pair complex. This ion pair complex is a contact ion pair during the reduction steps and can be observed as a protonated ion pair in the gas phase of the mass spectrometer. Additionally, it was possible to determine the time dependency of the reaction, where the initial reaction

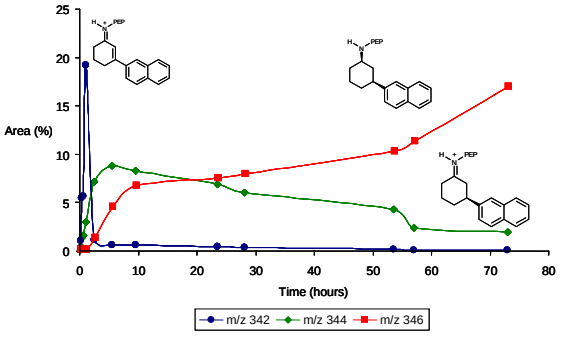


Fig. 2. Time dependency of cascade reaction.

steps take place within the first 15 minutes, while the subsequent reduction steps take more than 70 hours.

The third project currently under investigation deals with the most complex natural mixture: crude oil. Unfortunately, until sustainable resources for our energy supply are available in the necessary amounts to fuel the industrial and economical needs we are still dependent on fossil fuels. Since the light sweet crude oils are diminishing, the heavy fractions need chemical upgrading technologies. But first, the heavy resources need to be understood and chemical compositions need to be investigated. It must be noted that there is not one individual method alone that allows for the characterization of crude oil. High resolution mass spectrometry, however, is the most versatile method and plays an important role in understanding crude oils from unconventional resources. Additional analytical methods such as chemical derivatization, chromatography and the use of selective ionization methods result in higher selectivity and specificity. The use of different ionization methods displays different results from the same sample, as illustrated in Figure 3, where the spectra obtained with different ionization methods recorded from a vacuum gas oil (VGO) are shown. Different ionization methods favor different compounds. The use of different ionization methods can, therefore, be compared to watching the same sample through different windows, because each method favors certain compounds or discriminates others, meaning that the method needs to be adjusted based on what kind of compound classes are investigated.

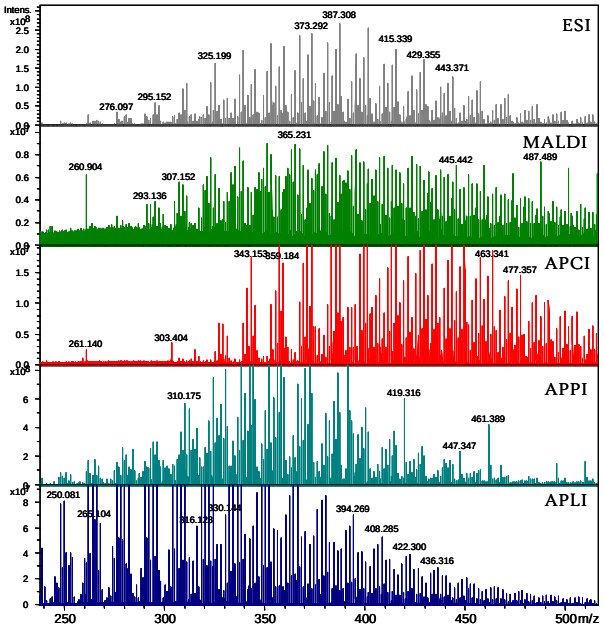


Fig. 3. Different ionization methods emphasize different compounds in complex crude oil samples.

Publications resulting from this research area: 77, 103, 105, 209, 227, 250, 251, 252, 255, 284, 297

External funding: Deutsche Forschungsgemeinschaft; Project Shell Global Solutions

Cooperations: J. T. Andersson (Münster, DE); T. Benter (Wuppertal, DE); M. Braun, H. D. Martin (Düsseldorf, DE); D. Enders (Aachen, DE); B. List, F. Schüth (Mülheim/Ruhr, DE)

3.4 Nuclear Magnetic Resonance (R. Mynott / C. Farès)

The NMR group provides a broad range of NMR techniques and analytical service to the entire institute. During the reporting period, approximately 35000 spectra have been recorded on a wide variety of samples ranging from organic and organometallic compounds in solution to coals and porous silicas in solids. To meet demands, the department is equipped with seven Bruker NMR spectrometers with field strengths corresponding to ^{1}H frequencies of 300 (x 2), 400 (x 2) and 600 MHz for analyses in solution and to 300 and 500 MHz for analyses in solid state. The department is also staffed with eight technical and scientific co-workers, skilled in NMR measurements and analyses as well as related soft- and hardware maintenance. The department is organized in four areas of service.

(1) NMR in Full Automation (R. Ettl / D. Bartels)
Basic NMR measurements in liquid state can be carried out in high throughput mode on two NMR spectrometers with ^{1}H frequencies of 400 and 300 MHz at room temperature. With minimal setup, scientific personnel from the institute can access these instruments round the clock and obtain NMR data which are acquired and processed fully automatically. The selection of available experiments is limited to those with high sensitivity, high information content and rapid execution with predefined parameters. These include experiments for 1D spectra of ^{1}H, ^{13}C, ^{31}P and ^{11}B as well as for 2D correlated NMR spectra such as ^{1}H/^{1}H COSY and ^{1}H/^{13}C HSQC. This service covers nearly 90% of all experiments run in our department.

(2) Routine NMR (R. Ettl / D. Bartels / W. Wisniewski / P. Philipps)
Liquid samples requiring special setup or treatment are submitted for measurement to our operators on two further 300 and 400 MHz spectrometers. The most common requests are for (a) experiments or nuclear frequencies not available in the automatic mode, (b) experiments at high or low temperature, (c) techniques requiring adjustment of acquisition parameters to optimize the spectra, and (d) spectroscopy of chemical reactions and kinetics followed in real time directly in the NMR tube.

(3) Advanced NMR Analyses (C. Wirtz / B. Gabor / P. Philipps)
Particularly challenging NMR studies of solution compounds are accepted for advanced analysis. For these samples, our technical staff members provide full measurement, analysis and interpretation assistance in close collaboration with the chemical research groups. The advanced techniques are carried out on our dedicated 600 and 400 MHz

NMR spectrometers. Since our last report, the 600 MHz spectrometer was implemented with a cryogenically cooled probehead, which considerably enhances signal-to-noise ratio up to a factor of 8 compared to conventional equipment. This important enhancement not only allows the full characterization of materials when the amounts are severely limited but also lowers the practical limits of powerful but less sensitive NMR experiments such as 2D-INADEQUATE. A large part of the analytical work is dedicated to determine or confirm structures, stereochemistries, conformations and dynamics. The most important spectroscopic projects are reported here:

- The NMR department has been closely involved in the spectroscopic assessment of the reaction steps leading to total syntheses of natural products from the Fürstner group. These included the berkelic acid, dictyodendrin alkaloids, the iejimalide-archazolid chimera, the lactimidomycin, the leiodolide B and the spirastrellolide F methyl ester. These studies entailed detailed structure and dynamics analyses which not only characterized the configuration of the products of every reaction step but also assisted in guiding the synthetic strategies.
- A number of organometallic complexes developed for catalysis were also characterized by advanced NMR. Strategies involving ^{1}H, ^{13}C, ^{31}P and ^{15}N nuclei allowed the identification of subtle chemical shift and coupling effects which helped to pinpoint the constitution of complexes involving gold, palladium, platinum and rhodium.
- NMR measurements over a temperature range were also used to characterize structural dynamics and reaction kinetics and mechanism. For instance, ^{1}H NMR was instrumental in unambiguously identifying carbenium cation species as the predominant reactive intermediates in gold-catalyzed rearrangement of cyclopropenone ketals.

(4) Solid-State NMR (B. Zibrowius / A. Rufińska)

Solid-state NMR spectroscopy remains one of the most important techniques for the characterization of solid catalysts and other new materials synthesized in the institute. 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. Specifically, the major fields of applications during the reporting period have been:

- Multinuclear (^{13}C, ^{29}Si, ^{31}P) MAS NMR investigations on the preparation of solid catalysts from mesoporous silicas (B. Zibrowius)
- Characterization of various complex aluminum hydrides and their (partially reversible) dehydrogenation by ^{27}Al NMR (B. Zibrowius)

- Characterization of doped sodium alanates applied as catalyst for partial hydrogenation of 1,3 butadiene by ^{27}Al, ^{23}Na and ^{13}C MAS NMR (B. Zibrowius)
- Mechanistic studies on the dehydrogenation process in sodium alanate by ^{27}Al and ^{23}Na MAS NMR (B. Zibrowius)
- Multinuclear (^{1}H, ^{13}C, ^{31}P) NMR investigations of structures, intra- and intermolecular dynamics and phase transitions of organometallic compounds at variable temperature (A. Rufińska).
- Investigations of products obtained from the catalytic hydrogenation/hydrogenolysis of different types of coals (A. Rufińska).

Methods Development (C. Wirtz)

With the hiring of a new group leader in 2010 (C. Farès) and the planned installation of a new 500 MHz instrument in 2011, the NMR department plans to develop new NMR methods applied to the field of chemical catalysis.

- Some preliminary work has been carried out to develop the use of residual dipolar couplings (RDC) for small chemical compounds. These parameters provide long-range information to complement the commonly-measured short-range NOE distance parameters. RDCs can determine stereochemistries, differentiate enantiomers and provide complementary conformational and dynamic information.
- The department has also begun the exploration of methods based on relaxation dispersion which permits the characterization of low-populated, high-energy intermediate states. Applied to transformation chemistry, this method can help identify the catalytically relevant transient intermediate and potentially help understand the important steps in reaction mechanisms.
- Finally, the tracking of catalytic transformation at atomic resolution in “real time” with rapid injection NMR technology is being prepared in order to identify short lived species and help reveal the progression of reactions.

Publications resulting from this area: 12, 164, 236, 258, 344, 404

3.5 Electron Microscopy and Chemical Crystallography (C. W. Lehmann)

Introduction: The new EmRay-Group has been amalgamated from the Electron Microscopy group and the X-ray Crystallography group following the retirement of Dr. Bernd Tesche in January 2008. The group continues to provide a service for solid state characterization and structure determination by means of single crystal and powder diffraction, X-ray photoelectron spectroscopy as well as transmission and scanning electron microscopy. By combining the existing crystallographic knowledge with the imaging expertise a synergetic effect is utilized for establishing the rapidly growing field of electron crystallography in the institute. In addition to these service tasks, research activities in high resolution electron density studies, crystal engineering as well as synchrotron crystallography and instrumentation are pursued.

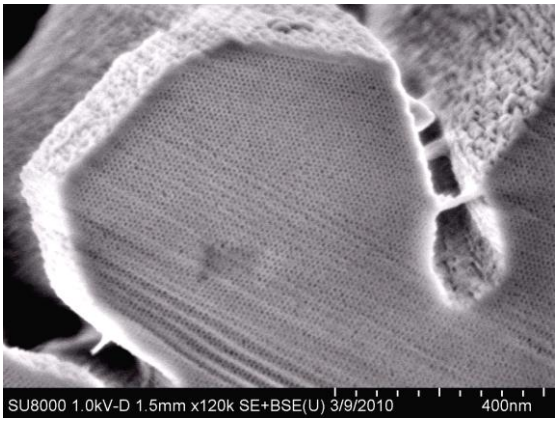
Service Activities: *i) Crystallography:* The service activities comprise diffraction techniques like single crystal structure analysis, powder diffraction and micro-diffraction, as well as spectroscopic methods, namely X-ray photoelectron spectroscopy (ESCA) and X-ray fluorescence analysis, using dedicated instruments operated by expert technical staff.

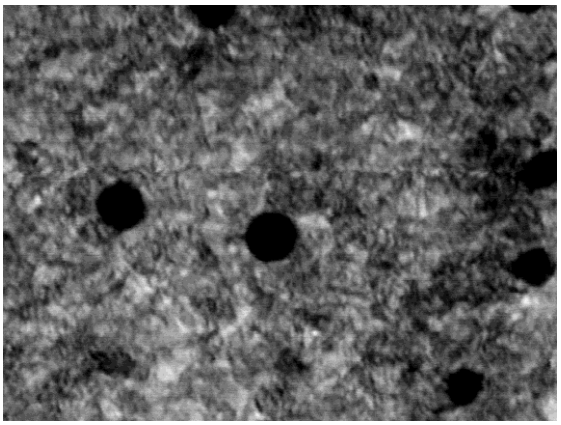
For single crystal structure analysis state-of-the-art technology is employed, comprising three area detector systems (including two 4k CCD detectors) in combination with Mo- and Cu-rotating anode X-ray generators and focusing X-ray optics (graded multilayer mirrors). A broad variety of samples, ranging from inorganic via organometallic and organic to macromolecular protein crystals comprise the approximately 500 data sets collected each year. An increasing number of samples yield only very small crystals with dimensions less than 20 μm. Selected samples are analyzed using synchrotron radiation, in particular using the single crystal beamline at ANKA in Karlsruhe. A small number of compounds, liquid at room temperature, have been crystallized *in-situ* on the diffractometer using a low temperature device. Their crystal structures have been elucidated successfully, providing insight into the molecular geometry of e.g. allenes and the intermolecular interactions employed in the solid state.

For the routine phase identification of polycrystalline materials three powder diffractometers are available. Two diffractometers make use of Mo-radiation in order to analyze more strongly absorbing samples, which are air and moisture sensitive and require sealed glass capillaries, which are measured in Debye-Scherrer geometry. *In-situ* X-ray diffraction studies of phase transformations both at low and high temperatures are carried out in order to investigate the formation of metastable phases and to follow solid state reactions. Recently a reaction chamber was added to one of the powder

diffractometers, which allows the investigation of structural changes in the presence of reactive gases at elevated temperatures.

ii) Electron Microscopy: During the reporting period changes with regard to the organization and equipment took place. An ultra-high-resolution scanning electron microscope has been installed, which offers a point resolution of 0.04 nm. In combination with bright and dark field STEM detectors and a nitrogen free EDX-System supported nano-sized metal catalysts and surface details of mesoporous compounds can be imaged and analyzed. Imaging of routine samples is now possible as a self-service based on an additional 125 keV TEM. Sample preparation for TEM and SEM has been further improved through the in-house development and manufacture of a new carbon coating device and the installation of a commercially available cross-section-polisher. The carbon coating device allows the preparation of ultra-thin carbon films (< 3 nm) used as sample support. The argon plasma cross-section polisher preserves fragile, sub-nm sized structures for SEM imaging. Samples submitted for TEM and SEM investigation show an increasingly complex composition on the nanoscopic scale. Consequently the demands for analyzing the spatial distribution of elements and for accurate quantitative analysis are growing. Future instrumentation should accommodate these requirements in the form of STEM and C_s-correction of the illumination system.





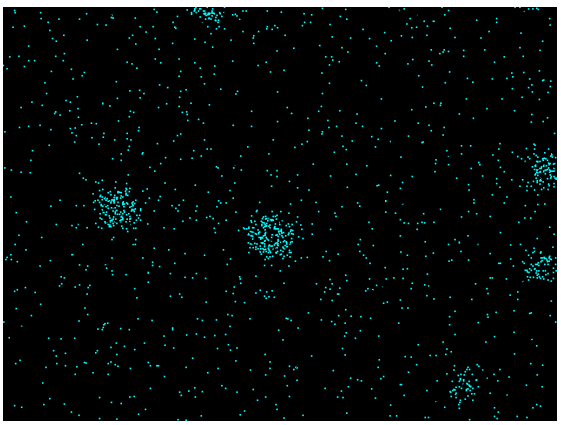


Fig. 1. a) (left): Cross section through SBA-15. b) (bottom left): Pd nano particles embedded in CMK-6. c) (bottom right): Pd-L EDX signal demonstrating spatial resolution.

Recent progress in electron microscopy allows recording of diffraction patterns with substantially reduced dynamic scattering. Together with improved software it comes within reach to solve crystal structures from sub-micron sized single crystals. The joined crystallography and electron microscopy group is in a unique position to exploit this development further.

Research Projects:

Electron Density Studies (T. Dols, F. Wang): The DFG priority program for "Experimental Charge Density as the Key to Understand Chemical Interactions" continued in three areas. In collaboration with F. Würthner (Würzburg) merocyanine dyes, which can be incorporated into organic solar cells as donor molecules in the photoactive layer, were characterized structurally and the experimental electron density of the highly effective MD376 was determined. The study of the electron density distribution in metal organic coordination polymers in cooperation with U. Englert (Aachen) was extended to characterize the non-bonding halogen-halogen and halogen-carbon interactions. Chemically closely related monomeric zinc-halogen-dipyridyl complexes have been included lately. Detailed *ab-initio* calculations of the monomeric building block as well as trimers were carried out and combined with the calculation of theoretical structure factors. This approach is suitable to improve the radial electron distribution parameters in the multipole refinement. Together with T. Spaniol (Aachen) Ti-based stereotactic polymerization catalysts of the mismatched interaction type were investigated, in order to characterize the weakly bonding sulfur-metal interaction.
Finally, NHC-transition metal catalysts were investigated and the topology of the electron density was analyzed.

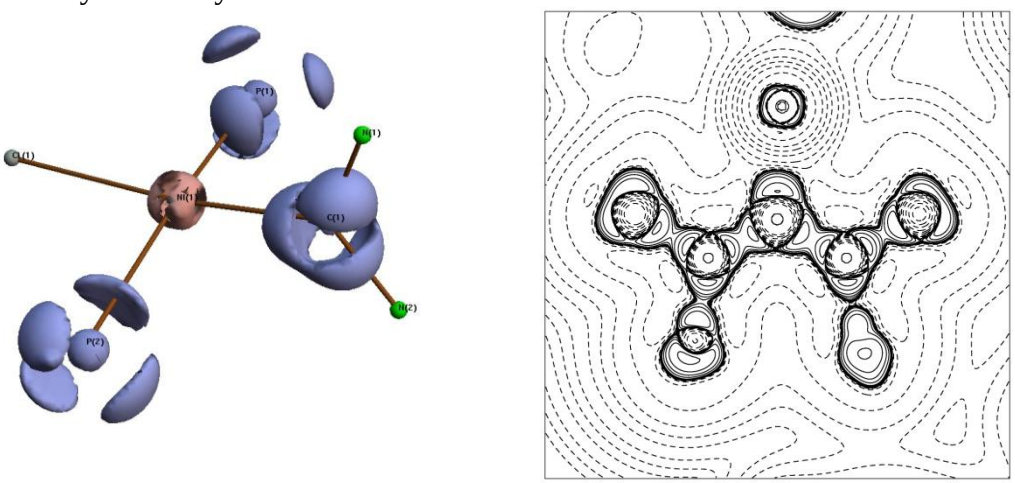


Fig. 2. Laplacian of the total electron density of a nickel carbene. Local valence shell concentrations on the phosphane and carbene point towards depletions in the Ni shell.

Crystal Engineering (D. Bock): Co-crystals are a specific implementation of supra-molecular chemistry, maximizing the use of intermolecular interactions. Since crystallization is usually employed as a means of purification and separation only strongly interacting supra-molecular aggregates will crystallize. In addition to solvent based crystallizations liquid assisted ball milling has proven to be very successful for obtaining co-crystals. This project aims at co-crystallizing chiral carboxylic acids with chiral amides; in particular it aims at the formation of diastereomers showing distinguishable powder diffraction patterns. In conjunction with crystal structure determination from powder data the influence of chirality in competition with structure directing supramolecular synthons is studied.

Chemical Crystallography Synchrotron Beamline: An extension to the PETRA III synchrotron laboratory at DESY in Hamburg will accommodate a dedicated chemical crystallography beamline. A consortium involving the University of Hamburg (U. Bismayer), the University of Dresden (D. Meyer), the University of Munich (W. Schmahl), the MPI für biophysikalische Chemie, Göttingen (S. Techert) and this group is responsible for planning, building and commissioning this beamline. Specific emphasis is being placed on handling reactive and sensitive samples in a state-of-the-art diffraction set-up. The beamline will permit high resolution single crystal data collections at variable energies up to at least 23 keV. A number of fixed energies up to 40 keV will be available as well.

Powder Diffraction Methodology: As a continuation and further development of the high-throughput polymorphism screen further research has been carried out into the application of powder diffraction for pharmaceuticals. X-ray powder diffraction using Mo-radiation has also been employed to develop a rapid screen for detecting counterfeit pharmaceutical products. The method allows to screen solid dosage forms (tablets) without removing these from their packaging or requiring further sample preparation like grinding.

Publications resulting from this area: 7, 12, 17, 18, 29, 30, 33, 34, 67, 81, 127, 149, 155, 158, 164, 183, 215, 236, 237, 262, 275, 285, 286, 288, 295, 298, 309, 310, 319, 325, 326, 327, 338, 342, 354, 358, 376, 381, 398, 399, 409, 418, 423

External Funding: Deutsche Forschungsgemeinschaft (priority program 1178 “Experimental Electron Densities”)

Cooperations: H. Butenschön (Hannover, DE); U. Englert, W. Leitner, T. Spaniol (Aachen, DE); G. Grundmeier (Paderborn, DE); K. Kleinermanns (Düsseldorf, DE); F. Mohr, H. Willner (Wuppertal, DE); F. Schüth (Mülheim,/Ruhr, DE); O. Terasaki (Stockholm, SE); F. Würthner (Würzburg, DE)

3.6 Library and Information Management (P. Fischer, R. Barabasch)

Our Library serves the five chemical departments by buying, collecting and archiving books and journals from the field of chemistry and chemical catalysis in general. It focuses on organometallic, theoretical, polymer and coal chemistry as well as on materials science. 17000+ books and monographs and 630 dissertations reflect various aspects of catalysis, which are electronically catalogued and searchable by the ALEPH program. The library contains a large collection of recent and many older print-journals. 120+ subscribed journals are electronically catalogued and linked with their digital equivalents.

On the other hand online information rapidly gains importance; most journals are now available online. All digital activities of the Max Planck Society are concentrated in the Max Planck Digital Library (MPDL). Since 2008 all needed processes for collaboration between MPDL and local libraries were established and work well now. As already mentioned in the last report, the "MPDL basic service" of the Max Planck Society allows online access to most of the core journals needed by our scientists. A list of all relevant publishers is part of the library intranet page of our institute.

The "MPDL basic service" allows us to receive many print journals for a deep discount price – e.g. the products from the American Chemical Society, the Royal Society of Chemistry, and the Wiley-VCH Group. Therefore, we keep selected journals from their journal list until the electronic long-term archive problem is solved either by the publishers themselves or by the Max Planck Society. Additionally we subscribe several other print journals, which are not included in the "MPDL basic service", bringing the total number to 80 journals. For scientific articles that are not available in our and other MPG libraries, we rely on loans through the SUBITO, British Library and Chemical Abstracts Service.

Apart from the Web of Knowledge (ISI/Thomson Scientific) which has been licensed through the MPG, the major source of information for our Institute is the Chemical Abstracts Service. In 2004 the Institute acquired 50 personal SciFinder licenses which were increased in the meantime to a total of 129. SciFinder enables users to run their own structural and bibliographic inquiries; the introduction of updated versions and the more intricate questions are handled by the library. The REAXYS files from Elsevier are also accessible.

Despite the large effort of publishing companies like Wiley or Elsevier to promote their e-books, neither the license modes nor the leasing offers have convinced us to switch from printed books. This may change in the future, and we are prepared to buy or lease single chapters as we buy review articles now. The problem of long-term archival storage seems to be solved only for printed media. A central digital book archive is being discussed within the MPG but without clear perspectives yet. Printed books still are of major importance for our library, and their number is constantly growing by ~ 260 titles per year. However, due to a strong scientific diversification many additional books are borrowed from other libraries.

Open Access to the scientific literature is a major theme in the MPG; however, activities in our institute are very limited: There is neither a central chemical open archive like the arXive.org for physicists nor high ranking open access journals in the field of chemistry. Presently we support the idea of using the eDoc server as a substitute for open access.

3.7 Computer Group (P. Fischer)

The general responsibilities of the IT group remain unchanged since the last evaluation. It supports both Mülheim Max Planck Institutes in the following areas:

- Operation and enhancement of the common local area network (LAN)
- Acquisition, operation and system management of central server computers 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 the case of failures

Electronic laboratory notebook (ELN) / Archive: Today information and results about experiments and analytic processes are stored and archived very heterogeneously. Accordingly our institute requires a system to manage these data and a long-term electronic archive where results can be archived and authenticity can be proved.

Some commercial ELNs were evaluated, but they did not fulfill the requirements of our institute. In 2009 Open Enventory (OE) was developed by F. Rudolphi in the Gooßen group (TU Kaiserslautern). Evaluation of OE showed that this ELN meets many of our requirements. Therefore it was decided to adjust this system to the specific needs of our Institute, in cooperation with F. Rudolphi. As a first step, OE was already put into operation for the administration of all chemicals.

Local area network: The common hierarchically structured LAN of both Mülheim institutes was described in the last report and remains unchanged. The link to the German science network (WiN) was upgraded from 75 to 155 Mbit/s.

For information security reasons an authentication by radius server was established for remote access, WLAN- and VPN- connections. Additionally MAC-address authentication was enabled.

Server computers: The IT group operates the central UNIX and Windows servers as well as the compute and file servers of the Department of Theory. A "grid engine queue system" was put into operation to manage the jobs from the Department of Theory.

The 4 central UNIX servers with Alpha architecture, which host the central services (external and internal logins, email dispatch and receipt, internet and intranet web pages, web cache, DNS, DHCP, RADIUS etc.) were substituted with new hardware and 64-bit LINUX.

The backup system was updated with a new HP backup server with 12 TB disc space, to meet the permanently growing amount of data. Together with this new server a new backup concept was established which is based on backup-to-disc-to-tape with synthetic full-backup.

Both Mülheim institutes share a common hierarchically structured Windows Server 2008 based Active Directory with one superordinate domain and two subdomains, one per institute. Each domain is hosted on two redundant domain controllers maintained by the IT group, except for the MPI-BAC domain controllers. Data are stored centrally on a highly redundant EMC Celerra NS80 network attached storage (NAS) server. This system was enhanced because of the permanently growing amount of data.

Linux clusters with a total of 15 dual-Opteron nodes, 81 quad-Opteron nodes (22 acquired since the last evaluation), 27 eight-way Opteron systems, 2 thirty-two way Opteron Nodes (acquired in 2008), 30 eight-way XEON systems (acquired in 03/2009) and 48 eight-way XEON blade systems (acquired in 10/2009) are in use as compute servers. Most systems are attached to the network using 1 Gbit/s ethernet. The EMC NAS server has a 10 Gbit/s ethernet connection.

Workstations and PCs: PCs represent the largest number of work place computers. There are ca. 400 in our institute and ca. 200 in the MPI-BAC. Most of them run Windows XP, whereas new PCs run with Windows 7. In the Department of Theory as well as in several other service and research groups, Linux- or UNIX-based workstations are used for more demanding applications. The workstations and PCs in the Departments of Theory and Homogeneous Catalysis have 1 Gbit/s connections to the network.

Computerization of experiments: From the real-time data acquisition systems which have been designed and implemented by the IT group in the past, the systems for the gas and liquid chromatography are still in use after more than two decades and continue to be supported. A new Software (Chromeleon of Dionex) was evaluated and will substitute the old system in the near future.

Application software: Safety data sheets on 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 the current legal regulations. Ordering of analyses can be done electronically for gas chromatography, X-ray crystallography and mass spectrometry. An elaborate book-keeping system for the samples in gas chromatography, designed and implemented by the IT group, is being maintained. Raw data and reports from mass spectrometry and gas chromatography are being archived. The IT group provides support to the libraries of both institutes concerning the Aleph 500 integrated library system. It also supports the Beilstein CrossFire database and the SciFinder interface to the Chemical Abstracts Service.

Development project: As already mentioned, the IT group develops an electronic laboratory notebook (ELN) on the basis of the Open Enventory system, in cooperation with F. Rudolphi. This involves a redesign of the software to adapt it to the needs of a larger institute and a rewriting of much of the code. In this context, the IT group will build a long-term central electronic archive that is compatible with the ELN software. The project is scheduled to be completed in 2012.

CHAPTER 4

The Training of Young Scientists

4 The Training of Young Scientists

The Institute considers the training of **young scientists** (**diploma** and **doctoral students**, **postdocs**) an important task. Their number amounts to more than 120 (cf. Figure 1 – the ratio of funding by the Institute's standard research budget and third party funds depends upon their relative contributions).

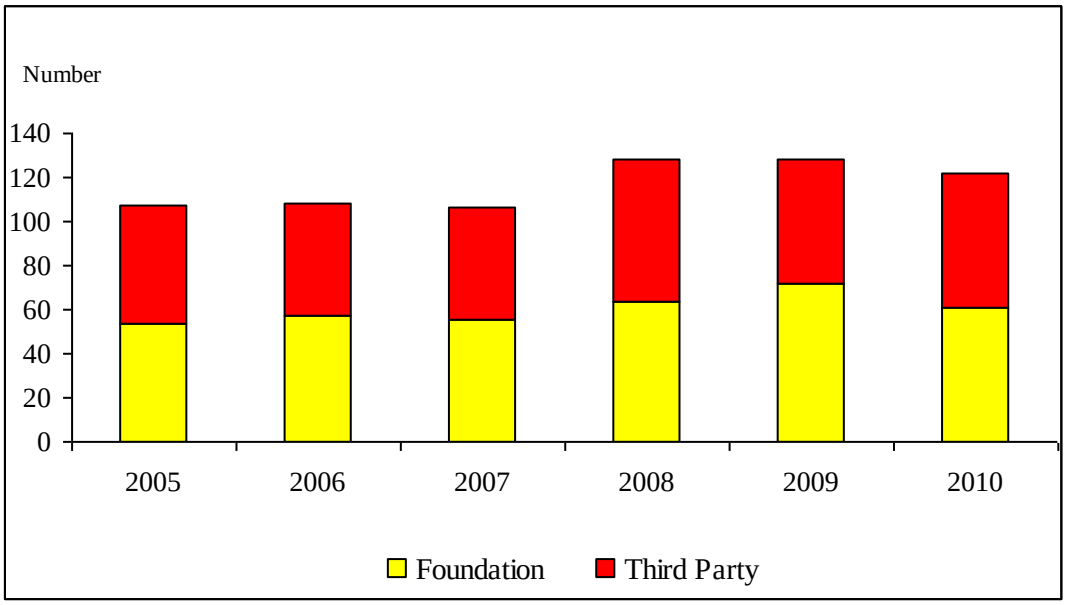


Fig. 1. Support for young scientists.

The financial resources of the Institute allow for the support of about 55 such positions in the five departments of the Scientific Members, including the positions of the research groups assigned to them. 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. During 2008 till 2010 the latter category includes 32 scholarship awardees (1 Emmy-Noether, 18 Alexander von Humboldt, 5 Deutscher Akademischer Austauschdienst, 1 Fulbright, 6 Kekulé, 1 Cusanus) and in addition 15 similar awards from abroad (Canada, China, Japan, Spain, The Netherlands).

Status 31.12.2008	Total	MPG and Foundation Funds	Third Party Funds	national (n) internat. (i)	female (f) male (m)
Diploma students	2		2	2 i	1 f 1 m
PhD students	57	25	32	27 n 30 i	17 f 40 m
Post-docs	69	39	30	6 n 63 i	14 f 55 m
Status 31.12.2009					
Diploma students	3		3	2 n 1 i	3 f
PhD students	62	31	31	30 n 32 i	22 f 40 m
Post-docs	63	41	22	6 n 57 i	17 f 46 m
Status 31.12.2010					
Diploma students	4		4	2 n 2 i	2 f 2 m
PhD students	58	31	27	21 n 37 i	24 f 34 m
Post-docs	57	33	24	6 n 51 i	18 f 39 m

Table 1. Young scientists.

The vast majority of the diploma and doctoral students come from German and European universities, including those at which the Institute's group leaders hold lectures. These are the Universities of Aachen, Berlin, Bochum, Köln, Dortmund, Duisburg/Essen, Düsseldorf, Münster, and Wuppertal.

PhD	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**
Bochum	4	3	11	5	5	10
Dortmund	3	4	4	4	3	1
Düsseldorf	2	2	2		2	1
Aachen			1			
Berlin	1	1	1			
Wuppertal					1	
Köln				2	3	1
Münster					1	
Duisburg/Essen						
Dalian (China)	1					
Total	11	10	19	11	15	13

Postdocs (country of origin)	2005	2006	2007	2008	2009	2010
Europe	22	24	23	34	32	27
USA / Canada	5	3	6	5	4	3
Latin & South America			2	3	3	6
Asia	18	20	17	25	24	21
Africa / Australia	1	3	1	2		
Total	46	50	49	69	63	57

The preceding tables specify, on an annual basis, the number of students that have received the PhD degree at a given university, as well as the geographical origin of the postdocs.

The training of the young scientists is supplemented by regular seminars within their department or group and by interdisciplinary colloquia including poster sessions. The latter are open to the whole Institute and held by the young scientists themselves. Once per year there is a 3-day long workshop for young scientists held by an internationally renowned scientist as part of the duties of the Karl Ziegler Guest Professorship. The daily lectures are supplemented by discussions. Special emphasis is laid on active participation of the young scientists. Since 2000 there is a four-semester cycle of lectures for the doctoral students and postdocs of the Institute. It covers the topics Biocatalysis (Reetz), Homogeneous Catalysis (Fürstner), Heterogeneous Catalysis (Schüth), Organocatalysis (List), Theoretical Methods in Catalysis (Thiel), and Industrial Catalysis (Hugl, Bayer AG). Since summer 2004 the Institute participates in the International Max Planck Research School (IMPRS) for Surface and Interface Engineering in Advanced Materials. In this school the Eisenforschung, Kohlenforschung, Ruhr-Universität Bochum and Institutes in China cooperate.

The Institute also contributes to the training of young scientists in the framework of large-scale research cooperations. Examples include two Collaborative Research Centers of the DFG, namely “Metal-surface Interactions in Heterogeneous Catalysis” lasting until summer 2012 (SFB 558) and “Molecular Response After Electronic Excitation” lasting until June 2010 (SFB 663), the Schwerpunktprogramm Organocatalysis of the DFG from March 2005 until April 2011 and two Max Planck Research Initiatives: “EnerChem” = Nanochemical Concepts for sustainable Energy Supply with 5 participating MPIs, and “Multiscale Materials Modeling” with 7 participating MPIs. Furthermore the institute participates with five research projects in the Exzellenzcluster “Tailor-made Fuels from Biomass” at the RWTH Aachen. In addition every year selected young scientists from our institute participate in workshops

on catalysis organized by Chemical Industry such as the Catalysis Research Laboratories (BASF together with the University of Heidelberg) or the Bayer PhD Student Course.

A survey of the diploma and doctoral theses completed in the reporting period is summarized at the end of this chapter. Students finished their doctoral studies between 2008 and 2010, on average, within a period of 3,9 years and were awarded their doctorates at the age of 29,1 years. The Rampacher Prize of the MPG, awarded annually since 1985 to the youngest doctoral student in the entire MPG to have completed his or her doctoral work in that year, has been won six times out of a possible twenty-four by students from the MPI für Kohlenforschung. In the reporting period 2 PhD candidates have won the Otto Hahn Medal by the Max Planck Society for their excellent thesis.

Special emphasis is put on the support of excellent postdocs for building up their independent research group. At present there are six such groups at our Institute (e.g. 5.1.3). During the period 2008-2010 seven Junior Scientists of the Institute have received calls from universities.

Name	**Year**	**University**
Mukherjee	2008	Bangalore, India
Trapp	2008	Heidelberg University
Yang	2009	Sungkyunkwan University, South Korea
Lu	2009	Dalian University, China
Moyeux	2009	Université de Paris, France
Palkovits	2010	RWTH Aachen
Zhang	2010	Dalian University, China

Doctoral Theses 2008

Ackerstaff, J.: Formale Totalsynthese von (–)-Haouamin A sowie Studien zur Makrozyklisierung gespannter Paracyclophane. Dortmund 2008.

Buchgraber, P.: Biologisch aktive Heterozyklen. Dortmund 2008.

Heilmann, E. K.: Totalsynthese von Isoflavonoiden mittels Platinkatalysierter Carboalkoxylierung – Neue Anwender freundliche Katalysatoren für die Alkinmetathese. Dortmund 2008.

Höbenreich, H.: Enantioselective Esterase Activities. Identification of new and Evolution of conventional Functionalities. Bochum 2008.

Hoffmann, S.: Organokatalytische asymmetrische Iminreduktion und dynamisch-kinetische Racematspaltung α-verzweigter Carbonylverbindungen. Köln 2008.

Kahakeaw, D.: Studies Enabling a Faster Directed Evolution. Evolving Stereoconvergent Epoxide Hydrolases. Bochum 2008.

Khalil, A .S. G.: Controlled Self-Assembly of Nanoporous Silica on Patterned Supports. Bochum 2008.

Korte, A.: Totalsynthese von Epohelmin B und Analoga sowie unsymmetrisch substituierte *N*-heterocyclische Carbene und ihr Einsatz in der Übergangsmetallkatalyse. Dortmund 2008.

Pan, S. C.: New Catalytic Routes to α-Amino Acids and Their Derivatives. Köln 2008.

Tüysüz, H.: Novel Mesostructured Metal Oxides. Bochum 2008.

Wüstefeld, H.-U.: Übergangsmetallkomplexe mit basischen N-Donor-Liganden in Katalyse und medizinischer Chemie. Bochum 2008.

Doctoral Theses 2009

Benítez Romero, M. J.: Self-assembled Magnetic Nanostructures: Synthesis and Characterization. Bochum 2009.

Bindl, M. F.: Totalsynthese von Cruentaren A und Analoga – Entwicklung neuer Molybdän-Nitrido-Katalysatoren für die Alkinmetathese. Dortmund 2009.

Creusen, C. M.: Phaseneigenschaften von pentakoordinierten 18-e-d^8-Übergangsmetall-π-Allyl-Komplexen. Düsseldorf 2009.

Flügge, S.: Totalsynthese von Amphidinolid V und Analoga sowie Studien zur homogenen Gold(I)-Katalyse. Dortmund 2009.

Handayani, P. P.: Development and Application of Mass Spectrometric Methods for the Investigations of Organocatalytic Reactions. Münster 2009.

Kampen, D.: Brønsted-Säure-katalysierte Hosomi-Sakurai-Reaktionen und Prolin-katalysierte Mannich-Reaktion von Acetaldehyd. Köln 2009.

Martin, N.: Organocatalytic Asymmetric Biomimetic Transfer Hydrogenations of Olefins. Köln 2009.

Metz, S.: QM/MM Investigations on the Hydroxylation Reactions of Molybdopterin-containing Enzymes. Düsseldorf 2009.

Nitz, J.-J.: Synthesis and Functionalization of Ordered Mesoporous Carbons for Catalytic Applications. Bochum 2009.

Paul, M.: Rattle-Type Structured Catalysts by the Encapsulation of Au and Pt Nanoparticles in Metal Oxide Hollow Spheres. Bochum 2009.

Rangaswamy, G. K.: Investigation of Biologically Active Vanadium-Containing Complexes using DFT-computed NMR parameters. Wuppertal 2009.

Schaack, B. B.: The Solid State Formation of Zeolitic Materials Studied by Mass Spectrometry. Bochum 2009.

Schlecker, A.: Metall-katalysierte Enin-Zyklisierungen. Dortmund 2009.

Stadler, M.: Heck Reactions of Crotonaldehyde and Organocatalytic, Asymmetric Mannich Reactions of N-Boc and Related Imines. Köln 2009.

Vukojević, S.: Copper Colloids and Nanoparticular Cu/ZrO_2-based Catalysts for Methanol Synthesis. Bochum 2009.

Doctoral Theses 2010

Bazula, P. A.: Nanostructured Oxidic Materials: Properties and Application of CoreQShell Spheres and Hollow Particles. Bochum 2010.

Benighaus, T.: Boundary Potentials for Hybrid Quantum Mechanical / Molecular Mechanical Simulations of Solvated Biomolecules. Düsseldorf 2010.

Berkermann, F.: Preparation and Application of Aqueous Iridium Oxide Colloids. Bochum 2010.

Cepak, A.: Ionenverteilung in kristallinen Katalysatoren. Bochum 2010.

Döring, J.: Gasphasenhydrierung von 1,3-Butadien an komplexen Metallhydriden. Bochum 2010.

Feyen, M.: Preparation of Novel Iron-Based Core-Shell Nanoparticles and Their Application in Heterogeneous Catalysis. Bochum 2010.

Gumulya, Y.: Exploration of evolutionary pathways *Aspergillus niger* epoxide hydrolase. Bochum 2010.

Kille, S.: Flavoproteins in Directed Evolution. Bochum 2010.

Kirchhoff, M.: High temperature stable supported catalysts and their application in the catalytic partial oxidation of methane to synthesis gas. Bochum 2010.

Liu, Y.: Novel Catalytic Materials for Glycerol Utilization and CO Oxidation. Bochum 2010.

Pawelke, R. H.: Arbeiten zu instabilen komplexen Hydriden des Aluminiums. Bochum 2010.

Reisinger, C.: Organocatalytic Asymmetric Epoxidations and Hydroperoxidations of α,β-Unsaturated Ketones. Köln 2010.

Stork, T.: Synthese und Anwendung neuer Cyclophanbasierter *N*-heterocyclischer Carbene sowie Studien zur Darstellung cyclischer bismetallischer Aminoylid Carbenkomplexe. Dortmund 2010.

Diploma Theses 2008

Paul, S.: Übergangsmetallkatalysierte Umlagerungsreaktionen. Freiberg 2008.

Spallek, M. J.: Asymmetric Catalysis with Camphor Derivatives. Synthesis of a Rigid, Chiral N-Heterocyclic Carbene Ligand and Immobilization of NHC Ligand on Polysiloxane Support. LMU München 2008.

Diploma Theses 2009

Kükrek, M.: Dehydratisierung von Fructose zu 5-Hydroxymethylfurfural und anschließende Oxidation zur Furandicarbonsäure als zuckerbasierter Terephthalsäureersatz. Düsseldorf 2009.

Tajvidi, K.: Zur Hydrogenolyse von Cellulose in wässriger Phase. Düsseldorf 2009.

Diploma Theses 2010

vom Stein, J.: Katalytische Umwandlungen von Holz in Gegenwart von ionischen Flüssigkeiten zur Herstellung von potentiellen Ausgangsstoffen für Biokraftstoffe. Düsseldorf 2010.

Master Thesis 2009

Galeano Nunez, C.: Synthesis of gold nanoparticles encapsulated in porous carbon shells. Bochum 2009.

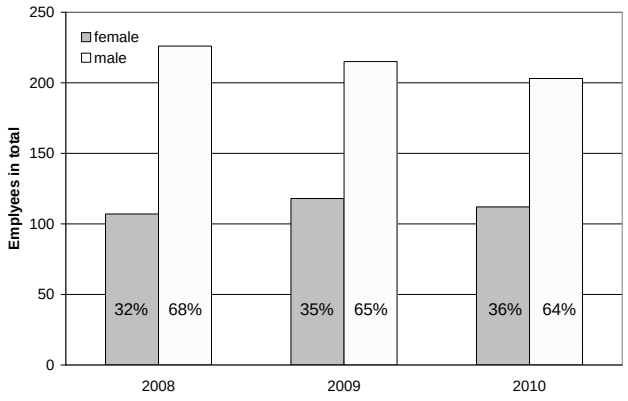
Gonthier, J.: Solvation effect on the asymmetric hydrogenation of itaconic acid dimethyl ester catalysed by $[Rh(P(O^{i}Pr)(R\text{-}BINOL))_2cod]BF_4$. EPFL Lausanne 2009.

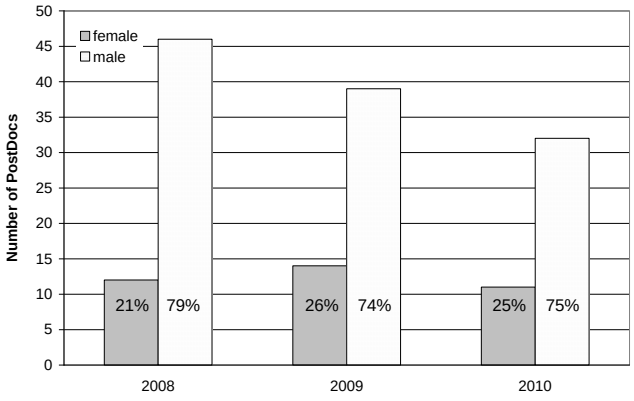
CHAPTER 5

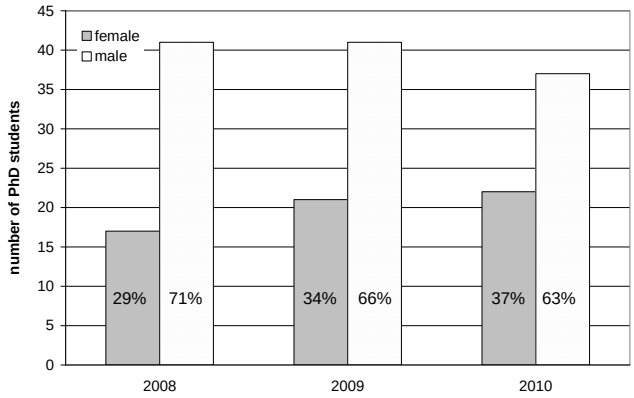
Equal Opportunities

5 Equal Opportunities

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. During the reporting period, this number could be slightly increased from 32% in 2008 to 36% in 2010. Although the most significant change has taken place in the group of the non-scientific staff (from 40% in 2008 to 52% in 2010, a percentage that actually exceeds the average of the CPTS section of the MPG (39.9% in 2009)), a very encouraging development was also noticed for female PhD students (from 29% in 2008 to 37% in 2010). The trend concerning women on postdoctoral positions was less steep but also positive during the last 3 years (21% in 2008 to 25% in 2010).







The number of female scientist on positions of the staff allocation plan of the Institute could not be improved over the last three years. Dr. Lisbeth Kværnø had been appointed as a group leader in the Department of Organometallic Chemistry after her winning of a "Max Planck Independent Research Group Leadership". For private reasons, however, Dr. Kværnø left the Institute after a stint of only 9 months (see Chapter 2.4). Currently, four female scientists are working at the Max-Planck-Institut für Kohlenforschung, two of them on permanent positions: Dr. Anna Rufińska (NMR department) and Dr. Claudia Weidenthaler (Department for Heterogeneous Catalysis). Dr. Sabrina Kille has a temporary position in the Department for Synthetic Organic Chemistry. Dr. Regina Palkovits (Department for Heterogeneous Catalysis) started here Habilitation in 2008 and was promoted to the rank of group leader in 2009. In October 2010 Dr. Palkovits has been appointed as W2 professor at the RWTH Aachen but will continue her research activities at the Institute until her laboratories in Aachen are renovated and fully operative.

To support young women scientists with small children during what is usually considered the most critical phase of their career, the Institute has signed an agreement with a newly founded local kindergarden in 2010. This agreement ensures care for two children under the age of three for a minimum of 30 h per weak each. The Institute supports these positions according to the child care allowances stipulated by the MPG and covers the risk in case these positions remain vacant. Depending on the experiences made during the first year, it is planned to develop this program further.

Dr. Claudia Weidenthaler was elected as the "equal opportunities representative" ("Gleichstellungsbeauftragte") of the Institute in 2009, with Dr. Regina Palkovits (until September 2010) and Sigrid Holle (since November 2010) as her deputies. 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 has been 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 in 2008, 4 in 2009 and 7 in 2010 were filed (see list of patent applications). For 6 applications from earlier years, patents were issued in 2008 to 2010 in Europe, Canada, and USA.

License agreements exist in the reporting period for the electrochemical coating with aluminum and with aluminum/magnesium-alloys, a process for the production of monodispersable magnetic nanocolloids, the production of chiral phosphorus compounds ("Quinaphos") and their use as catalysts or catalyst components for the preparation of optically active products, for mixtures of chiral monophosphorus compounds, chiral monophosphites, chiral diphosphonites as well as for ferrocene-based diphosphonites for asymmetrical catalysis, the method for decarboxylating C-C bond formation of carboxylic acid with carbon electrophiles, and the use of different software.

Over the period 2008 to 2010 15 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. Oliver Trapp, who was group leader in the Department of Heterogeneous Catalysis until 2008 has – after discussions with SGK – founded a company which intends to exploit the high-throughput multiplexing gas chromatography methods developed by him at the institute. A license contract is being discussed.

General managers ("Geschäftsführer") of the Studiengesellschaft are Professor Dr. Manfred T. Reetz and Professor Dr. Ferdi Schüth. Operational functions are performed by Dr. Ruth Christophersen, a patent lawyer, who works for the Institute for about 6 days/month on a freelance contract, and who has per pro for SGK. To foster the licensing activities, the Institute has signed a contract in 2009 with Max Planck Innovation, Munich, as the central technology transfer agency of the Max Planck Society.

Patent Applications 2008

1. Verfahren zur Herstellung von chiralen α,β-Epoxyketonen
   (Benjamin List, Corinna Reisinger, Xingwang Wang)

2. Verfahren zur Depolymerisation von Zellulose
   (Ferdi Schüth, Roberto Rinaldi, Regina Palkovits)

3. Probenträger für die Röntgen-Pulverdiffraktometrie (utility patent)
   (Klaus Hauschild, Wolfgang Kersten)

4. Wasserstoffspeicher
   (Ferdi Schüth, Michael Felderhoff, Borislav Bogdanović, Claudia Weidenthaler, André Pommerin)

5. Verfahren zur Herstellung von Alkalimetallcyanoborat
   (Roland Pawelke)

Patent Applications 2009

1. Chirale Disufonsäuren und Disulfonimide
   (Benjamin List, Frank Lay, Pilar García-García)

2. Verfahren zur Hydrolyse von Celluloserohstoffen
(Ferdi Schüth, Roberto Rinaldi, Philip Engel, Antje Spieß, Jochen Büchs)

3. Verfahren zur Oxidation von Methan
(Ferdi Schüth, Regina Palkovits, Markus Antonietti, Christian Baltes, Arne Thomas)

4. Verfahren zur Herstellung von Kohlenstoff-Schaumstoffen
(Ferdi Schüth, Manfred Schwickardi)

Patent Applications 2010

1. Verfahren zur Herstellung von aromatischen Verbindungen unter Bildung von Kohlenstoff-Kohlenstoffbindungen oder einer Kohlenstoff-Sauerstoff-Bindung im Rahmen einer Kupplungsreaktion
(Martin Klußmann, Aron Pintér, Abhishek Sud, Devarajulu Sureshkumar)

2. Neue und benutzerfreundliche Katalysatoren für die Alkinmetathese
(Alois Fürstner, Johannes Heppekausen, Voker Hickmann, Robert Stade)

3. Bipyridinkomplexe als Katalysatoren für die Alkinmetathese
(Alois Fürstner, Johannes Heppekausen, Robert Stade)

4. Verfahren zum Auflösen von Zellulose
(Roberto Rinaldi)

5. Verfahren zur Oxidation von organischen Verbindungen
(Felipe Emilio Zilly, Manfred T. Reetz)

6. Process for preparing carbon protected superparamagnetic or magnetic nanospheres
(Ferdi Schüth, Mathias Feyen, An-Hui Lu, Wen-Cui Li, Guang-Hui Wang, Tao Sun)

7. Verfahren zur säurekatalysierten Depolymerisation von Cellulose
(Ferdi Schüth, Roberto Rinaldi, Niklas Meine)

CHAPTER 7

Appendices

7.1 List of Publications 2008-2010

2008

1. *Adair, G., S. Mukherjee and B. List:* TRIP – A Powerful Brønsted Acid Catalyst for Asymmetric Synthesis. Aldrichim. Acta **41**, 31-39 (2008).

2. *Altun, A., D. Kumar, F. Neese and W. Thiel:* Multireference Ab Initio Quantum Mechanics/Molecular Mechanics Study on Intermediates in the Catalytic Cycle of Cytochrome P450cam. J. Phys. Chem. A **112**, 12904-12910 (2008).

3. *Balbo Block, M.A. and S. Hecht:* Poly(propylene oxide)–Poly(phenylene ethynylene) Block and Graft Copolymers. Macromolecules **41**, 3219-3227 (2008).

4. *Baltes, C., S. Vukojević and F. Schüth:* Correlations between synthesis, precursor, and catalyst structure and activity of a large set of $CuO/ZnO/Al_2O_3$ catalysts for methanol synthesis. J. Catal. **258**, 334-344 (2008).

5. *Bazula, P.A., A.-H. Lu, J.-J. Nitz and F. Schüth:* Surface and pore structure modification of ordered mesoporous carbons via a chemical oxidation approach. Microporous Mesoporous Mater. **108**, 266-275 (2008).

6. *Becker, S., H. Höbenreich, A. Vogel, J. Knorr, S. Wilhelm, F. Rosenau, K.-E. Jaeger, M.T. Reetz and H. Kolmar:* Single-Cell High-Throughput Screening To Identify Enantioselective Hydrolytic Enzymes. Angew. Chem. **120**, 5163-5166 (2008); Angew. Chem. Int. Ed. **47**, 5085-5088 (2008).

7. *Bejan, D., H. Willner, N. Ignatiev and C.W. Lehmann:* Synthesis and Characterization of Bis[bis(pentafluoroethyl)phosphinyl]imides, $M^+N[(C_2F_5)_2P(O)]_2^-$, M = H, Na, K, Cs, Ag, Me_4N. Inorg. Chem. **47**, 9085-9089 (2008).

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11. *Bogdanović, B., M. Felderhoff and F. Schüth:* Complex Hydrides. In: Hydrogen as a Future Energy Carrier. (Eds.) A. Züttel, A. Borgschulte, L. Schlapbach. Wiley-VCH, Weinheim 2008, 211-237.

12. *Buchgraber, P., T.N. Snaddon, C. Wirtz, R. Mynott, R. Goddard and A. Fürstner:* A Synthesis-Driven Structure Revision of Berkelic Acid Methyl Ester. Angew. Chem. **120**, 8578-8582 (2008); Angew. Chem. Int. Ed. **47**, 8450-8454 (2008).

13. *Bühl, M. and V. Golubnychiy:* Density-functional computational of ^{99}Tc NMR chemical shifts. Magn. Reson. Chem. **46**, S36-S44 (2008).

14. *Bühl, M., N. Sieffert, V. Golubnychiy and G. Wipff:* Density Functional Theory Study of Uranium(VI) Aquo Chloro Complexes in Aqueous Solution. J. Phys. Chem. A **112**, 2428-2436 (2008).

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16. *Chen, D., M. Schmitkamp, G. Franciò, J. Klankermayer and W. Leitner:* Enantioselective Hydrogenation with Racemic and Enantiopure Binap in the Presence of a Chiral Ionic Liquid. Angew. Chem. **120**, 7449-7451 (2008); Angew. Chem. Int. Ed. **47**, 7339-7341 (2008).

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27. *Fürstner, A. and J. Ackerstaff:* Formal total synthesis of (−)-haouamine A. Chem. Commun. (Cambridge, U. K.) **2008**, 2870-2872.

28. *Fürstner, A., M. Alcarazo, V. César and H. Krause:* Preparation of a Non-Symmetrical Imidazolium Salt: 1-Adamantyl-3-mesityl-4,5-dimethylimidazolium Tetrafluoroborate. Org. Synth. **85**, 34-44 (2008).

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47. *Kahakeaw, D. and M.T. Reetz:* A Cell-Based Adrenaline Assay for Automated High-Throughput Activity Screening of Epoxide Hydrolases. Chem.–Asian J. **3**, 233-238 (2008).

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410. *Theyssen, N., K. Scovell and M. Poliakoff:* High-pressure Methods and Equipment. In: Handbook of Green Chemistry. (Ed.) P. Anastas. Vol. 4. Wiley-VCH, Weinheim 2010, 31-75.

411. *Trapp, O., L. Sahraoui, W. Hofstadt and W. Könen*: The Stereodynamics of 1,2-Dipropyldiaziridines. Chirality **22**, 284-291 (2010).

412. *Vellalath, S., I. Čorić and B. List: N*-Phosphinyl Phosphoramide–A Chiral Brønsted Acid Motif for the Direct Asymmetric N,O-Acetalization of Aldehydes. Angew. Chem.**122**, 9943-9946 (2010); Angew. Chem. Int. Ed. **49**, 9749-9752 (2010).

413. *vom Stein, T., P. Grande, F. Sibilla, U. Commandeur, R. Fischer, W. Leitner and P. Domínguez de María:* Salt-assisted organic-acid-catalyzed depolymerization of cellulose. Green Chem. **12**, 1844-1849 (2010).

414. *Wakchaure, V.N. and B. List:* A New Structural Motif for Bifunctional Brønsted Acid/Base Organocatalysis. Angew. Chem. **122**, 4230-4233 (2010); Angew. Chem. Int. Ed. **49**, 4136-4139 (2010).

415. *Wakchaure, V.N., J. Zhou, S. Hoffmann and B. List*: Catalytic Asymmetric Reductive Amination of α-Branched Ketones. Angew. Chem. **122**, 4716-4718 (2010); Angew. Chem. Int. Ed. **49**, 4612-4614 (2010).

416. *Weidenthaler, C. and M. Felderhoff:* Complex Metal Hydrides. In: Handbook of Hydrogen Storage, New Materials for Future Energy Storage. (Ed.) M. Hirscher. Wiley-VCH, Weinheim 2010, 117-157.

417. *Weiss, V.C., B. Heggen and F. Müller-Plathe:* Critical Parameters and Surface Tension of the Room Temperature Ionic Liquid [bmim][PF_6]: A Corresponding-States Analysis of Experimental and New Simulation Data. J. Phys. Chem. C, **114**, 3599-3608 (2010).

418. *Werner, G., C.W. Lehmann and H. Butenschön:* The First Anionic Thia-Fries Rearrangements at Ferrocene: Ready Access to Trifluoromethylsulfonyl-Substituted Hydroxyferrocenes and an Extremely High Interannular Stereoinduction between Cyclopentadienyl Ligands. Adv.Synth. Catal. **352**, 1345-1355 (2010).

419. *Wu, S., J.P. Acevedo and M.T. Reetz*: Induced allostery in the directed evolution of an enantioselective Baeyer-Villiger monooxygenase. Proc. Natl. Acad. Sci. U. S. A. **107**, 2775-2780 (2010).

420. *Yachmenev, A., S.N. Yurchenko, P. Jensen, O. Baum, T.F. Giesen and W. Thiel:* Theoretical Rotation-Torsion Spectra of HSOH. Phys. Chem. Chem. Phys. **12**, 8387-8397 (2010).

421. *Yachmenev, A., S.N. Yurchenko, I. Paidarova, P. Jensen, W. Thiel and S.P.A. Sauer:* Thermal Averaging of the Indirect Nuclear Spin-Spin Coupling Constants of Ammonia: The Importance of the Large Amplitude Inversion Mode. J. Chem. Phys. **132**, 114305/1-15 (2010).

422. Y*urchenko, S.N., M. Carvajal, A. Yachmenev, W. Thiel and P. Jensen:* A Theoretical-Spectroscopy, Ab-Initio-Based Study of the Electronic Ground State of $^{121}SbH_3$. J. Quant. Spectrosc. Radiat. Transf. **111**, 2279-2290 (2010).

423. *Zeng, X., H. Beckers, H. Willner and C.W. Lehmann:* Bis(methanesulfonyl) Peroxide, $CH_3S(O)_2OOS(O)_2CH_3$: Spectroscopic, Structural, and Thermal Properties. Z. Anorg. Allg. Chem. **636**, 2447-2453 (2010).

424. *Zhang, Y., F. Lay, P. García-García, B. List and E.Y.-X. Chen:* High-Speed Living Polymerization of Polar Vinyl Monomers by Self-Healing Silylium Catalysts. Chem.–Eur. J. **16**, 10462-10473 (2010).

425. *Zheng, H., D. Kahakeaw, J.P. Acevedo and M.T. Reetz:* Directed Evolution of Enantioconvergency: The Case of an Epoxide Hydrolase-Catalyzed Reaction of a Racemic Epoxide. ChemCatChem **2**, 958-961 (2010).

426. *Zheng, H. and M.T. Reetz*: Manipulating the Stereoselectivity of Limonene Epoxide Hydrolase by Directed Evolution Based on Iterative Saturation Mutagenesis. J. Am. Chem. Soc. **132**, 15744-15751 (2010).

427. *Zheng, W.Q., J. Zhang, B. Zhu, R. Blume, Y.L. Zhang, K. Schlichte, R. Schlögl, F. Schüth and D.S. Su:* Structure-Function Correlations for Ru/CNT in the Catalytic Decomposition of Ammonia. ChemSusChem **3**, 226-230 (2010).

428. *Zumbansen, K., A. Döhring and B. List:* Morpholinium Trifluoroacetate Catalyzed Aldol Condensation of Acetone with both Aromatic and Aliphatic Aldehydes. Adv. Synth. Catal. **352**, 1135-1138 (2010).

7.2 List of Invited Talks Given by Members of the Institute (2008-2010)

2008

Alcarazo, M.

- Universidad de Santiago de Compostela, ES, 10 November 2008

Erhardt, S.

- 37th Inorganic Reaction Mechanisms Group Meeting, Barcelona, ES, 1 January 2008
- Universität Marburg, DE, 22 January 2008
- MGMS Spring Meeting, Cardiff, UK, 1 April 2008
- Conference on Multiscale Methods for the Design of Biofunctional Molecules, Essen, DE, 4 April 2008

Felderhoff, M.

- Deutsche Physikalische Gesellschaft, Berlin, DE, 28 February 2008
- Midterm Meeting of the European Hydrogen Network, University Reykjavik, IS, 17 September 2008

Fernández, L.

- BioNoCo Course, Jülich, DE, 12 March 2008

Fürstner, A.

- Derome Lecture (I), University of Oxford, UK, 7 February 2008
- Derome Lecture (II), University of Oxford, UK, 8 February 2008
- DSM Kaiseraugst, CH, 3 April 2008
- 13th Eli Lilly Foundation Scientific Symposium, Madrid, ES, 17 April 2008
- 5th Asian-European Symposium on "Meal-Mediated Efficient Organic Synthesis", Obernai, FR, 26 May 2008
- University of Namur, BE, 2 June 2008
- Syngenta Crop Protection AG, Basel, CH, 5-6 June 2008
- Academy of Science of the Czech Republic, Prague, CZ, 12 June 2008
- Firmenich Synthesis Symposium, Geneva, CH, 27 June 2008
- International Conference on Organometallic Chemistry, ICOMC 2008, Rennes, FR, 15 July 2008
- Janssen Pharmaceutical Prize for Creativity in Organic Chemistry, Gent, BE, 17 July 2008
- Chemistry Symposium in Honor of Professor Jack E. Baldwin (Oxford, UK), Roche Pharmaceuticals, Basel, CH, 25 August 2008

- Institut Català d'Investigació Química, Tarragona, ES, 5 September 2008
- Merck, Pomezia, IT, 26 September 2008
- Ischia Advanced School of Organic Chemistry, IASOC 2008, Ischia, IT, 29 September 2008
- AstraZeneca, Lund, SE, 9-10 October 2008
- Westschweizer Graduierten-Kolleg (3ème Cycle) (I), Université de Genève, Geneva, CH, 27 October 2008
- Westschweizer Graduierten-Kolleg (3ème Cycle) (II), Université de Neuchatel, CH, 28 October 2008
- Westschweizer Graduierten-Kolleg (3ème Cycle) (III), Université de Neuchatel, CH, 29 October 2008
- Westschweizer Graduierten-Kolleg (3ème Cycle) (IV), Université de Fribourg, CH, 30 October 2008
- Westschweizer Graduierten-Kolleg (3ème Cycle) (V), Université de Fribourg, CH, 31 October 2008
- DIP Symposium on Asymmetric Catalysis, MPI für Kohlenforschung, Mülheim/Ruhr, DE, 5 November 2008
- AstraZeneca, Macclesfield, UK, 17 November 2008
- Sir Robert Robinson Distinguished Lecture, University of Liverpool, UK, 18 November 2008
- Syngenta, Jealott's Hill, UK, 1-2 December 2008

Keal, T.W.

- DFG 490 Retinal Research Group Workshop, Braunschweig, DE, 23 April 2008

Klußmann, M.

- Technische Universität Darmstadt, DE, 7 January 2008
- ACS National Meeting, New Orleans, USA, 7 April 2008
- Universität zu Köln, DE, 24 June 2008
- Microsymposium on Asymmetric Synthesis, Polish Academy of Science, Warsaw, PL, 5 September 2008

List, B.

- University Haifa, IL, 28 February 2008
- University Tel Aviv, IL, 2 March 2008
- Saltigo, Leverkusen, DE, 11 March 2008
- Sanofi Aventis Meeting, Lalonde, FR, 1 April 2008
- Wageningen Symposium, NL, 3 April 2008
- Bürgenstock Meeting, CH, 12 April 2008
- SelChem Meeting, Stockholm, SE, 22 April 2008

- AstraZeneca, Lund, SE, 24 April 2008
- Freie Universität Berlin, DE, 6 May 2008
- Beilstein Symposium, Bozen, I, 27 May 2008
- Sanofi Aventis, Paris, FR, 9-10 June 2008
- Universität zu Köln, DE, 23 June 2008
- Gordon Conference, RI, USA, 17 July 2008
- EUCHEMS, Torino, IT, 17 September 2008
- Young Chemists 2008, Cracow, PL, 16 October 2008
- Max Planck Society, Berlin, DE, 23 October 2008
- FAST, Philadelphia, USA, 28 October 2008
- Seoul National University, KR, 4 November 2008
- KAIST, Seoul, KR, 5 November 2008
- Sungkyunkwan University, Seoul, KR, 7-8 November 2008
- POSTECH, Pohang, KR, 10-11 November 2008
- SIOC, Shanghai, CN, 13 November 2008
- DFG-Organocatalysis Meeting, Berlin, DE, 4 December 2008

Haenel, M. W.

- Engler-Bunte-Institut, Universität Karlsruhe (TH), DE, 7 January 2008
- German-Turkish Symposium "Development and Technology of Carbons", Istanbul Technical University, TR, 24 April 2008
- DGMK International Conference "Future Feedstock for Fuels and Chemicals", Berlin, DE, 1 October 2008

Lehmann, C. W.

- Stockholm University, SE, 28 January 2008
- IQPC 4th Annual Forum on Polymorphism and Patenting, Frankfurt/Main, DE, 28 May 2008
- Kristallographie Sommerschule, Hardehausen, DE, 8 September 2008
- Bergische Universität Wuppertal, 16 October 2008
- IQPC Developing IP Strategies for Crystalline Forms, London, UK, 10 November 2008

Leitner, W.

- ProcessNet Arbeitsausschuss "Kinetik und Reaktionsmechanismen", Frankfurt/Main, DE, 7 January 2008
- Catalysis and Advanced Materials Seminar, Imperial College, London, UK, 24 January 2008
- Katalytikertreffen, Weimar, DE, 27 February 2008

- Séminaire de l' UMR Sciences Chimiques, Rennes, FR, 03 April 2008
- Green Chemistry Gordon Conference, Bates College, Lewiston, USA, 6 August 2008
- 236th ACS Meeting, Philadelphia, USA, 18 August 2008
- Expertenrunde "Stoffliche Nutzung von CO_2", DECHEMA, Frankfurt/Main, DE, 3 September 2008
- 125. Versammlung der Gesellschaft Deutscher Naturforscher und Ärzte, Tübingen, DE, 22 September 2008
- Green Solvents – Progress in Science and Application, Friedrichshafen, DE, 28 September 2008
- Seminar des Exzellenz Clusters "Unifying Concepts in Catalysis", TU Berlin, DE, 29 October 2008
- CATSA Eminent Visitor Lecture Tour, Johannesburg/Parys, ZA, 10 November 2008
- CATSA Eminent Visitor Lecture Tour, University of Kwa-Zulu Natal, Durban, ZA, 13 November 2008
- CATSA Eminent Visitor Lecture Tour, North West University, Potchefstroom, ZA, 13 November 2008
- CATSA Eminent Visitor Lecture Tour, University of Stellenbosch / University of Cape Town, Stellenbosch, ZA, 14 November 2008
- Société Française de Chimie, Paris, FR, 2 December 2008
- FFC, Toulouse, FR, 16 December 2008

Marlow, F.

- Phys.-Chem. Kolloquium, Universität Duisburg-Essen, DE, 10 June 2008
- Graduate Lecture, Universität Paderborn, DE, 25 June 2008
- International Conference on Materials Science and Engineering, Nürnberg, DE, 4 September 2008
- Physikalisches Kolloquium, Universität Duisburg-Essen, DE, 26 November 2008

Maulide, N.

- Instituto Superior Técnico, Lisbon, PT, 24 November 2008

Palkovits, R.

- Tutorial Workshop on Green Chemistry and Catalysis, Universität Aachen, DE, 25 April 2008
- University Amsterdam, NL, 28 May 2008
- GKSS (Helmholtz Center), Geesthacht, DE, 23 October 2008

Pörschke, K.-R.

- University of South Florida, Tampa, USA, 20 March 2008
- University of Florida, Gainesville, USA, 28 March 2008
- University of South Alabama, Mobile, USA, 4 April 2008
- ACS National Meeting, New Orleans, USA, 9 April 2008

Reetz, M. T.

- Novozymes Technology Conference, Bagsvaerd, DK, 15 January 2008
- GDCh, Technische Universität Kaiserslautern, DE, 22 January 2008
- 5th Knud Lind Larsen Symposium, Danish Academy of Technical Sciences, Copenhagen, DK, 25 January 2008
- UCB Pharma, Medicinal Chemistry Department, London, UK, 4 February 2008
- BioNoCo Course, Forschungszentrum Jülich, DE, 12 March 2008
- Delft University, NL, 2 April 2008
- University of Manchester, UK, 17 April 2008
- Industrial Biotransformations Conference, San Francisco, USA, 24 April 2008
- DSM Life-Science Synthesis Days, Bad Herrenalb, DE, 18 June 2008
- 16th Int. Symposium on Homogeneous Catalysis, Florence, IT, 8 July 2008
- Medical School Hannover, DE, 2 October 2008
- Forschungszentrum Dresden-Rossendorf, DE, 13 October 2008
- ESF-EMBO Symposium, Sant Feliu de Guixols (Costa Brava), ES, 28 October 2008
- Hans-Fischer-Symposium "Weiße Biotechnologie", TU München, DE, 3 November 2008
- Solvias Science Day, Basel, CH, 18 November 2008

Rinaldi, R.

- ProcessNet Jahrestagung 2008, Karlsruhe, DE, 8 August 2008
- Future Feedstocks for Fuels and Chemicals, DGMK Meeting, Berlin, DE, 1 October 2008

Schaack, B. B.

- British Association for Crystal Growth, Loughborough University, UK, 7 September 2008

Schmidt, W.

- Bergakademie Freiberg, DE, 9 January 2008
- Indo-German Workshop on Advances in Reaction and Separation Processes, Chennai, IN, 19 February 2008

- Workshop “Charakterisierung von feinteiligen und porösen Festkörpern”, Bad-Soden, DE, 19 November 2008

Schrader, W.

- Workshop “Hochauflösende Massenspektrometrie” at the 41. Jahrestagung der DGMS, Gießen, DE, 2 March 2008
- TU Darmstadt, DE, 21 May 2008
- Bergische Universität Wuppertal, 10 June 2008
- Kolloquium Shell Global Solutions, Amsterdam, NL, 8. July 2008
- Division of Fuel Chemistry, ACS Fall Meeting, Philadelphia, PA, USA, 17 August 2008

Schüth, F.

- NRSC-Catalysis Conference, Amsterdam, NL, 9 January 2008
- Knud Lind Larsen Symposium on Catalysis in Synthesis, Copenhagen, DK, 26 January 2008
- GDCh, Bayer, Leverkusen, DE, 31 January 2008
- GDCh, Universität Konstanz, DE, 7 February 2008
- GDCh, Frankfurt/Main, DE, 8 February 2008
- 17. Diskussionstagung Anorganisch-Technische Chemie, Dechema, Frankfurt/Main, DE, 28 February 2008
- GDCh, TU Bergakademie Freiberg, DE, 16 April 2008
- 75 Jahre DGMK, Berlin, DE, 22 May 2008
- 408. WE Heraeus Seminar, Physikzentrum Bad Honnef, DE, 27 May 2008
- Adolf-Martens-Kolloquium, Berlin, DE, 28 May 2008
- Science College, Ruhr-University Research School, Bochum, DE, 12 July 2008
- Cluster EnergieForschung NRW, Zeche Zollverein, Essen, DE, 16 June 2008
- Heidelberger Chemische Gesellschaft, Universität Heidelberg, DE, 17 June 2008
- A scientific and academic ceremony on the occasion of the 65th birthday of Professor Pierre Jacobs, Universität Leuven, BE, 17 September 2008
- GDNÄ, Tübingen, DE, 19 September 2008
- TU Darmstadt, DE, 8 October 2008
- 10 Years Institute of Nanotechnology, KNMF, Karlsruhe, DE, 13 October 2008
- Innovation NRW Kongress, Düsseldorf, DE, 23 October 2008
- Werkstoffdialog NRW 2008, Dortmund, DE, 17 November 2008
- GDCh, Kassel, DE, 18 November 2008
- GDCh, Kaiserslautern, DE, 25 November 2008
- SPD Bundestagsfraktion im Austausch mit der Max-Planck-Gesellschaft, Berlin, DE, 18 December 2008

Theyssen, N.

- Sektionstreffen "Tailor-Made Fuels from Biomass", Aachen, DE, 1 September 2008
- Netzwerktreffen der Alumnibeauftragten, Berlin, DE,16 October 2008

Thiel, W.

- RSC Conference: Computational Biophysics, Antigua, AG, 14 January 2008
- QUASAAR Winter School: Quantitative Spectroscopy, Saas-Almagell, CH, 23 January 2008
- Danish Chemical Society, Aarhus, DK, 1 February 2008
- DPG Symposium: Modern Developments in Multiphysics Materials Simulations, Berlin, DE, 28 February 2008
- Sanofi-Aventis Seminar, Frankfurt/Main, DE, 27 March 2008
- Nordrhein-Westfälische Akademie der Wissenschaften, Düsseldorf, DE, 25 April 2008
- WGF International Symposium: Theoretical Biochemistry, Stockholm, SE, 15 May 2008
- GDCh, Universität Regensburg, DE, 2 June 2008
- DSM Workshop, Geleen, NL, 5 August 2008
- ACS National Meeting, Symposium: Electronic Structure of Transition Metal Systems, Philadelphia, USA, 20 August 2008
- 20th International HRMS Conference, Prague, CZ, 2 September 2008
- Latsis Symposium, ETH Zürich, CH, 8 September 2008
- WATOC2008 Conference, Sydney, AU, 18 September 2008
- TACC2008 Conference, Shanghai, CN, 24 September 2008
- DIP Symposium, Mülheim/Ruhr, DE, 5 November 2008
- Lise Meitner-Minerva Symposium, Jerusalem, IL, 13 November 2008
- Anorganisch-chemisches Seminar, Universität Hamburg, DE, 1 December 2008
- Symposium: Gas-Phase Ion Chemistry, Kloster Eberbach, DE, 13 December 2008

Trapp, O.

- New York University, USA, 10 January 2008
- Merck & Co., Rahway, NJ, USA, 11 January 2008
- Universität Mainz, DE, 14 February 2008
- Indo-German Workshop, Chennai, IN, 19 February 2008
- 41. Jahresteffen Deutscher Katalytiker, Weimar, DE, 28 February 2008
- Dechema, Frankfurt/Main, DE, 12 March 2008
- Chemie-Dozententagung, Kaiserslautern, DE, 19 March 2008

- Chemie-Dozententagung, Kaiserslautern, DE, 20 March 2008
- TU Berlin, DE, 19 May 2008
- TU Dortmund, DE, 27 May 2008
- RWTH Aachen, DE, 30 May 2008
- Freie Universität Berlin, DE, 3 June 2008
- BASF, Ludwigshafen, DE, 4 June 2008
- TU Darmstadt, DE, 18 June 2008
- Chirality-2008 (ISCD 20), Geneva, CH, 9 July 2008
- TU München, DE, 29 July 2008
- Analytica China, Shanghai, CN, 23 September 2008
- 5th Conference on ht-Techniques, Seeon, DE, 30 September 2008

Weidenthaler, C.

- Jahrestagung der Deutschen Mineralogischen Gesellschaft, Berlin, DE, 16 September 2008
- Universität Bremen; DE, 7 November 2008

2009

Alcarazo, M.

- 9th International Congress in Heteroatom Chemistry, ICHAC-9, Oviedo, ES, 1 July 2009

Benighaus, T.

- Winter School: Intermolecular Interactions, Mariapfarr, AT, 20 February 2009
- International Workshop on Multiscale Materials Modeling, Fritz-Haber-Institut, Berlin, DE, 12 March 2009

Fink, G.

- Leibniz-Institut für Oberflächenmodifizierung, Leipzig, DE, 14 May 2009

Fürstner, A.

- MPI-RIKEN Bilateral Conference on Interdisciplinary Cooperation, Munich, DE, 21 January 2009
- Organisch-Chemisches Kolloquium, Westfälische Wilhelm-Universität Münster, DE, 5 February 2009
- Synthesefest 2009, Ludwig-Maximilians-Universität München, DE, 18 March 2009
- ETH Zürich, CH, 27 April 2009

- CGC Symposium 2009, Chemical Genomics Center of the MPG, Dortmund, DE, 8 May 2009
- XVIIIth International Conference on Olefin Metathesis and Related Chemistry (ISOM XVIII), Leipzig, DE, 7 August 2009
- 13th Brazilian Meeting on Organic Synthesis, São Carlos, SP, BR, 4 September 2009
- Sanofi-Aventis, Frankfurt/Main, DE, 23-24 September 2009
- Eli Lilly, Windlesham, Surrey, UK, 1 October 2009
- University of Tokyo, JP, 5 October 2009
- Astellas Pharmaceuticals, Takahagi, JP, 6 October 2009
- Tokyo Institute of Technology, JP, 7 October 2009
- Astellas Pharmaceuticals, Tsukuba, JP, 8 October 2009
- Eisai Co., Tsukuba, JP, 9 October 2009
- Solvias Science Day, Basel, CH, 2 November 2009
- Heidelberg Forum of Molecular Catalysis 2009, Heidelberg, DE, 6 November 2009
- 15th Anniversary Symposium of the Holland Research School of Molecular Chemistry (HRSMC), Amsterdam, NL, 12 November 2009
- Royal Society of Chemistry, London, UK, 30 November 2009
- University of Birmingham, UK, 1 December 2009
- Almac, Craigavon (Belfast), UK, 2-3 December 2009

Haenel, M. W.

- Innovationsforum "Innovative Braunkohlen Integration in Mitteldeutschland (ibi)", Bergakademie Technische Universität Freiberg, DE, 26 February 2009
- 237th ACS National Meeting, Salt Lake City, Utah, USA, 26 March 2009
- 70. Sitzung des DGMK-Arbeitskreises Kohlenveredlung, Bergakademie Technische Universität Freiberg, DE, 24 April 2009

Lan, Z.

- University of Alcala, ES, 17 April 2009
- Tsinghua University, Beijing, CN, 3 September 2009
- 45th Symposium on Theoretical Chemistry, Neuss, DE, 12 September 2009
- 2nd Annual GCCCD Workshop, Universität Duisburg-Essen, DE, 19 December 2009

Lehmann, C. W.

- Polish Patent Office, Warsaw, PL, 23 March 2009
- 12th BCA Intensive Teaching School in X-ray Structure Analysis, Durham, UK, 27 March 2009

- Universität Bonn, DE, 9 October 2009
- Bergische Universität Wuppertal, DE, 29 October 2009

Leitner, W.

- CCS Kongress des IZ Klima e.V., Berlin, DE, 23 January 2009
- Anorganisch-Chemisches Kolloquium, Ludwig-Maximilians-Universität München, DE, 5 February 2009
- Bucharest, RO, 12 February 2009
- Imperial College, London, UK, 3 March 2009
- AoC Kolloquium "Catalytic Processes", Evonik Degussa, Marl, DE, 24 March 2009
- SusChem-D, Dechema, Frankfurt/Main, DE, 8 April 2009
- Achema 2009, Frankfurt/Main, DE, 14 May 2009
- Universitat Rovira i Virgili, Tarragona, ES, 15 July 2009
- CS^3 Workshop, Kloster Seeon, DE, 24 July 2009
- GSC-4 und AOGSC-2, Beijing, CN, 21 August 2009
- Wissenschaftsforum der GDCh, Frankfurt/Main, DE, 31 August 2009
- Wirtschaftsrat, Berlin, DE, 1 September 2009
- ProcessNet Jahrestagung, Mannheim, DE, 8 September 2009
- Clemens-Winkler-Kolloquium, TU Bergakademie Freiberg, DE, 22 October 2009
- Technische Universität München, DE, 30 October 2009
- 1. Energie-Kolloqium der Chemiegesellschaften, Frankfurt/Main, DE, 17 November 2009
- GDCh, Johann Wolfgang Goethe-Universität Frankfurt/Main, DE, 24 November 2009

List, B.

- GDCh, Ruhr-Universität Bochum, DE, 29 January 2009
- 74th Meeting ICS, Tel Aviv, IL, 8-9 February 2009
- Superior School in Organic Synthesis, Campinas, BR, 12-13 February 2009
- Instituto di Química – Unicamp, Sao Paulo, BR, 16-17 February 2009
- Synthesefest, Ludwig-Maximilians-Universität München, DE, 17 March 2009
- CarLa Winterschool, Unversität Heidelberg, DE, 19 March 2009
- GDCh, Bayer, Monheim, DE, 2 April 2009
- Sepracor, Boston, MA, USA, 23 April 2009
- McGill University, Montreal, CA, 28 April 2009
- Boehringer Ingelheim, Montreal, CA, 29 April 2009
- University of Montreal, Montreal, CA, 30 April 2009

- MPG/Bayer Symposium, Monheim, DE, 18 May 2009
- Pfizer, Groton, USA, 16 June 2009
- ROCCAT, Münster, DE, 20 June 2009
- GDCh, Universität Leipzig, DE, 2 July 2009
- HRSMC Summer School, Maastricht, NL, 8-9 July 2009
- ASMC Conference, Kiev, UA, 27 August 2009
- GECO, Obernai, FR, 3 September 2009
- ICIQ, Tarragona, ES, 10 September 2009
- XXXII Biennial Meeting of the RSEQ, Oviedo, ES, 14 September 2009
- Summer School, Universität Graz, AT, 28 September 2009
- Yale University, New Haven, CT, USA, 2 November 2009
- Penn State University, Pennsylvania, USA, 4 November 2009
- University of Michigan, Ann Arbor, USA, 6 November 2009
- University of California, Irvine, USA, 10 November 2009
- University of California, Davis, USA, 12 November 2009
- Syngenta, Jealott's Hill, UK, 8 December 2009
- 27th SCI Process Development Symposium, Pfizer, Cambridge, UK, 9 December 2009
- UCB Pharma, Slough, UK, 10 December 2009

Maulide, N.

- Encontro Nacional de Química Orgânica, Aveiro, PT, 2 July 2009
- Ruhr-Universität Bochum, DE, 16 July 2009

Palkovits, R.

- 8th French-Japanese Seminar on Nanomaterials, Tsukuba, JP, 15 June 2009
- Summer school on catalysis, University Liverpool, UK, 15 July 2009
- Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Golm, DE, 12 August 2009
- Sino-German Workshop on Designed Materials for Energy Related Catalytic Processes, Dalian, CN, 29 September 2009
- Universität Aachen, DE, 2 November 2009
- Robert-Bosch Foundation, Stuttgart, DE, 16 November 2009
- TU Hamburg-Harburg, DE, 24 November 2009

Podtetenieff, J.

- DFG-Tagung (SPP 1170), Universität Regensburg, DE, 20 September 2009

Pörschke, K.-R.

- University of Massachusetts at Amherst, USA, 15 October 2009
- State University of New York at Albany, USA, 20 October 2009
- University of Vermont, Burlington, USA, 22 October 2009

Reetz, M. T.

- Hanse-Wissenschaftskolleg (HWK), Delmenhorst, DE, 4 February 2009
- Fourth Annual Merck Symposium in Organic Chemistry, Stanford, CA, USA, 6 February 2009
- Humboldt-Universität zu Berlin, DE, 11 February 2009
- Johnson and Johnson Pharmaceutical R&D, Beerse, BE, 3 March 2009
- University Stockholm, SE, 10 March 2009
- LOST II Symposium, Facultes Universitaires Notre-Dame de la Paix (FUNDP), Namur, BE, 20 March 2009
- Max-Planck-Haus, Munich, DE, 20 April 2009
- Biocenter University of Oulu, FI, 28 April 2009
- Tag der Chemie, Ruhr-Universität Bochum, DE, 26 June 2009
- 41st National Organic Symposium, University of Colorado, Boulder, USA, 10 June 2009
- 42nd IUPAC Congress, Glasgow, UK, 4 August 2009
- Europacat-IX, Salamanca, ES, 1 September 2009
- McGill University, Montreal, CA, 3 September 2009
- ISHHC XIV, Stockholm University, SE, 15 September 2009
- Enzyme Engineering XX, Groningen University, NL, 20 September 2009
- Int. Symposium on the Interface of Asymmetric Catalysis & F-Chemistry, Tokyo, JP, 24 October 2009
- Institut Català d'Investigació Química, Tarragona, ES, 30 October 2009

Rinaldi, R.

- 42. Jahrestreffen Deutscher Katalytiker, Weimar, DE, 1 March 2009
- 2nd International Workshop of the Excellence Cluster Tailor-Made Fuels from Biomass, Aachen, DE, 24 August 2009
- Europacat IX, Salamanca, ES, 30 August 2009
- 1st Sino-German Workshop, Dalian, CN, 28 September 2009
- 15th Brazilian Congress on Catalysis, Buzios/RJ, BR, 14 September 2009

Sanchez-Garcia, E.

- Seminars on Advanced Studies of Molecular Design and Bioinformatics, Havanna, CU, 25 August 2009

- Nano Bio Info Chemistry Symposium, Hiroshima, JP, 13 December 2009

Schmidt, W.

- Österreichische Akademie der Wissenschaften, Graz, AT, 26 February 2009

Schrader, W.

- Universität Duisburg-Essen, DE, 29 January 2009
- Universität Leipzig und Helmholz-Zentrum Leipzig, DE, 1 April 2009
- Kolloquium Shell Global Solutions, Houston, TX, USA, 15 April 2009
- Symposium of Oilfield Chemistry, Society of Petroleum Engineers, The Woodlands, TX, USA, 21 April 2009

Schüth, F.

- GDCh, Mainz, DE, 8 January 2009
- Universität Tübingen, DE, 29 January 2009
- Akademie der Wissenschaften und der Literatur, Mainz, DE, 30 January 2009
- BASF, Ludwigshafen, DE, 4 March 2009
- EMPA-Akademie, Dübendorf, CH, 6 March 2009
- Science Media Academy, Berlin, DE, 13 March 2009
- Auer von Welsbach Lecture, Österreichische Akademie der Wissenschaften, Wien, AT, 18 March 2009
- ACS National Meeting, Salt Lake City, USA, 22 March 2009
- Universität Zürich, CH, 3 April 2009
- University of California, Santa Barbara, USA, 6 April 2009
- Universität Stuttgart, DE, 21 April 2009
- Steinheimer Gespräche, Rödermark, DE, 25 April 2009
- Achema, Frankfurt/Main, DE, 13 May 2009
- GDCh, Universität Leipzig, DE, 4 June 2009
- TU Darmstadt, DE, 19 June 2009
- Ruhr-Universität Bochum, DE, 26 June 2009
- GDCh-Wissenschaftsforum, Frankfurt/Main, DE, 31 August 2009
- Universität Leipzig, DE, 4 September 2009
- ProcessNet Jahrestagung, Mannheim, DE, 9 September 2009
- Institut für Energie- und Umwelttechnik, Duisburg, DE, 11 September 2009
- Wissenschaft im Rathaus, Dresden, DE, 16 September 2009
- 3rd Workshop on Industry-Academia Partnerships in Catalysis (IDECAT), Berlin, DE, 27 October 2009

- 16. Umwelttreffen der MPG, Hohenroda, DE, 3 November 2009
- GDCh, Oldenburg, DE, 4 November 2009
- Wirtschaftsrat, Berlin, DE, 12 November 2009
- Max-Planck-Institut für Plasmaphysik, Garching, DE, 13 November 2009
- Dechema, Frankfurt/Main, DE, 17 November 2009
- BASF, Ludwigshafen, DE, 19 November 2009
- Universität Konstanz, DE, 19 November 2009
- Leibniz-Lecture, DFG, Hanoi, VN, 23 November 2009
- Guest Professor, Peking, CN, 25 November 2009
- Dalian Institute of Chemical Physics, CN, 26 November 2009
- Norwegian Catalysis Symposium 2009, Trondheim, NO, 30 November 2009
- Leibniz-Institut für Festkörper- und Werkstoffforschung, Dresden, DE, 10 December 2009
- Römer-Lecture, Munich, DE, 11 December 2009

Theyssen, N.

- ACHEMA 2009, Frankfurt/Main, DE, 11 May 2009

Thiel, W.

- GDCh, Universität Konstanz, DE, 14 January 2009
- GDCh, Universität Darmstadt, DE, 3 February 2009
- Annual Meeting of the Israel Chemical Society, Tel Aviv, IL, 9 February 2009
- Winter School: Intermolecular Interactions, Mariapfarr, AT, 20 February 2009
- Winter School: Multiscale Simulation Methods, Jülich, DE, 3 March 2009
- Triple-M International Workshop, Berlin, DE, 11 March 2009
- Academy of Sciences: IOCB Invited Lecture Series, Prague, CZ, 14 May 2009
- University of St. Andrews, UK, 27 May 2009
- University of Glasgow, UK, 28 May 2009
- International Congress of Quantum Chemistry, Helsinki, FI, 26 June 2009
- Catalan Symposium on Theoretical Chemistry, Barcelona, ES, 1 July 2009
- Symposium on Theory and Simulations of Complex Molecular Systems, Kyoto University, JP, 20 July 2009
- Conference: Molecular Interactions, Varadero, CU, 26 August 2009
- Symposium: Modeling and Simulation of Complex Systems, Mainz, DE, 21 September 2009
- CAS-MPG Symposium on Computational Biology, Potsdam, DE, 22 September 2009
- Indo-German Symposium on Modeling Chemical and Biological Reactivity, Wildbad Kreuth, DE, 4 October 2009

- Norwegian Computational Chemistry Meeting, Bergen, NO, 13 October 2009
- Kavli Institute of Theoretical Physics, UC Santa Barbara, USA, 10 November 2009
- UC Berkeley, USA, 23 November 2009
- Stanford University, USA, 24 November 2009
- Physical Chemistry Seminar, UC Santa Barbara, USA, 30 November 2009

Yachmenev, A.

- Conference: QUASAAR Winter School, Jasna Chopok, SK, 24 February 2009

Zilly, F. E.

- University of Technology, Delft, NL, 23 March 2009

2010

Alcarazo, M.

- Academy of Sciences of Seville, ES, 8 February 2010
- Institute of Organometallic Chemistry "Enrique Moles", Oviedo, ES, 18 February 2010
- 93rd Canadian Chemistry Conference and Exhibition, Toronto, CA, 31 May 2010
- Ruhr-Universität Bochum, DE, 15 November 2010
- Institute of Chemical Research of Catalonia, Tarragona, ES, 10 December 2010

Barbatti, M.

- CECAM Workshop, CECAM-HQ-EPFL, Lausanne, CH, 1 November 2010
- Universität Potsdam, DE, 24 November 2010

Benson, S.

- VCI Stipendiatentreffen, Heinrich-Heine-Universität Düsseldorf, DE, 18 February 2010

Farès, C.

- MPI for Polymer Research, Mainz, DE, 1 December 2010

Felderhoff, M.

- World Hydrogen Energy Conference (WHEC), Messe Essen, DE, 20 May 2010
- CIC Energigune, Energy Cooperative Research Centre, Minano-Alava, ES, 22 June 2010

- European Materials Research Society (EMRS) Meeting, Warsaw, PL, 15 September 2010

Fink, G.

- Universität Konstanz, DE, 15 October 2010

Fürstner, A.

- Knud Lind Larsen Symposium "Visions in Chemistry", Copenhagen, DK, 29 January 2010
- 22. Irseer Naturstofftage der DECHEMA, Kloster Irsee/Kaufbeuren, DE, 26 February 2010
- Dead Sea Symposium, En Bokek, IL, 9 March 2010
- Frontiers in Medicinal Chemistry, GDCh/DPhG Annual Meeting, Münster, DE, 17 March 2010
- Bristol-Myers Squibb Lectures, Boston College, MA, USA, 17-18 April 2010
- COST Innovation-IV Meeting on Innovative Catalysis, Ankara, TR, 25 May 2010
- Balticum Organicum Syntheticum (BOS 10), Riga, LT, 28 June 2010
- European Colloquium on Heterocyclic Chemistry, Technische Universität Wien, AT, 24 August 2010
- DSM Geleen, NL, 20 September 2010
- French Chemical Society Symposium, Palaiseau, FR, 22 September 2010
- Eli Lilly, Science Day, Madrid, ES, 24 September 2010
- Dr. Paul Janssen Invited Lecture, Johnson & Johnson Pharmaceutical Research and Development, Beerse, BE, 27 September 2010
- Peking University-Eli Lilly Symposium, Beijing, CN, 26 October 2010
- GDCh, Bayer Schering Pharma AG, Wuppertal, DE, 1 December 2010

Haenel, M. W.

- Goethe Universität Frankfurt am Main, DE, 21 June 2010

Klußmann, M.

- Universität Karlsruhe, DE, 19 January 2010

Lan, Z.

- Winter School: Dynamics in Excited States, Mariapfarr, AT, 16-17 February 2010
- 3rd Annual GCCCD Workshop, Universität zu Köln, DE, 19 June 2010
- Dalian Institute of Chemical Physics, CN, 3 December 2010

Lehmann, C. W.

- Kristallographie Sommerschule, Hardehausen, DE, 6 September 2010
- IQPC Developing IP Strategies for Crystalline Forms, London, UK, 7 December 2010

Leitner, W.

- ProcessNet Kolloquium: Industrielle Nutzung nachwachsender Rohstoffe, Frankfurt/Main, DE, 21 January 2010
- DFG/FHI Rundgespräch "Catalysis: Principles and Applications", Bad Honnef, DE, 18 February 2010
- 1st International JARA-Energy Conference, Aachen, DE, 9 March 2010
- 239th Meeting of the American Chemical Society, San Francisco, USA, 23 March 2010
- IDECAT Conference "Frontiers in Catalysis", Porquerolles, FR, 14 May 2010
- Deutsche Bundesstiftung Umwelt, Neue Perspektiven für die Nutzung von CO_2, Berlin, DE, 11 June 2010
- 17th International Symposium on Homogeneous Catalysis (ISHC 17), Poznan, PL, 6 July 2010
- Süd-Chemie AG, Heufeld, DE, 1 August 2010
- PIRE Summer School 2010, Kloster Seeon, DE, 4 August 2010
- Internationales Graduiertenkolleg SeleCa: Biological and Chemical Approaches to Selective Processes, Aachen, DE, 7 September 2010
- Chemical Sciences and Society Symposium - CS3: Sustainable Materials, London, UK, 9 September 2010
- 9th Congress on Catalysis Applied to Fine Chemicals (CAFC9), Zaragoza, ES, 14 September 2010
- RWE Symposium: CO_2 - Ein neuer Rohstoff, Düsseldorf, DE, 21 September 2010

List, B.

- Symposium RWTH, Aachen, DE, 22 January 2010
- Irseer Naturstofftage der DECHEMA, Irsee, DE, 26 February 2010
- GDCh, Bayer Schering Pharma, Wuppertal, DE, 10 March 2010
- Recontres de Chimie Organique (RCO), Université Pierre et Marie Curie Paris, FR, 15 April 2010
- "Third European Workshop in Drug Synthesis", University of Siena, IT, 26 May 2010
- ISOμ 2010, MPI f. Kohlenforschung, Mülheim/Ruhr, DE, 15 July 2010
- ICIQ Summer School, Tarragona, ES, 19-20 July 2010
- SCI "A Celebration of Organic Chemistry", GlaxoSmithKline, Stevenage, UK, 13 September 2010

- Gregynogg Synthesis Symposium, Gregynogg, UK, 25 September 2010
- GDCh, Universität Konstanz, DE, 28 October 2010
- BASF Insights, Mannheim, DE, 8 November 2010
- GDCh, Universität Kaiserslautern, DE, 16 November 2010
- University of Science and Technology of China, Hefei, CN, 7 December 2010
- SIOC, Shanghai, CN, 9 December 2010
- National University of Singapore, SG, 10 December 2010
- Nanyang Technological University, Singapore, SG, 13 December 2010
- Pacifichem, Hawaii, USA, 15 December 2010

Marlow, F.

- Kolloquium Humboldt-Universität Berlin, DE, 3 February 2010
- Seminarvortrag, FhI für Werkstoffmechanik, Halle, DE, 7 June 2010

Maulide, N.

- Ruprecht-Karls-Universität Heidelberg, DE, 22 July 2010
- 19th Nachwuchswissenschaftler-Symposium (BioOrg), Göttingen, DE, 29 September 2010

Oliveira, M. T.

- 1st JCS Ruhr-Symposium, Bochum, DE, 9 September 2010

Palkovits, R.

- IDECAT Conference on Catalysis, Proquerolles, FR, 15 May 2010
- Deutsches Bergbaumuseum, Bochum, DE, 22 June 2010
- 3rd Symposium “Frontiers in Heterogeneous Catalysis”, Garching, DE, 22 October 2010
- GDCh Stöckhardt-Kolloquium, Chemnitz, DE, 16 December 2010

Pörschke, K.-R.

- 239th ACS National Meeting, San Francisco, USA, 22 March 2010
- UC Santa Barbara, USA, 30 March 2010
- University of Nevada, Las Vegas, USA, 6 April 2010

Reetz, M. T.

- GDCh, Philipps-Universität Marburg, DE, 27 January 2010
- Ludwig-Maximilian-Universität München, DE, 8 February 2010
- University of Barcelona, ES, 12 March 2010

- Delft University, NL, 12 April 2010
- Evonik Degussa GmbH, Marl, DE, 7 May 2010
- Trends in Enzymology, Ascona, CH, 14 June 2010
- 35th FEBS Congress, Gothenburg, SE, 1 July 2010
- 1. Deutsch-Japanisches Symposium, Aachen, DE, 6 September 2010
- Trilateral Symposium, Paris, FR, 7 October 2010
- Seminar, Washington University, St. Louis, USA, 9 November 2010
- Zing Conference Biocatalysis, Cancún, MX, 11 December 2010

Rinaldi, R.

- 3rd International Workshop of the Excellence Cluster "Tailor-Made Fuels from Biomass", Aachen, DE, 23 June 2010
- Frontiers in Biorefining, Biobased Products from Renewable Carbon, Georgia, USA, 20 October 2010

Sanchez-Garcia, E.

- Leopoldina Symposium: Complexity Connecting Biomolecular Structure and Solvation Dynamics, Bochum, DE, 27 May 2010
- Conference on Reactive Intermediates and Unusual Molecules, Heron Island, AU, 14 July 2010
- University of Queensland, Brisbane, AU, 26 July 2010
- Pacifichem 2010, Honolulu, USA, 19 December 2010

Schrader, W.

- Thermo Seminar at the 9th European Fourier Transform Mass Spectrometry Workshop, Lausanne, CH, 7 April 2010
- Workshop "Energy and Mass Spectrometry", 58th ASMS Conference, Salt Lake City, UT, USA, 24 May 2010
- International Symposium on Organocatalysis ISOμ 2010, Reporting colloquium SPP1179, MPI f. Kohlenforschung, Mülheim/Ruhr, DE, 14 July 2010

Schüth, F.

- Dechema, Frankfurt/Main, DE, 14 January 2010
- ACS Meeting, San Francisco, USA, 22 March 2010
- Internationale Graduiertenschule TU München, Freising, DE, 8 April 2010
- Deutsche Hochschule für Verwaltungswissenschaften, Speyer, DE, 13 April 2010
- Promovierendenforum, Campus Essen, DE, 23 April 2010
- Sächsischer Landtag, Dresden, DE, 27 April 2010

- International Symposium Nanomaterials and Functionality, Valencia, ES, 25 May 2010
- Osamu Teraski Symposium, Stockholm, SE, 28 May 2010
- NanoFormulation 2010, Stockholm, SE, 10 June 2010
- GDCh, Berlin, DE, 21 June 2010
- KIT, Karlsruhe, DE, 24 June 2010
- EuChem, Nürnberg, DE, 30 August 2010
- Meeting of the section "Fourier-transform mass spectrometry (FTMS)" of the German Society for Mass Spectrometry, Mülheim/Ruhr, DE, 2 September 2010
- Weltkongress Chemie, Karlsruhe, DE, 3 September 2010
- ProcessNet Jahrestagung, Aachen, DE, 22 September 2010
- 1st International Workshop ENMIX, Antwerp, BE, 5 October 2010
- GeoDarmstadt 2010, Darmstadt, DE, 11 October 2010
- Solvay Science for Innovation, Brussels, BE, 14 October 2010
- 10. Münchener Wissenschaftstage, Munich, DE, 26 October 2010
- Wissenschaft für Jedermann, Deutsches Museum München, DE, 27 October 2010
- 8th iCeMS International Symposium, Kyoto, JP, 11 November 2010
- Gender Mainstreaming, Stuttgart, DE, 29 November 2010
- Thermoelectrics goes Automotive, Berlin, DE, 10 December 2010

Silva-Junior, M. R.

- Federal University of Natal, BR, 4 February 2010

Teller, H.

- VCI Stipendiatentreffen, Heinrich-Heine-Universität Düsseldorf, DE, 18 February 2010
- 4th Annual Workshop of the International Research Training Group (GRK 1038), University of Basel, CH, 11 June 2010

Theyssen, N.

- Sektionstreffen "Tailor-Made Fuels from Biomass", Aachen, DE, 21 May 2010
- International Workshop "Tailor-Made Fuels from Biomass", Aachen, DE, 23 June 2010

Thiel, W.

- Belgian Quantum Chemistry Meeting, Louvain, BE, 26 January 2010

- Winter School: Dynamics in Excited States, Mariapfarr, AT, 17-18 February 2010
- SFB 749 Symposium, Kloster Irsee, DE, 22 March 2010
- Conference: First Principles Quantum Chemistry, Bad Herrenalb, DE, 16 April 2010
- Stockholm University, SE, 12 May 2010
- Conference: Molecular Quantum Mechanics, UC Berkeley, USA, 28 May 2010
- SFB 623 Seminar, Universität Heidelberg, DE, 25 June 2010
- Faraday Discussion on Bioinorganic Chemistry, Nottingham, UK, 6 July 2010
- RSC Theoretical Chemistry Symposium, Nottingham, UK, 7 July 2010
- British Biophysical Society Meeting, Cambridge University, UK, 17 July 2010
- 17th Canadian Symposium on Theoretical Chemistry, Edmonton, CA, 27 July 2010
- 8th European Computational Chemistry Conference, Lund, SE, 26 August 2010
- Computational Biology Symposium, Oxford University, UK, 13 September 2010
- CECAM Workshop: Approximate Quantum Methods, Bremen, DE, 22 September 2010
- SFB 813 Symposium, Bad Honnef, DE, 24 September 2010
- Chemical Physics IX Congress, Cesme, TR, 15 October 2010
- CECAM Workshop: Nonadiabatic Dynamics, Lausanne, CH, 2 November 2010
- Weihnachtskolloquium, Universität Heidelberg, DE, 6 December 2010
- Forschungszentrum Jülich, DE, 17 December 2010

Valerio, V.

- 1st JCS Ruhr-Symposium, Bochum, DE, 9 September 2010

Weidenthaler, C.

- Ruhr-Universität Bochum, DE, 20 January 2010

Weingart, O.

- Winter School: Dynamics in Excited States, Mariapfarr, AT, 18 February 2010

Yachmenev, A.

- University of Tromso, NO, 18 June 2010
- POLAR2010 Conference: Quantum Chemistry beyond the Arctic Circle, Sommaroy-Tromso, NO, 25 June 2010
- Karlsruher Institut für Technologie, Karlsruhe, DE, 15 July 2010

7.3 Scientific Honors, Name Lectureships, Awards

Alcarazo, M.

- Ramon-y-Cajal Fellowship 2008
- Global Young Faculty Member der Stiftung Mercator und des Kulturwissenschaftlichen Instituts Essen 2009
- Young Scientist Award from the Academy of Sciences of Seville, ES 2010
- Thieme Journal Award 2010

Bloom, A.

- Fulbright Scholarship 2009-2010

Fürstner, A.

- Andrew Derome Lecture, UK 2008
- Janssen Pharmaceutica Prize for Creativity in Organic Synthesis, BE 2008
- Westschweizer Graduierten Kolleg (3ème Cycle), CH 2008
- Sir Robert Robinson Distinguished Lecture, UK 2008
- Astellas Lectureship, JP 2009
- Alexander Todd – Hans Krebs Lectureship, Royal Society of Chemistry, UK 2009

Güttel, R.

- Global Young Faculty Member der Stiftung Mercator und des Kulturwissenschaftlichen Instituts Essen 2009

Haenel, M. W.

- Honorary Member of the Working Group “Coal Processing” of the DGMK, German Society for Petroleum and Coal Science and Technology, 2010

Klußmann, M.

- Thieme Journal Award 2008
- Global Young Faculty Member der Stiftung Mercator und des Kulturwissenschaftlichen Instituts Essen 2009

Lehmann, C. W.

- Honorar-Professor, Bergische Universität Wuppertal, 2009

Leitner, W.

- CATSA Eminent Visitor Award der Catalysis Society of South Africa 2008

- Wöhler-Preis der Gesellschaft Deutscher Chemiker 2009
- Fellow of the Royal Society of Chemistry (FRSC) 2010

List, B.

- Visiting Professorship, Sungkyunkwan University, KR 2008
- Thomson Reuters Citation Laureate, 2009
- Organic Reactions Lectureship, USA 2009
- Boehringer-Ingelheim Lectureship, CN 2009
- High Levels Lectureship for Graduate Students, University of Science and Technology of China, Hefei, CN 2010
- New Honors Program Lectureship, National University of Singapore, SG 2010

Maulide, N.

- Member of the Global Young Faculty der Stiftung Mercator und des Kulturwissenschaftlichen Instituts Essen 2009
- Thieme Journal Award 2010

Palkovits, R.

- Junior Professorship of the Robert Bosch Foundation 2008
- GKSS Award for "Comprehensible Science" (Helmholtz Society) 2009
- Member of Global Young Faculty of Stiftung Mercator and of the Kulturwissenschaftliches Institut Essen 2009
- Jochen Block Award of the German Catalysis Society 2010
- Junior Professorship of Robert Bosch Foundation for Utilization of Renewable Natural Resources 2010
- Member of Junge Akademie an der Berlin-Brandenburgischen Akademie der Wissenschaften and of Akademie der Naturforscher Leopoldina 2010
- Innovation Award of North Rhine-Westphalia 2010

Prechtl, M. H. G.

- Preisträger im Rahmen des Rückkehrerprogramms des Innnovationsministeriums des Landes Nordrhein-Westfalens 2009

Reetz, M. T.

- Lilly Lecture, Organic Chemistry Colloquia Oxford, UK, 2008
- Lilly Organic Chemistry Postgraduate Prize Day, Windlesham, Surrey, UK, 2008
- Cope Award ACS, Salt Lake City, UT, USA, 2009
- Lilly Distinguished Lectureship Award, Prague, CZ, 2009

- Cope Award ACS Nat. Meeting, Washington, DC, USA, 2009
- Yamada Koga Prize, Tokyo, JP, 2009
- Thomas Lecture, University of Missouri-Columbia, USA, 2010

Rinaldi, R.

- Member of Global Young Faculty der Stiftung Mercator und des Kulturwissenschaftlichen Instituts Essen 2009
- Sofja Kovalevskaja Award, Alexander von Humboldt Foundation 2010
- TMFB Outstanding Project Award, Shell Global Solutions 2010

Ruppert, A.

- Poster Award, Netherlands' Catalysis and Chemistry Conference 2010

Sanchez-Garcia, E.

- Liebig-Stipendium, Fonds der Chemischen Industrie, 2010

Schaack, B. B.

- Otto-Hahn-Medaille 2009
- Wolfgang-Paul-Award, Deutsche Gesellschaft für Massenspektrometrie, 2010

Schüth, F.

- Member of Deutsche Akademie der Naturforscher Leopoldina, 2008
- Guest Professor Beijing University, 2009
- ERC Advanced Grant, 2009
- Auer von Welsbach Lecture, Österreichische Akademie der Wissenschaften, Vienna, A, 2009
- Leibniz Lecture, Deutsche Forschungsgemeinschaft, Hanoi, VN, 2009
- Römer-Lecture, LMU München, DE, 2009
- Heisenberg-Medaille of the Alexander von Humboldt-Stiftung, 2010
- Member of the Nordrhein-Westfälische Akademie der Wissenschaften und der Künste, 2010
- Nominated for Deutscher Zukunftspreis 2010

Soorholtz, M.

- Poster Award, Jahrestreffen Deutscher Katalytiker, Weimar, DE, 2010

Stade, R.

- Poster Award, CaRLa Winter School on Homogeneous Catalysis, Heidelberg, DE, 2010

Stork, T.

- Poster Award, CaRLa Winter School on Homogeneous Catalysis, Heidelberg, DE, 2009

Tajvidi, K.

- DAAD Prize for outstanding achievements of international students, Heinrich-Heine-Universität Düsseldorf, DE, 2008
- Poster Award on ProcessNet Conference, Mannheim, DE, 2009
- Dechema-Studentenpreis, ProcessNet Conference 2010

Thiel, W.

- Member of Nordrhein-Westfälische Akademie der Wissenschaften, 2008
- Festschrift, Journal of Physical Chemistry A 2009, 113 (43), 11455-12044

Trapp, O.

- Member of the Young College of the Northrhine Westphalian Academy of Sciences 2008
- ADUC-Prize of the German Chemical Society (GDCh) for the Best Habilitation Thesis 2008
- Heinz Maier-Leibnitz Award of the German Research Foundation (DFG) 2008
- Innovation Award of the Northrhine-Westphalian Ministry of Innovations 2008

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. Moreover, in 1994 the Institute signed an agreement with the Louis Pasteur Université Strasbourg/France and in 2010 with the Ruhr-Universität Bochum (RUB) outlining official co-operation between the respective institutions. During the period 2008-2010 the following lectures/workshops were held:

Alcarazo, M.

- Organometallic Chemistry I, Technische Universität Dortmund, SS 2010

Fink, G.

- Spezielle Organische Chemie: Polymertechnik – Stereospezifische Polymerisation, Heinrich-Heine-Universität Düsseldorf, SS 2008
- Spezielle Organische Chemie: Polymertechnik – Stereospezifische Polymerisation II, Heinrich-Heine-Universität Düsseldorf, WS 2008/2009
- Kinetik und Mechanismen von Polyreaktionen sowie Polymertechnik, Heinrich-Heine-Universität Düsseldorf, SS 2009
- Stereospezifische Polymerisation – Polymertechnik, Heinrich-Heine-Universität Düsseldorf, SS 2010

Fürstner, A.

- Stereoselektive Synthesen I, Technische Universität Dortmund, WS 2008/2009
- Stereoselektive Synthesen II, Technische Universität Dortmund, SS 2009
- Naturstoffsynthese I, Technische Universität Dortmund, WS 2007/2008, WS 2009/2010
- Naturstoffsynthese II, Technische Universität Dortmund, SS 2008, SS 2010

Haenel, M. W.

- Übergangsmetalle in der Organischen Synthese, Heinrich-Heine-Universität Düsseldorf, WS 2007/2008, WS 2008/2009
- Spezielle Aromatenchemie: Cyclophane – polycyclische Aromaten – Fullerene – Nanotubes, Heinrich-Heine-Universität Düsseldorf, DE, SS 2008, SS 2009

Klußmann, M.

- Kalorimetrie und Kinetik, Universität zu Köln, SS 2008, WS 2008/2009, WS 2009/2010, WS 2010/2011

Lehmann, C. W.

- Seminar Synthesechemie, Bergische Universität Wuppertal, WS 2008/2009, WS 2009/2010, WS 2010/2011
- Seminar zum Praktikum Synthesechemie, Bergische Universität Wuppertal, WS 2008/2009, WS 2009/2010, WS 2010/2011
- Praktikum Anorganische Materialien, Bergische Universität Wuppertal, SS 2010
- Seminar zum Praktikum Anorganische Materialien, Bergische Universität Wuppertal, SS 2010

Leitner, W.

- Allgemeine Technische Chemie und Makromolekulare Chemie, Universität Aachen, SS 2008, WS 2008/2009, SS 2009, WS 2009/2010, SS 2010
- Einführung in die Technische Chemie und Makromolekulare Chemie, Universität Aachen, SS 2008, WS 2008/2009, SS 2009, WS 2009/2010
- Technische Chemie F, Universität Aachen, WS 2008/2009, WS 2009/2010, WS 2010/2011
- Technische Chemie IVa, Universität Aachen, SS 2008, WS 2008/2009, SS 2009, WS 2009/2010
- Technische und Makromolekulare Chemie I, Universität Aachen, WS 2008/2009, WS 2009/2010
- Faszination Technik, Universität Aachen, WS 2008/2009, WS 2009/2010, WS 2010/2011
- Angewandte Molekulare Katalyse, Universität Aachen, WS 2009/2010, WS 2010/2011
- Katalysatorimmobilisierung und Mehrphasenkatalyse, Universität Aachen, WS 2009/2010, WS 2010/2011

List, B.

- Organokatalyse, Universität zu Köln, WS 2007/2008, SS 2008, WS 2008/2009, SS 2009, WS 2009/2010, WS 2010/2011
- CarLa Winter School, Universität Heidelberg, March 2009
- HRSMC Summer School, Maastricht, University of Amsterdam, NL, July 2009
- Summer School Graz, Universität Graz, AT, September 2009
- ICIQ Summer School, University of Tarragona, ES, July 2010

Marlow, F.

- Physikalische Chemie Nanostrukturierter Systeme IV (Molekulare Materialien), Freie Universität Berlin, WS 2007/2008, SS 2008
- Electronic and Optical Properties of Thin Films, Blockvorlesung für Doktoranden im Ausbildungsprogamm der IMPRS SurMat (Ruhr-Universität Bochum, MPI Mülheim and MPI Düsseldorf), 2008

- Aktuelle Probleme der Nanostrukturphysik, Vorlesung für Master- und Diplomstudenten, Universität Duisburg-Essen, SS 2010, WS 2010/2011
- Optical Properties of Solids and Photonic Crystals, Blockvorlesung und Laborpraktikum, Blockvorlesung für Doktoranden im Ausbildungsprogramm der IMPRS SurMat (Ruhr-Universität Bochum, MPI Mülheim und MPI Düsseldorf), 2010
- Projektpraktikum für Ingenieure 5. Semester: Herstellung und spektroskopische Charakterisierung von photonischen Kristallen, Fachbereich Physik, Universität Duisburg-Essen, WS 2010/11

Maulide, N.

- Strategies and Tactics in Organic Synthesis, Ruhr-Universität Bochum, SS 2010

Palkovits, R.

- Grundzüge der Chemie für Studierende des Maschinenbaus, Umwelttechnik und Ressourcenmanagement und Sales Engineering and Product Management, Ruhr-Universität Bochum, WS 2009/2010
- Einführung in die Technische und Makromolekulare Chemie, Universität Aachen, WS 2010/2011
- Metallorganische Komplexchemie, Heinrich-Heine-Universität Düsseldorf, SS 2008, WS 2008/2009, SS 2009, WS 2009/2010, SS 2010, WS 2010/2011

Reetz, M. T.

- Advanced Course "Biocatalysis", University of Technology, Delft, NL, 2008, 2010
- Basic Biocatalysis, Ruhr-Universität Bochum, SS 2008, SS 2009, SS 2010

Schrader, W.

- Introduction to Modern Mass Spectrometry and Hyphenated Methods, Universität Münster, SS 2008
- Advanced Mass Spectrometry, Universität Duisburg-Essen, SS 2009, SS 2010

Schüth, F.

- Chemie Anorganischer Materialien, Ruhr-Universität Bochum, SS 2008, SS 2009
- Moderne Aspekte der Chemie und Biochemie: Seminar des SFB 558: Metall-Substrat-Wechselwirkungen in der heterogenen Katalyse, Ruhr-Universität Bochum, SS 2008, WS 2008/2009, SS 2009, SS 2010
- HTE, Nanokatalyse, Ruhr-Lehrverbund Katalyse, Technische Universität Dortmund, WS 2008, WS 2010
- Präparation heterogener Katalysatoren, Ruhr-Lehrverbund Katalyse, Technische Universität Dortmund, WS 2008, WS 2010

- Inorganic Functional Materials, Porous Materials, Ruhr-Universität Bochum, SS 2010
- The structure of solids and defects in solids. Lectures for students in the training program of the IMPRS SurMat (Ruhr-Universität Bochum, MPI Mülheim and MPI Düsseldorf), WS 2010

Schüth, F. and R. Palkovits

- Grundzüge der Chemie für Studierende des Maschinenbaus, Umwelttechnik und Ressourcenmanagement (UTRM) und Sales Engineering and Product Management (SEPM), Ruhr-Universität Bochum, WS 2008/2009, WS 2009/2010

Schüth, F. and R. Rinaldi

- Grundzüge der Chemie für Studierende des Maschinenbaus, Umwelttechnik und Resourcenmanagement (UTRM) und Sales Engineering and Product Management (SEPM), Ruhr-Universität Bochum, WS 2010/2011

Trapp, O.

- Fortgeschrittenenpraktikum Synthesechemie, Ruhr-Universität Bochum, WS 2007/2008
- Massenspektrometrie im Rahmen des Synthesechemieseminars, Ruhr-Universität Bochum, WS 2007/2008
- Grundzüge der Chemie für Studierende des Maschinenbaus und des Studiengangs Umwelttechnik und Ressourcenmanagement, Ruhr-Universität Bochum, WS 2007/2008

Weidenthaler, C.

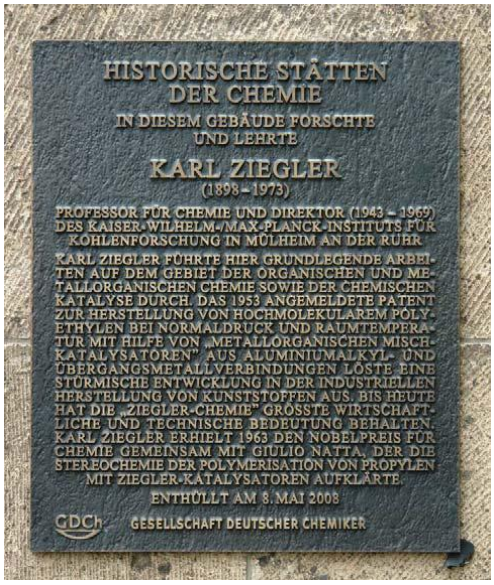
- Untersuchungsmethoden von Materialien unter “non ambient” Bedingungen, Ruhr-Universität Bochum, WS 2010/2011
- Pulverdiffraktometrie unter “non ambient” Bedingungen, Universität Innsbruck, AT, SS 2010
- Ringvorlesung: Hydrogen Storage: Methods and Materials, Universität Bremen, WS 2009/2010

7.5 Special Events and Activities

"Historical Landmark of Chemistry" Award

Inaugural act with lectures and unveiling of a plaque: the *Gesellschaft Deutscher Chemiker* (GDCh, German Chemical Society) honored the Max-Planck-Institut für Kohlenforschung as a Historical Landmark of Chemistry in remembrance of the achievements of Karl Ziegler.

8 May 2008



Alexander von Humboldt Laureate

Professor Gérard Férey
Institut Lavoisier, Université de Versailles Saint-Quentin-en-Yvelines, FR
Hybrid porous solids: A new world
20 August 2008
A strange behavior in solid-state sciences: The breathing effect
27 August 2008

Alexander von Humboldt Senior Awardee

Professor Dr. Osamu Terasaki
Stockholm University, SE
November 2008 and 13-19 December 2009

Liebig Lectureship

Dr. Paolo Melchiorre
University of Bologna, IT
Asymmetric amino catalysis: After the gold rush
11 November 2008

Visiting Scientists

Dr. Herbert Hugl
(formerly with Bayer, Leverkusen, DE)
Workshop Industrial Catalysis
12-16 January 2009

Professor Dr. Mu-Hyun (Mookie) Baik
Department of Chemistry, Indiana University, Bloomington, USA
25 May 2009 - 31 December 2009
Host: Professor Walter Thiel

Karl-Ziegler-Lectureship 2010

Professor Scott E. Denmark

University of Illinois, Urbana-Champaign, USA

Workshop I, 3 May 2010: *Silicon-Based Cross-Coupling Reactions: Methodology, Synthesis and Mechanism*

Main Lecture, 4 May 2010*: Lewis Base Activation of Lewis Acids: A New Paradigm in Main Group Chemistry*

Workshop II, 5 May 2010: *Toward a Fundamental Understanding of Asymmetric Phase Transfer Catalysis*

Lecture course on catalysis, a four-semester program, 2008-2010

Ferdi Schüth *Basic Heterogeneous Catalysis* (10 - 26 August 2009, 22 h)

Manfred T. Reetz *Basic Biocatalysis* (31 May - 10 June 2010, 12 h)

Introduction into crystallography and X-ray powder diffraction methods

16-20 March 2009, 23-26 November 2010

Organizer: Dr. Claudia Weidenthaler

Workshop on microstructure analysis from powder diffraction data

9 - 11 November 2009

Organizer: Dr. Claudia Weidenthaler

Seminars of the Institute

In addition to poster sessions with 23-28 posters each, the following oral presentations were given:

Coordination chemistry at carbon
Dr. Manuel Alcarazo (Fürstner group)
Alternative pathways for conventional products
Dr. Regina Palkovits (Schüth group)
25 February 2009

Total synthesis of spirastrellolide F methyl ester
Stefan Benson (Fürstner group)
QM/MM studies on the reaction mechanism in molybdopterin containing enzymes
Sebastian Metz (Thiel group)
15 December 2009

Different routes to depolymerize cellulose
Jan Niklas Meine (Schüth group)
STRIP Catalyzed kinetic resolution of homoaldols via an intramolecular transacetalization – from an academic curiosity to useful applications
Steffen Müller (List group)
17 November 2010

Max-Planck Delegation at the 74th Annual Meeting of the Israel Chemical Society

8-9 February 2009
Organizer: Professor Benjamin List

Organocatalysis in Germany

Meeting of nation-wide DFG Priority Program (SPP1179) "Organocatalysis", sponsored by the German Research Foundation, Berlin, DE
4-5 December 2008
Conference Organizer: Professor Benjamin List

7.5.1 Symposia Organized by the Institute

International Symposium on Theoretical and Computational Chemistry

Colloquium on the Occasion of the 60th Birthday of Professor Dr. Walter Thiel

28 February – 2 March 2010

21 plenary lectures, 190 participants

28 February 2010

Professor Reinhart Ahlrichs (Karlsruhe Institute of Technology, DE)
Homoatomic clusters

Professor Martin Quack (ETH Zürich, CH)
The fundamental and approximate symmetries of space, time and matter and the dynamics of their violations in the spectroscopy and kinetics of molecules and clusters

Professor Gustavo Scuseria (Rice University, Houston, USA)
Constrained-pairing mean-field theory

Professor Sason Shaik (Hebrew University, Jerusalem, IL)
Is there anything new in electron-pair bonding? Charge-shift bonding and its manifestations

Professor Hans-Joachim Werner (Universität Stuttgart, DE)
Explicitly correlated local coupled-cluster methods: approaching the CCSD(T) basis set limit for enzyme reactions

1 March 2010

Professor Marcus Elstner (Karlsruhe Institute of Technology, DE)
Multi-scale methods for the investigation of biological structures and processes

Professor Jürgen Gauss (Johannes Gutenberg-Universität Mainz, DE)
Interplay of theory and experiment in rotational spectroscopy

Professor Jeremy N. Harvey (University of Bristol, UK)
Reactivity and selectivity in organic and biological chemistry: QM and QM/MM studies

Professor Martin Head-Gordon (University of California, Berkeley, USA)
Approximating CASSCF with increasingly perfect coupled cluster models for strong correlations -- perfect pairs, quadruples and hextuples

Professor Jürg Hutter (University of Zurich, CH)
Efficient and stable Hartree-Fock exchange in periodic systems

Professor William L. Jorgensen (Yale University, New Haven, USA)
QM/MM Simulations of organic and enzymatic reactions

Professor Hans Lischka (University of Vienna, AT)
On-the-fly non-adiabatic dynamics: program development and application to photochemical and photobiological simulations

Professor Christel Marian (Heinrich-Heine Universität Düsseldorf, DE)
Environment and substitution effects on the triplet generation in flavins

Professor Keiji Morokuma (Kyoto University, JP)
ONIOM Studies of photochemical processes and chemical reactions of biomolecular systems in proteins

Professor Frank Neese (Rheinische Friedrich-Wilhelms-Universität Bonn, DE)
Usages of theoretical spectroscopy

Professor Wilfred van Gunsteren (ETH Zürich, CH)
Force-field development for computer simulation of biomolecular systems: the GROMOS case

2 March 2010

Professor Michael Bühl (University of St. Andrews, UK)
Insights into uranyl(VI) chemistry from CPMD simulations

Professor Gernot Frenking (Universität Marburg, DE)
The chemistry of divalent carbon(0) compounds and heavier homologues – a challenge for theory and experiment

Professor Joachim Sauer (Humboldt Universität Berlin, DE)
Selective oxidation of C-H bonds by vanadium oxides – clusters in the gas phase and supported on SiO_2 and CeO_2

Professor Henry F. Schaefer (University of Georgia, Athens, USA)
From donor-acceptor complexes to gallium nitride nanorods

Professor Helmut Schwarz (Technische Universität Berlin, DE)
Oxidative dehydrosulfurization and selective bond activation by "roll-over" cyclometalated Pt(II) complexes: theory and experiment in concert

International Symposium on Organocatalysis ISOμ 2010

Meeting of nation-wide DFG Priority Program (SPP 1179) "Organocatalysis", sponsored by the German Research Foundation

14-17 July 2010

Conference Organization: Professor Benjamin List

14 July 2010

Reporting colloquium SPP1179 presented by:

Professor Thorsten Bach (Technische Universität München, DE)
Professor Albrecht Berkessel (Universität zu Köln, DE)
Professor Carsten Bolm (RWTH Aachen, DE)
Professor Stefan Bräse (Karlsruhe Institute of Technology, DE)
Tamilselvi Chinnusamy (Universität Regensburg, DE)
Professor Mathias Christmann (Technische Universität Dortmund, DE)
Professor Frank Glorius (Westfälische Wilhelms-Universität Münster, DE)
Professor Stefan Hecht (Humboldt-Universität zu Berlin, DE)
Professor Lukas Hintermann (Technische Universität München, DE)
Professor Jürgen Liebscher (Humboldt-Universität zu Berlin, DE)
Professor Rainer Mahrwald (Humboldt-Universität zu Berlin, DE)
Giuseppe Rulli (Friedrich-Alexander-Universität Erlangen-Nürnberg, DE)
Markus Schmid (Universität Regensburg, DE)
Professor Christoph Schneider (Universität Leipzig, DE)
Dr. Wolfgang Schrader (MPI für Kohlenforschung, Mülheim/Ruhr, DE)
Professor Peter Schreiner (Universität Giessen, DE)
Professor Armido Studer (Westfälische Wilhelms-Universität Münster, DE)
Professor Svetlana Tsogoeva (Friedrich-Alexander-Universität Erlangen-Nürnberg, DE)
Dr. Kirsten Zeitler (Universität Regensburg, DE)
Professor Hendrik Zipse (Ludwig-Maximilians-Universität München, DE)

15 July 2010

Professor Alexandre Alexakis (Université de Genève, CH)
Asymmetric conjugate addition of carbonyl compounds to unsaturated nitro, sulfone and phosphonate substrates

Professor Ken Houk (University of California Los Angeles, USA)
Computational modeling of mechanisms and stereoselectivities in organocatalysis

Professor Eric Jacobsen (Harvard University, USA)
Attractive, non-covalent interactions in organocatalysis

Professor Benjamin List (Max-Planck-Institut f. Kohlenforschung, DE)
Asymmetric Lewis acid organocatalysis

Professor David MacMillan (Princeton University, USA)
Photoredox catalysis in organic synthesis

Professor Keiji Maruoka (Kyoto University, JP)
Design of high-performance bifunctional organocatalysts

Professor Herbert Mayr (Ludwig-Maximilians-Universität München, DE)
Nucleophilic organocatalysis from a physical organic chemist's point of view

Professor Petri Pihko (University of Jyväskylä, FI)
A is for α-acroleins, B is for β-acroleins

Professor Yoshiji Takemoto (Kyoto University, JP)
Asymmetric catalysis with new hydrogen-bond donors

Professor Helma Wennemers (University of Basel, CH)
Peptides as asymmetric catalysts

Professor Hisashi Yamamoto (University of Chicago, USA)
Chiral Brønsted acid catalysis for asymmetric synthesis

Professor Shuli You (Shanghai Institute of Organic Chemistry, CN)
Asymmetric Friedel-Crafts alkylation reactions by chiral Brønsted acids

16 July 2010

Professor Takahiko Akiyama (Gakushuin University, Tokyo, JP)
Chiral Brønsted acid catalyzed asymmetric reactions

Professor Carlos Barbas (The Scripps Research Institute, San Diego, USA)
Organocatalysis: A pervasive catalytic approach

Professor Jeffrey Bode (University of Pennsylvania, Philadelphia, USA)
An enantioselective Claisen rearrangement catalyzed by chiral N-heterocyclic carbenes

Professor Yingchun Chen (Sichuan University, Chengdu, CN)
Asymmetric reactions catalyzed by Lewis basic amines

Professor Li Deng (Brandeis University, Waltham, MA, USA)
Asymmetric reactions with cooperative and multifunctional catalysis

Professor Gregory Fu (Massachusetts Institute of Technology, Cambridge, USA)
Asymmetric nucleophilic catalysis

Professor Matthew Gaunt (University of Cambridge, UK)
New catalytic strategies for chemical synthesis

Professor Yujiro Hayashi (Tokyo University, JP)
Organocatalytic and practical synthesis of Tamiflu

Professor Shu Kobayashi (University of Tokyo, JP)
Catalytic carbanion reactions: Formation and reactions of carbanions using catalytic amounts of bases

Professor Scott Miller (Yale University, New Haven, USA)
Asymmetric reactions catalyzed by amino acids and peptides

Professor Takashi Ooi (Nagoya University, JP)
Unique asymmetric catalysis of supramolecularly assembled chiral tetraaminophosphonium phenoxides

Professor Viresh Rawal (University of Chicago, USA)
Exploration of new scaffolds for hydrogen bonding catalysts

Professor Magnus Rüping (RWTH Aachen, DE)
Asymmetric metal-free catalysis – Concepts and applications

Professor Yian Shi (Colorado State University, Fort Collins, USA)
Progress on chiral ketone-catalyzed asymmetric epoxidation of olefins

Professor Masahiro Terada (Tohoku University, Sendai, JP)
Chiral phosphoric acids as versatile catalysts for enantioselective carbon-carbon bond forming reactions

17 July 2010

Professor Dieter Enders (RWTH Aachen, DE)
Asymmetric organocatalysis with proline and derivatives, Brønsted acids and N-heterocyclic carbenes

Professor Liu Zhu Gong (University of Science and Technology of China, Beijing, CN)
Organocatalytic three-component 1,3-dipolar cycloaddition reactions with azomethine ylides

Professor Karl Anker Jørgensen (Aarhus University, DK)
The organocatalytic-LEGO concept

Professor Paolo Melchiorre (Institute of Chemical Research of Catalonia, Tarragona, ES)
Unconventional reactivity profiles induced by chiral primary amine catalysis

Professor Vinod Singh (Indian Institute of Science, Bangalore, IN)
Enantioselective organocatalytic direct aldol reaction

Professor Tibor Soós (Hungarian Academy of Science, Budapest, HU)
Design and application of bifunctional metal-free catalysts: From epi-quinine thioureas to frustrated Lewis pairs

Professor Choong Eui Song (Sung Kyun Kwan University, Seoul, KR)
Self-association-free, acid-base bifunctional organocatalysts: Unprecedented catalytic activity and enantioselectivity

Professor Wei Wang (University of New Mexico, Albuquerque, USA)
New strategies in developing powerful enantioselective organocatalytic cascade reactions

Meeting of the Section "Fourier-transform mass spectrometry (FTMS)" of the German Society for Mass Spectrometry

2-3 September 2010

Organizer: Dr. Wolfgang Schrader

2 September 2010

Professor Helmut Schwarz (TU Berlin, DE)
Gasphasenkatalyse mit Atomen und kleinen Metallclustern

Dr. Jürgen Grotemeyer (Christian-Albrechts-Universität zu Kiel, DE)
Ungewöhnliche Fragmentierungen von Rhodaminen

Dr. Thomas Möhring (Thermo Fisher Scientific, Bremen, DE)
Accelerating spectral acquisition rate of Orbitrap mass spectrometry

Dr. Jürgen H. Gross (Universität Heidelberg, DE)
H/D-Austauschreaktionen von Peptid-Fragmenten in der Gasphase

Dr. Marianne Engeser (Universität Bonn, DE)
Mass spectrometric investigations of gold(I) N-heterocyclic carbene complexes

Dipl.-Ing. Monika Taucher (Universität Innsbruck, AT)
Identifizierung, Lokalisierung, und relative Quantifizierung von Pseudouridin in RNA mit Tandem-Massenspektrometrie von Hydrolyseprodukten

Professor Jan T. Andersson (Westfälische Wilhelms Universität Münster, DE)
Ultrahigh resolution mass spectrometric investigations on asphaltene deposits

Dr. Matthias Witt (Bruker Daltonik GmbH, Bremen, DE)
Analysis of gasoil by GC/APCI-FT-ICR mass spectrometry

Dr. Fabiane M. Nachtigall (Max-Planck Institut für Kohlenforschung, Mülheim/Ruhr, DE)
Metal ion extraction and derivatization as combined analytical tools to selectively characterize N-species in crude oils

MSc Sami Lababidi (Max-Planck-Institut f. Kohlenforschung, Mülheim/Ruhr, DE)
LC/FT-ICR MS Coupling for the investigation of nitrogen species in crude oil

Dr. Andras Gaspar (Helmholtz Zentrum München, DE)
Variously charged constituents in Suwannee River dissolved organic matter

Professor Ferdi Schüth (Max-Planck Institut für Kohlenforschung Mülheim/Ruhr, DE)
Speicherung von Energie – Eine Herausforderung an die Chemie

3 September 2010

Dr. Andreas Römpp (Justus Liebig Universität, Giessen, DE
Fourier transform mass spectrometry imaging of biological samples at cellular resolution

Yvonne Schober (Justus Liebig Universität Giessen, DE)
Accurate mass MALDI imaging - improving confidence in protein identification

Dr. Michael Mormann (Westfälische Wilhelms-Universität Münster, DE)
Infrared matrix-assisted laser desorption/ionization Fourier-transform ion cyclotron resonance mass spectrometry with a glycerol matrix for applications in proteomics, glycoproteomics and glycomics

Dipl.-Chem. Nicole Zehethofer (Forschungszentrum Borstel, DE)
Sensitive Lipidanalytik von biologischen Proben: Kopplung von chromatographischen Trennverfahren mit hochauflösender Massenspektrometrie

Dr. Andreas Springer (Freie Universität Berlin, DE)
Strukturaufklärung von Supramolekülen und Clustern

Marius Ionuț Iurașcu (Universität Konstanz, DE)
Structural characterization of ß-amyloid peptide and aggregates revealed by Fourier transform – ion cyclotron resonance and ion mobility mass spectrometry

Bogdan Bernevic (Universität Konstanz, DE)
The identification of postmortem pig muscle L. dorsi protein degradation by high resolution FT-ICR mass spectrometry

Professor Andrea Sinz (Martin-Luther-Universität Halle-Wittenberg, DE)
A novel cleavable cross-linker for protein structure analysis: reliable identification of cross-linking products by tandem MS

Presentation of the “Young Scientists Awards” Sponsored by Springer Publisher

7.6 List of Talks Given by Guests (2008-2010)

2008

15 January 2008	Professor Andy Phillips (University of Colorado, Boulder, USA) *From targets to strategies and back again: some examples from complex molecule synthesis*
30 January 2008	Dr. Ourida Saidi (University of Liverpool, UK) *Hydroformylation of functionalised olefins*
10 March 2008	Professor Wilhelm T. S. Huck (University of Cambridge, UK) *Adaptive surfaces using polymer brushes*
14 March 2008	Dr. Eric Kantchev (Institute of Bioengineering and Nanotechnology, Singapore, SG) *Highly active and versatile N-heterocyclic carbene-Pd coupling catalyst*
17 March 2008	Dr. Wei Chen (Dalian Institute of Chemical Physics, CN) *Catalytic behavior of metal nanoparticles confined inside carbon nanotubes*
18 March 2008	Professor Yao Zhang (Dalian Institute of Chemical Physics, CN) *Some complex hydrides studied in DICP*
19 March 2008	Professor Xinhe Bao (Dalian Institute of Chemical Physics, CN) *Catalysis chemistry of the confined nano systems*
28 April 2008	Professor Petra de Jongh (University of Utrecht, NL) *Synergy between catalytic and hydrogen storage materials*
14 May 2008	Professor Angeliki Lemonidou (University of Thessaloniki, GR) *Nanostructured Ni-Nb-O catalysts for the effective oxidative dehydrogenation of ethane to ethylene*
19 May 2008	Professor Ole M. Lovvik (University of Oslo, NO) *First principles modelling of materials for solid state hydrogen storage*
21 May 2008	Dr. Takafumi Ueno (Nagoya University, JP) *Coordination design of artificial metalloproteins using protein vacant species*
23 May 2008	Dr. Petri Pihko (Helsinki University, FI) *Adventures in selective catalysis*

26 May 2008	Kamalakannan Kailasam (Universität Stuttgart, DE) *Synthesis and characterization of alkyl-grafted MCM-41 silica spheres*
30 May 2008	Professor Dongyuan Zhao (Fudan University, Shanghai, CN) *Large-scale synthesis of ordered mesoporous carbon molecular sieves and their applications*
5 June 2008	Kerstin Nowak (Sloning BioTechnology GmbH, Puchheim, DE) *A new quality level in tailoring genetic diversity for protein engineering*
13 June 2008	Dipl.-Chem. Ilija Coric (University of Zagreb, HR) *Synthesis of resveratrol-biotin conjugate*
17 June 2008	Dr. Polly L. Arnold (University of Edinburgh, UK) *Reduction and activation reactions in organometallic f-block complexes*
7 July 2008	Professor Chun-Hua Yan (Peking University, CN) *Synthesis and properties of rare earth nanocrystals*
23 July 2008	Professor Nigel G. J. Richards (University of Florida, USA) *Hybrid DFT studies of Mn(II)-dependent oxalate-degrading enzymes*
14 August 2008	Dr. Karl Mayrhofer (TU München, DE) *Electrocatalysis of low-temperature fuel cell reactions*
20 August 2008	Professor Gérard Férey (Institut Lavoisier Versailles, FR) Alexander von Humboldt Laureate *Hybrid porous solids: A new world*
25 August 2008	Professor Jochen Büchs (RWTH Aachen, DE) *Don't miss your best hit – Novel approaches to control protein expression*
27 August 2008	Professor Gérard Férey (Institut Lavoisier Versailles, FR) Alexander von Humboldt Laureate *A strange behavior in solid-state sciences: The breathing effect*
24 September 2008	Professor David Cole-Hamilton (University of St. Andrews, Scotland, UK) *Highly selective syntheses of linear esters, amides and amines using homogeneous catalysis*

24 September 2008	Dr. Arne Thomas (MPI für Kolloid- und Grenzflächenforschung, Golm, DE) *Porous materials: From hard to soft functional frameworks*
10 October 2008	Dipl.-Chem. Marcus Fischer (TU Kaiserslautern, DE) *2,2'-Ditriazolyl-1,1'-binaphtyl, a new ligand for enantioselective catalysis*
16 October 2008	Professor Tohru Fukuyama (University of Tokyo, JP) *Total synthesis of natural products and development of synthetic methodologies*
16 October 2008	Dipl.-Ing. Robert Güttel (TU Clausthal, DE) *Monolithische Wabenkörper in der Fischer-Tropsch-Synthese*
28 October 2008	Dr. Markus Mreyen (Shimadzu Europa GmbH, Duisburg, DE) *Discover the unknown – Charakterisierung von Substanzen mittels LCMS*
29 October 2008	Dr. Sam de Visser (University of Manchester, UK) *The mechanism of oxygen activation of L-arginine by nitric oxide synthase enzymes, a theoretical study*
2 December 2008	Dr. Nuno Maulide (Catholic University of Louvain, BE and Stanford University, USA) *New strategies for the construction of ring systems: from orthoesters to transition metals*
10 December 2008	Dr. Michal Michalak (CNRS-Ècole Polytechnique, Palaiseau, FR) *Total synthesis of terpenoids with cyclopentacyclooctane carbon skeleton*

German Chemical Society (GDCh), Ruhr Section

10 April 2008	Professor Uwe Bornscheuer (Universität Greifswald, DE) *Solving organic synthesis problems with modern biocatalysis tools: Examples for the development of highly enantioselective enzymatic reactions*
19 June 2008	Professor A. Greiner (Universität Marburg, DE) *Elektrogesponnene Polymer-Nanofasern – eine Spielwiese für Chemiker, Physiker, Biologen, u.v.a.*
9 October 2008	Professor Klaus-Peter Dinse (TU Darmstadt, DE) *High frequency EPR in material sciences and catalysis*

20 November 2008 Professor Rolf Müller (Universität des Saarlandes, Saarbrücken, DE)
Biotechnology of myxobacteria – promising resources for novel bioactive natural products

27 November 2008 Professor Christian Hertweck (Universität Jena, DE)
Exploring and engineering polyketide diversity in microorganisms

2009

14 January 2009 Blanca Ines Tejedor (Universidad del Pais Vasco, Leioa, Bizkaia, ES)
New insights in the chemistry of palladium pincer complexes towards tailor-made efficient, sustainable catalysts

21 January 2009 Dr. Yewen Fang (Université Louis Pasteur de Strasbourg, FR)
Syntheses of exo-cyclic ethers via copper-catalyzed intramolecular O-vinylation

21 January 2009 Professor Siegfried R. Waldvogel (Universität Bonn, DE)
Oxidative coupling reaction of arenes – from innovative concepts to novel detection principles for explosives

28 January 2009 Dr. Vivek Tukaram Khedkar (MPI für molekulare Physiologie, Dortmund, DE)
New catalytic reaction strategies for compound collection synthesis

28 January 2009 Professor Ulrich Schwaneberg (Jacobs Universität Bremen, DE)
Steering directed evolution: from strategies managing the combinatorial complexity of mutant libraries over understanding of structure-function relationships to reengineering of protein functions

30 January 2009 Viviane Valerio (University of Rome "La Sapienza", IT)
Design and synthesis of benzamide derivatives as inhibitors of histone deacetylases

5 February 2009 Professor Helge Willner (Bergische Universität Wuppertal, DE)
Weakly coordinating anions. From academic curiosity to industrially important compounds

11 February 2009	Johannes Kloesges (University of Oxford, Oriel College, UK) *Novel asymmetric synthesis of terminal aziridines*
11 February 2009	Samir El Hajjaji (University of Nottingham, UK) *Asymmetric metal-catalysed methyl addition to imines with chiral phosphine ligands*
18 February 2009	Dr. Claire Madelaine (ICSN, Gif-sur-Yvette, FR) *Oxidation of aminocyclopropanes prepared via the Kulinkovich-de Meijere reaction*
20 February 2009	Dr. Than Binh Nguyen (University of Maine, Le Mans, FR) *New methodology development of dipolar cycloaddition of nitrones*
25 February 2009	Frédéric Frébault (University of Birmingham, UK) *The total synthesis of brevianamide B and malbrancheamide B and progress towards the stephacidin A*
2 March 2009	Professor Helma Wennemers (Universität Basel, CH) *The many different faces of peptides – from supramolecular assemblies to asymmetric catalysis*
11 March 2009	Dr. Subhrangsu Roy (University of York, UK) *Enantioselective total synthesis of bioactive epoxyquinoid natural products*
25 March 2009	Denis Chusov (A.N. Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Science, Moscow, SU) *Synthesis and application of new binuclear asymmetric catalysts*
26 March 2009	Nico Erdmann (Universität Gießen, DE) *New reaction pathways to swainsonine derivatives*
27 March 2009	Thomas Fenlon (St. John's College, University of Oxford, UK) *Studies towards the biomimetic synthesis of (±)-lindenatriene and related natural products*
31 March 2009	Professor Michael Müller (Universität Freiburg, DE) *From biosynthesis to drug synthesis: conceptual design of chemoenzymatic strategies*
1 April 2009	Dr. Yan Xiong (University College Dublin, IE) *Amino-catalysis in asymmetric carbon-carbon bond formation reactions*

3 April 2009	Guillaume Bordeau (Université Pierre et Marie Curie, Paris, FR) *New triarylamine-based two-photon absorbing fluorophores for microscopy and photovoltaic devices*
3 April 2009	Dr. Subhrangsu Roy (University of York, UK) *Enantioselective total synthesis of bioactive epoxyquinoid natural products*
15 April 2009	Dr. Kamil Weinberg (Technical University of Lodz, PL) *Azasugar adventures, heterocyclic highlights*
20 April 2009	Louay Alsamman (Ruhr-Universität Bochum, DE) *Synthesis and analytical study of new type of compounds [precursor]@MOF*
20 April 2009	Professor Antonio Garcia (Arizona State University, Tempe, USA) *Control of aqueous fluid drops using superhydrophobic surfaces: Some technological applications in medicine and nanomaterials manufacturing*
22 April 2009	Mohamed El-Shazly (Jacobs Universität, Bremen, DE) *Chiral amine synthesis with significantly enhanced stereoselectivity*
28 April 2009	Mario Soorholtz (Universität Oldenburg, DE) *Basenkatalysierte Aldolkondensation von linearen Aldehyden in der Flüssigphase*
6 May 2009	Fikr Sen (Technische Universität Clausthal, DE) *Auswertung reaktionskinetischer Messungen an einem konventionellen und neuartigen Dampfreformerkatalysator*
12 May 2009	Professor Bernard Offmann (Université de la Réunion, Saint Denis, FR) *A mixed in vitro/in silico approach for identifying combination of single point amino acid substitutions with improved fitness*
13 May 2009	Xavier Bugaut (Institut de Chimie des Substances Naturelles ICSN, Gif-sur-Yvette, FR) *Palladium-catalyzed cross-couplings of potassium (Z)-2-chloroalk-1-enyl trifluoroborates / Approach of the total synthesis of the aglycone of landomyin A*

15 May 2009	Ana Aljarilla Jiménez (University of Madrid, ES) *New norbornene derivatives as chiral building blocks. Application in metathesis reactions*
20 May 2009	Nicolas Demoulin (Institut de Chimie des Substances Naturelles ICSN, Paris, FR) *Total synthesis of ecteinascidins and analogs*
28 May 2009	Professor Michael J. Krische (University of Texas at Austin, USA) *Formation of C-C bonds via catalytic hydrogenation and transfer hydrogenation*
29 May 2009	Alexander Zhdanko (Moskow State University, SU) *Recent research in the Ugi-related chemistry*
3 June 2009	Alberto Martinez Cuezva (University of Burgos, ES) *Brønsted acid-catalyzed nucleophilic substitution reactions of alcohols*
3 June 2009	Marco Luparia (University of Pavia, IT) *Development of the gold(I)-catalyzed enantioselective cycloaddition of munchnones with electron-deficient alkenes*
5 June 2009	Aron Wosylus (Max-Planck-Institut für chemische Physik, Dresden, DE) *Phase transitions in silicon and germanium networks: Synthesis and in-situ characterization at elevated pressures and temperatures*
5 June 2009	Thierry Jousseaume (Institut de Chimie des Substances Naturelles, CNRS at Gif Sur Yvette, FR) *Studies toward the synthesis of (-)-gymnodimine*
10 June 2009	Manuel Hamburger (Technische Universität Darmstadt, DE) *Polyquinoxalines: stereoregular, helically chiral backbone for biaryl-organocatalysts*
12 June 2009	Matthew Webber (Imperial College London, UK) *Towards the total synthesis of (–)-euonyminol*
16 June 2009	Professor Tamás Ungár (Eötvös University Budapest, HU) *Microstructure in terms of crystallite size, microstrain and planar defects from X-ray line profile analysis*

17 June 2009	Professor Karl A. Scheidt (Northwestern University, Evanston, Illinois, USA) *New discoveries with carbene catalysis*
19 June 2009	Raphael Rahmani (Institut des Sciences Moleculaire de Marseille, FR) *Synthesis of polycylic spirolactones using a Diels-Alder reaction*
26 June 2009	Georgy Varseev (Universität Tübingen, DE) *Total synthesis of the natural products (±)-symbioimine, (+)-neosymbioimine and formal synthesis of platencin*
29 June 2009	Professor Huimin Zhao (University of Illinois, USA) *Surfing the third wave of biotechnology: Turning trash into cash*
2 July 2009	Professor Ajayan Vinu (National Institute for Materials Science, Ibaraki, JP) *Novel nanoporous materials with multiple functions*
2 July 2009	Felix Richter (TU München, DE) *Synthesis and characterization of crosslinked PHPMA gel-nanoparticles*
2 July 2009	Kristina Pupovac (Heinrich-Heine-Universität Düsseldorf, DE) *Pyrazoles as bichromophores*
3 July 2009	Dr. Joyram Guin (University of Geneva, CH) *Intermolecular radical hydroamination, carbene-catalyzed oxidations of aldehydes and cationic helicenes in asymmetric synthesis*
6 July 2009	Professor Julius Rebek (The Scripps Research Institute, La Jolla, USA) *The inner space of molecules*
7 July 2009	Rahime Cinar (Heinrich-Heine-Universität Düsseldorf, DE) *Synthesis of quinoline derivates*
8 July 2009	Chaoqun Li (University of Liverpool, UK) *Highly enantioselective synthesis of amines by asymmetric hydrogenation*
30 July 2009	Professor Bert D. Chandler (Trinity University, San Antonio, Texas, USA) *Dendrimer templates for new Au and Au-based heterogeneous catalysts*

18 August 2009	Dr. Jevgenij Raskatov (Tokyo Institute of Technology, JP) *Physical organic studies of chiral ion pairing for asymmetric catalysis*
19 August 2009	Professor Detlef Bahnemann (Leibniz Universität Hannover, DE) *Reductive photocatalytic synthesis: Efficient generation of complex organic compounds and molecular hydrogen*
21 August 2009	Dipl.-Chem. Sabrina Bremer (Universität Heidelberg, DE) *On-column reaction chromatography and electrophoresis – A unified tool to investigate reaction mechanisms*
25 August 2009	Dipl.-Chem. Daniel Schunk (Universität Duisburg-Essen, DE) *Metallic nanoparticles in mesoscopic systems*
28 August 2009	Professor Nobuyuki Nishimiya (Nihon University, JP) *Solidification of hydrogen for energy carrier using alloy hydrides, mesoporous materials and nanomaterials with high specific surface area*
28 August 2009	Jérôme Clerc (Chemical Genomics Centre of the Max-Planck Society, Dortmund, DE) *Synthesis and biological evaluation of syringolins*
8 September 2009	Dr. Annika Bande (University of Kyoto, JP) *Quantum Monte Carlo methods*
8 September 2009	Jennifer N. Reece (Purdue University, West Lafayette, USA) *Reactivity studies of pyridine-based tetraradicals*
21 September 2009	Anna Kulik (Universität Braunschweig, DE) *Katalysatoren für die Oxidation von Alkoholen*
25 September 2009	Chuanbo Gao (University of Stockholm, SE) *Mesoporous materials: Synthesis, formation mechanism and application in drug delivery*
7 October 2009	Dr. Horst Puschmann (Durham University, Durham, UK) *Olex2 – Ein Programmsystem zur Lösung, Verfeinerung und Darstellung von Kristallstrukturen*
8 October 2009	Professor Makoto Ogawa (Waseda University, Tokyo, JP) *Functional hybrid materials based on layered materials*
14 October 2009	Xingyu Wang (Technische Universität München, DE) *Controlled growth of ultralong single walled carbon nanotubes array under electric field*

16 October 2009	Dr. Mario Barbatti (Universität Wien, AT) *Dynamics of photoactivated molecules and materials: What simulations can tell us*
21 October 2009	Dr. Grigory Lazarev (LMU München, DE) *Laser interference microscopy for precise surface characterization*
26 October 2009	Qiong Tong (Universität Konstanz, DE) *Nanoscale polymer crystals*
29 October 2009	Dr. Tibor Soós (Hungarian Academy of Sciences, Budapest, HU) *Bifunctionality as a key concept in metal-free synthetic method developments*
9 November 2009	Dr. Matteo Leoni (Department of Materials Engineering and Industrial Technologies, University of Trento, IT) *Evaluation of microstructure properties of solids from powder diffraction data*
10 November 2009	Professor Philippe Sautet (Université de Lyon, Institut de Chimie de Lyon, FR) *Modeling active sites and mechanisms in heterogeneous catalysis*
24 November 2009	Dr. Peter Nussbaumer (Lead Discovery Center GmbH, Dortmund, DE) *Labelled natural products by cross-metathesis reaction and their applications*
25 November 2009	Dr. Florence Collet (Institut de Chimie des Substances Naturelles ICSN - Gif-sur-Yvette, FR) *Stereoselective catalytic nitrene transfer: Intermolecular C-H amination, imination of sulfides and application to the synthesis of N-acetylcolchinol analogues*
7 December 2009	Ivy Lim (TU München/BASF Ludwigshafen, DE) *Aliphatic polycarbonates*
9 December 2009	Dr. Eszter Takács (University of Pannonia, Veszprém, HU) *Application of aminocarbonylation in the synthesis of new steroidal compounds*
11 December 2009	Leticia Espinosa Alonso (Utrecht University, NL) *Space and time resolved spectroscopy during the preparation of hydrogenation catalyst bodies*

German Chemical Society (GDCh), Ruhr Section

2 April 2009	Professor Matthias Drieß (TU Berlin, DE) *Silylenes in concert for catalysis and more*
7 May 2009	Professor Dietmar Stalke (Universität Göttingen, DE) *What synthetic chemists learn from experimental charge densities*
14 May 2009	Professor Klaus Gerwert (Ruhr-Universität Bochum, DE) *From protein reactions mechanisms towards protein networks*
2 July 2009	Professor Mario Thevis (DSHS Köln, DE) *Detection of new drugs and methods of doping*
15 October 2009	Professor Carsten Schmuck (Universität Duisburg-Essen, DE) *What have anion sensors, enzyme inhibitors and nanoparticles in common? Interacting molecules*
19 November 2009	Professor Lukas J. Gooßen (TU Kaiserslautern, DE) *New catalytic transformations - On the way to "dream reactions"*
26 November 2009	Professor Carsten Strohmann (TU Dortmund, DE) *From structure formation principles and reactivity of organolithium compounds to chiral reagents*

2010

7 January 2010	Carolina Neudeck (TU München, DE) *Green routes for preparation of functional nanoparticles*
8 January 2010	Dr. Helena Kaper (Institute de Chimie Séparative de Marcoule, FR) *Synthesis of nanostructures in ionic liquids*
13 January 2010	Professor Sir John Meurig Thomas (University of Cambridge, UK) *Exploring the interface between heterogeneous and homogeneous catalysis*
22 January 2010	Dr. Shutian Zhou (Technical University of Denmark, Lyngby, DK) *Acetylene selective hydrogenation over new intermetallic compounds*

26 January 2010	Dr. Walter Heckmann (BASF, Ludwigshafen, DE) *Das Elektronenmikroskop als analytisches Instrument in der angewandten Polymerforschung*
3 February 2010	Rafik Rajjak Shaikh (University of Camerino, IT) *Synthesis of 3-substituted indoles via alkylideneindolenine intermediates generated from arylsulfonylalkyl indoles*
3 February 2010	Dr. Guodong Wen (Dalian Institute of Chemical Physics, Dalian, CN) *Direct conversion of cellulose into hydrogen by aqueous-phase reforming process*
3 February 2010	Dr. Róbert Rémiás (University of Szeged, HU) *Study of Pt/SBA-15, Rh/SBA-15 and Ni/C catalysts in a model hydrogenation reaction*
5 February 2010	Dr. Célia Brancour (Université Pierre et Marie Curie, Paris, FR) *Platinum(II)-catalyzed cycloisomerization and [5+1]-cycloaddition reaction of enynes*
10 February 2010	Davide Audisio (Université Paris-Sud, FR) *Synthesis of simplified denoviose compounds related to novobiocin as potential inhibitors of heat shock protein 90 (Hsp90)*
19 February 2010	Dr. Eugen S. Andreiadis (Ecole Nationale Supérieure de Chimie de Paris, FR) *Tetrazole-based luminescent architectures: from monometallic lanthanide to polymetallic iridium-lanthanide complexes*
22 February 2010	Rui Carvalho (Instituto Superior Técnico, Lisbon, PT) *1. Peroxidative oxidation of alkanes, 2. Extraction and synthetic applications of naturally occurring labdanolic acid*
1 March 2010	Christine Minke (TU Clausthal, DE) *Weiterentwicklung von Cobalt-Katalysatoren für die Fischer-Tropsch-Synthese*
2 March 2010	Dr. Andras Gaspar (Institut für Ökologische Chemie, Helmholtz Zentrum München, Neuherberg, DE) *Unravelling the interactions of boron with natural organic matter (NOM) on a molecular level*
2 March 2010	Professor Michael Filatov (University of Groningen, NL) *Theoretical studies on molecular motors*

3 March 2010	Bora Karasulu (Koc University, Istanbul, TR) *Reaction path analysis of histone demethylation process of histone tails using QM and QM/MM methods*
10 March 2010	Dr. Gilles Galvani (Université Paris-Sud XI, FR) *An approach towards a convergent asymmetric synthesis of Leustroducsin B via an asymmetric nitroso Diels-Alder reaction and some unexpected chemistry of 1,2-oxazines*
7 April 2010	Dr. Wen Yang (MPI für Kolloid- und Grenzflächenforschung, Golm, DE) *Using ionic liquids and nucleobase as precursors for highly nitrogen-doped carbon materials and their application in oxygen reduction*
12 April 2010	Dr. İlknur Kayacan (Gazi University, Ankara, TR) *Production of sodium borohydride by hydrogenation of anhydrous borax at high temperature and pressure in the presence of the magnesium*
13 April 2010	Andranik Kazaryan (Rijksuniversiteit Groningen, NL) *An ensemble DFT method and its applications in photochemistry*
15 April 2010	Dr. Vadim Korotkov (RWTH Aachen, DE) *Catalytic insertions into the cyclopropane ring. Syntheses of various belactosin C congeners and analogues*
21 April 2010	Dr. G. Gopakumar (Vrije Universiteit Amsterdam, NL) *Computational studies on oxidation catalysis by metaloxo systems*
22 April 2010	Eliot Boulanger (Université Catholique de Louvain, Louvain-la-Neuve, BE) *A dipole-field/QM approach to inductive effects*
26 April 2010	Alexandre Barthelme (École Nationale Supérieure de Chimie de Mulhouse, Université de Haute-Alsace, FR) *Research participations in organic synthesis*
28 April 2010	Professor Bruce H. Lipshutz (University of California, Santa Barbara, USA) *Need to make a bond? Try in water @ RT*
28 April 2010	Jan Goetze (Universität Potsdam, DE) *Structure/spectra relationship in BLUF and the RuBisCO carbon isotope effect*

29 April 2010	Igor D. Jurberg (Laboratoire de synthèse organique, Ecole Polytechnique, FR) *Unusual approach to branched 3-alkynylamides and development of new Au(I)-mediated transformations*
12 May 2010	Quentin A. Huchet (University of Oxford, UK) *Studies toward the total synthesis of (±)-frondosin B*
18 May 2010	Dr. Katja Hübel (MPG EU-Regionalbüro Rhein-Ruhr, Max-Planck-Institut für molekulare Physiologie, Dortmund, DE) *The Marie-Curie actions*
19 May 2010	Professor Suzanne A. Blum (University of California - Irvine, USA) *Lights... Camera... Catalysis! Single-molecule tools & novel synthetic methods*
26 May 2010	Dr. Vitalie Stavila (Sandia National Labs, Livermore, CA, USA) *Factors affecting hydrogen release and absorption in complex metal hydrides*
31 May 2010	Dr. Thanh Tung Dang (Université Paul Sabatier, Toulouse, FR) *Regioselective palladium-catalyzed cross-coupling, C-H allylic amination and alkoxylation reactions*
9 June 2010	Claudia Loerbroks (Universität Marburg, DE) *The reaction mechanism of an unusual alkyne nitrile metathesis*
10 June 2010	Sofia Mariana Riaño Torres (National University of Colombia, Bogotá, CO) *Oxidative cleavage of vic-diols catalyzed by manganese (III) complexes in ionic liquids*
14 June 2010	Dr. Céline Réthoré (Institut für Organische Chemie des Karlsruher Instituts für Technologie, DE) *Organic conductors, asymmetric catalysis and molecular frameworks*
15 June 2010	Wojciech Supronowicz (Universität Oldenburg, DE) *Isomorphous substitution of Si atoms in porous silicates*
17 June 2010	Thorsten vom Stein (RWTH Aachen, DE) *Catalytic biomass conversion*

22 June 2010	Dr. Mehmet Ali Celik (Universität Marburg, DE) *Is it gold click chemistry? Quantum chemical study on the formation of C-bound (1,4-triazolato) gold(I) derivatives: A gold mediated Huisgen [3+2] cycloaddition*
23 June 2010	Professor Helmut Schwab (University of Technology, Graz, AT) *Converting enzyme function and enantioselectivity of enzymes*
23 June 2010	Dr. Daan Gercke (Freie Universität Amsterdam, NL) *Polarizable biomolecular force field development*
1 July 2010	Dr. Thomas E. Storr (University of York, UK) *Direct arylation approach to highly fluorescent purine nucleoside analogues*
2 July 2010	Desislava Petkova (Sofia University St. Kliment Ohridski, Faculty of Chemistry, BG) *I. Synthesis of polysubstituted 3,4-dihydroisocoumarins. II. Synthesis and physico-chemical properties of guanidinium- based ionic liqiuds*
5 July 2010	Dr. Luca Pretali (University of Pavia, IT) *Photosubstitution and photofragmentation reaction, the versatility of (hetero)aromatics*
7 July 2010	Dr. Valeria Tagliazucca (University of Trento, IT) *Nanostructured hybrid organic/inorganic materials by the nanobuilding block (NBB) approach*
12 July 2010	Alice Ghidini (Department of Organic and Industrial Chemistry, Parma, IT) *Functionalized cyclodextrins with positively charged groups in position 6: Synthesis and applications in fluorescence and electrophoresis analysis*
12 July 2010	Dr. Martin Korth (University of Cambridge, UK) *Accurate thermochemistry with fixed node diffusion Monte Carlo*
12 July 2010	Dr. Mika Lindén (Abo Akademi, Turku, FN) *Mesoporous silica nanoparticles for cell specific targeting and drug delivery*
12 July 2010	Dr. Andreas Kuschel (Universität Konstanz, DE) *Mesoporous organosilica materials with tuneable architecture*

12 July 2010	Dr. Heqing Jiang (Leibniz Universität Hannover, DE) *Coupling of energy/environment related reactions in perovskite catalytic membrane reactors*
13 July 2010	Dr. Kevin Jones (Cardiff University, UK) *A novel metal-free dihydroxylation procedure*
13 July 2010	Ali Younes (University of Rennes, FR) *Total synthesis of alkaloids derivative - An electrochemical approach*
14 July 2010	Matthias Heyden (Ruhr-Universität Bochum, DE) *Water seen through THz glasses: Picosecond dynamics and THz vibrational modes in water and aqueous solutions*
23 July 2010	Marcus Rose (TU Dresden, DE) *Novel nanoporous organic framework materials*
28 July 2010	Céline Joie (Université catholique de Louvain, BE) *Development of the cycloaddition [4+1] between dienes and ylides*
10 August 2010	Dr. Claudio Pirovano (University of Milano, IT) *Design of nanostructured catalysts for efficient transformations*
11 August 2010	Manuel Mahlau (Institut für Organische Chemie und Biochemie der Universität Freiburg, DE) *Synthetic studies towards the enantioselective total synthesis of arizonin C1*
16 August 2010	Emmanouil Passas-Lagos (Technische Universität Darmstadt, DE) *Investigations of organics oxidation on thermally prepared IrO_2 based dimensionally stable anodes*
20 August 2010	Caroline Souris (Pharmaceutical Chemistry and Pharmacy, University of Chatenay-Malabry, Paris, FR) *Scaffolds obtained by photocycloaddition and their application in library synthesis*
24 September 2010	Kiril Dimitrov (University of Chemical Technology and Metallurgy, Sofia, BG) *Electromagnetic shielding - challenging field for new materials development*

24 September 2010	Dr. Mehmet Zahmakiran (Middle East Technical University, Ankara, Turkey, TR) *Nanoparticle catalysis*
29 September 2010	Jenna Head (University of Edinburgh, UK) *Methodology development for C-H activation of indoles, pyrroles, and anilines via benzyne addition*
30 September 2010	Professor Kizashi Yamaguchi (Osaka University, JP) *Historical review of the development of broken-symmetry methods for open-shell systems at Osaka University*
1 October 2010	Professor Michinori Suginome (Kyoto University, JP) *Organic synthesis toward/with polyarenes: Boron-masking strategy for the iterative cross-coupling and chirality - switchable chiral polymer ligand for asymmetric synthesis*
7 October 2010	Sebastian Klimczyk (Ruhr-Universität Bochum, DE) *Palladium-catalyzed arylations of cyclopentadiene derivatives*
8 October 2010	César Solorio Alvarado (Institut Català d'Investigació Química, Tarragona, ES) *Gold and palladium-catalyzed synthesis of novel polycyclic aromatic hydrocarbons*
5 November 2010	Professor Guy Bertrand (University of California, Riverside, USA) *Novel families of carbon ligands, novel catalytic reactions*
15 November 2010	Professor Scott A. Snyder (Columbia University, New York, USA) *Lessons in chemoselectivity: Total synthesis of polyphenolic natural products*
16 November 2010	Professor Martin U. Schmidt (Johann Wolfgang Goethe-Universität, Frankfurt, DE) *Pair-distribution function analyses of nanocrystalline organic compounds*
22 November 2010	Professor Bettina Lotsch (Ludwig-Maximilians-Universität, München, DE) *Chemistry in diminishing dimensions: functional nanostructures for sensing and energy conversion*
30 November 2010	Professor Zhang-Jie Shi (Peking University, CN) *Transition-metal catalyzed C-O/H activation*

7 December 2010	Dr. Na Ji (Dalian Institute of Chemical Physics, CN) *Catalytic conversion of cellulose into ethylene glycol over tungsten carbide catalyst*
16 December 2010	Professor Susanne Ullrich (University of Georgia, Athens, USA) *The photoprotective properties of adenine: Fs time-resolved photoelectron spectroscopy at different excitation wavelengths*

German Chemical Society (GDCh), Ruhr Section

4 March 2010	Professor Thomas J. J. Müller (Heinrich-Heine-Universität Düsseldorf, DE) *Transition metal catalysis as an entry to multicomponent synthesis of heterocycles*
29 March 2010	Professor Gerald Henkel (Universität Paderborn, DE) *Bis-guanidines and guanidin-thiolate-hybrides - Ligands with biomimikry-potential*
10 June 2010	Dr. Heiner Jendralla (Sanofi-Aventis, Frankfurt, DE) *Industrial scale enantioselective synthesis of a 1,3-aminoalcohol with three chiral centres. Unprecedented four-component Mannich reaction with crystallization-driven dynamic resolution*
24 June 2010	Professor Holger Braunschweig (Universität Würzburg, DE) *Borylene complexes as reagents in organic and organometallic synthesis*
1 July 2010	Professor Carsten Bolm (RWTH Aachen, DE) *Ligand effects in metal catalysis*
19 August 2010	Professor Yitzhak Apeloig (Technion, Haifa, IL) *Recent studies on low-coordination silicon compounds. Multiple bonds, metallosilanes and silyl radicals*
16 September 2010	Professor Judith A. K. Howard (University Durham, UK) *Structure-property relationships explored by diffraction methods*
4 November 2010	Professor Martin Winter (Universität Münster, DE) *State of the art and future scenarios of large lithium-ion-batteries*

7.7 Local Activities of the Young Chemists Forum (JCF) of the German Chemical Society (GDCh)

List of Talks Given by Guests

24 January 2008	Professor Dieter Jahn (BASF, Ludwigshafen, DE) *"Young chemists meet industry": BASF – The chemical company*
7 February 2008	Dr. Helmut Haning (Bayer HealthCare, Wuppertal, DE) *"Young chemists meet industry": Chemie als Innovationstreiber in der Pharmaforschung*
29 April 2008	Dr. Henning Priepke (Boehringer Ingelheim Pharma, Ingelheim am Rhein, DE) *"Young chemists meet industry": Structure based design of coagulation inhibitors*
15 May 2008	Professor Klaus Müller and Dr. Willy Kinzy (F. Hoffmann-La Roche, Basel, CH) *"Young chemists meet industry": How fit for Roche?*
12 June 2008	Dr. Gerda Grund and Dr. Guido Streukens (Evonik Degussa, Marl, DE) *"Young chemists meet industry": Intelligente Technologie sichert effiziente Verfahren für Jahre*
4 December 2008	Dr. Dirk Seinsche (Landeskriminalamt Nordrhein-Westfalen, Düsseldorf, DE) *Chemie und Kriminaltechnik*
23 January 2009	Dr. Rainer Bürstinghaus (BASF, Ludwigshafen, DE) *Industrial research projects: Challenges for young chemists*
29 May 2009	Dr. Carsten Schaffer and Dr. Horst Höbenreich (Merck, Darmstadt, DE) *Fascinating fields for flexible scientists – In-house consulting*
23 June 2009	Dr. Johannes Panten (Symrise, Holzminden, DE) *Fascinating fields for flexible scientists: Current trends in the evaluation of novel aroma molecules*
22 October 2009	Dr. Matthias Lamm (AREVA NP, Erlangen, DE) *Fascinating fields for flexible chemists: AREVA - Solutions for the world's great energy challenges*
12 November 2009	Dr. Helga Neidlein (Gille Hrabal Struck Neidlein Prop Roos – German and European Patent and Trademark Attorneys, Düsseldorf, DE)

	Intellectual property law – A fascinating field for flexible scientists
14 December 2009	Dr. W. Klotzbücher (MPI for Bioanorganic Chemistry, Mülheim/Ruhr, DE) *Die Energien der Zukunft*
24 March 2010	Dr. Michael Paul (hte, Heidelberg, DE) *"My first year in industry": Bridging the gap between lab and business – The Chemist as business development manager*
9 April 2010	Professor Thomas Müller-Kirschbaum (Henkel, Düsseldorf, DE) *Performance based on sustainability: How researchers develop sustainable innovations*
17 June 2010	Dr. Sonja Grothe (Sachtleben Chemie, Duisburg, DE) *Great solutions with small particles*
29 July 2010	Dr. Sven K. Weber (Merck, Darmstadt, DE) *"My first year in industry" as an analytical chemist at Merck KGaA*
30 September 2010	Dr. Jörg-Joachim Nitz, Dr. Jens Döring and Dr. Jörg Sauer (Evonik Industries, Marl, DE) *"My first year in industry": Process and technology development at Evonik*
16 December 2010	Dr. Asif Karim (Mannheim, DE) *Moleküle aus Luft gebaut*

Other Activities

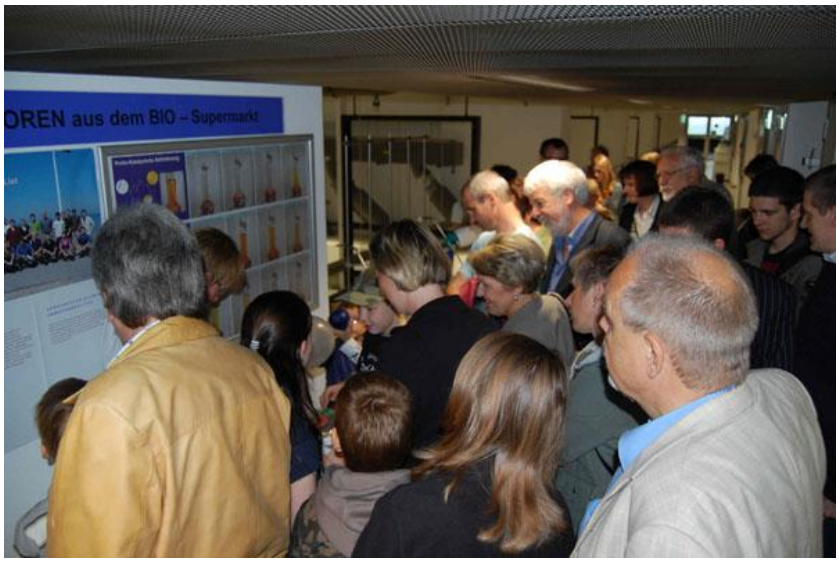
11-14 March 2009	11th JCF Frühjahrssymposium (Universität Duisburg/Essen, DE) *The symposium was organized by the JCFs of Bochum, Essen, Mülheim and Dortmund.*
30 June 2009	3rd Annual Summer Barbecue (MPI für Kohlenforschung, Mülheim, DE)
29 July 2010	4th Annual Summer Barbecue (MPI für Kohlenforschung, Mülheim, DE)
9 September 2010	1st 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, Essen, Mülheim and Dortmund.*

7.8 Public Relations

3 April 2008 — Visit of ca. 30 students of the *Studienstiftung des Deutschen Volkes*

24 April 2008 — Girls' Day (Organizer: Dr. Claudia Weidenthaler)

17 May 2008 — Open Day of the Institute with ca. 3000 visitors



2 June 2008 — Visit of representatives of the new Ruhr Museum, Essen

15 August 2008 — Experimental Lecture “Chemie und Wahnsinn- ein wilder Ritt durch die Chemiegeschichte”, Open Air Theater Mülheim/Ruhr (Organizer: Professor Ferdi Schüth)

20 October 2008 — Visit of a delegation with ca. 20 Romanian scientists

26 January 2009 — Laying of the cornerstone of the new lecture hall

9 March 2009 — Visit of ca. 15 young chemists of the Northeastern Section of the American Chemical Society within an exchange program between the ACS and the GDCh

23 April 2009 — Girls’ Day (Organizer: Dr. Claudia Weidenthaler)

5 June 2009 — Visit of a delegation of the Chinese Academy of Science

29 January 2010 — Visit of a delegation from Finland and of representatives of the municipality of the City of Mülheim

22 April 2010	Girls' day (Organizer: Dr. Claudia Weidenthaler)
23 April 2010	Visit of scientists from Turkey within an EU-Leonardo-da-Vinci project
30 April 2010	Opening of the new lecture hall building

May - August 2010	"The Future of Energy", Science Year of Energy 2010, Exhibition on Mainau Island, DE The Institute has contributed to the MPG exhibition pavilion
5-7 June 2010	"Wissenschaftssommer (Science Summer)", Science Year of Energy 2010, Magdeburg, DE The Institute has contributed to the MPG exhibition pavilion

26 June 2010	Day of architecture The new lecture hall building has been opened for interested visitors

12 August 2010	Panel Discussion with Professor Ferdi Schüth, “Vom Feuerstein zum Antimaterie-Reaktor? – Energienutzung im Wandel der Zeit” Science Boat “MS Wissenschaft”, Harbor of Duisburg, DE
4 September 2010	Exhibition at the “19. Mülheimer Umweltmarkt” Topic: Energy conversion, energy storage
13 September 2010	Experimental Lecture “Feuer und Flamme für Mülheim” Open Air Theater Mülheim/Ruhr (Organizer: Professor Ferdi Schüth)
25-26 September 2010	“Day of Energy”, Science Year of Energy 2010, Exhibition, Potsdamer Platz, Berlin

60 reports in the local and nation-wide media on activities of the Institute and/or on awards received by our staff members.

School Contact Program (Dr. Claudia Weidenthaler)

11 September 2009	Visit of students from Luisenschule (secondary school) at the Department for Electron Microscopy
7 October 2009	Experimental Lecture, Gustav-Heinemann Gesamtschule (secondary school)
5 March 2010	Experimental Lecture, Grundschule Trooststraße (elementary school)
17 and 21 May 2010	Experimental Day, Willy Brandt Schule (secondary school) Experiments and background information on heterogeneous catalysis
19 May 2010	Experimental Day, Willy Brandt Schule (secondary school) Experiments and background information on homogeneous catalysis
22 June 2010	Experimental Day, Gymnasium Broich (secondary school) Experiments and background information on heterogeneous catalysis
6 July 2010	Visit of students from chemistry classes of Gymnasium Heißen (secondary school)
30 September 2010	Experimental Lecture, Gustav-Heinemann Gesamtschule (secondary school)

7.9 Special Equipment (> € 25.000)

Instrument	**Department and responsible person**
	Homogeneous Catalysis
GC – Apparatus, Agilent – 7890-N, for normal GC	*Professor List*
GC – Apparatus, Agilent – 6890-N, for normal GC	
GC – Apparatus, Agilent – 6890-N, for chiral GC	
GC – Apparatus, Agilent – 6890-N + GC / MS – Detector, Agilent, 5973-N	
GC – Apparatus, Agilent – 7890-N + GC / MS – Detector, Agilent, 5975-N	
HPLC Station, complete, Shimadzu–LC 2010C	
HPLC Station, complete, Shimadzu–LC 2010C + LC/MS–Detector, LC 2010A	
Multidimensional HPLC Station, Shimadzu–LC 20AD, + DAD–Detector	
Microwave reactor system, CEM – Explorer – NX 2044	
ReactIR 15, FTIR analyzer, Mettler Toledo	
Polarimeter, Autopol IV, Rudolph Research Analytical	
FTIR-Spectrometer, ATR, Spectrum 100, Perkin Elmer	
Preparative Chromatography, Sepacore System, BÜCHI (4x)	
NMR-Spectrometer, Avance III 500 MHz, Bruker	
Spectrometer, Molecular Devices – Spectramax M2 – microplate reader	
HPLC Station, complete, Shimadzu–LC 20A	*Dr. Klußmann*
Reaction calorimeter, Omnical Insight	
GC – Apparatus, Agilent – 7890-A + GC / MS – Detector, Agilent, 5975-C	*Dr. Klußmann / Dr. Maulide*
Combiflash Rf 200 (Isco)	*Dr. Maulide*

	Heterogeneous Catalysis
Physisorption unit, ASAP 2000C (Micromeritics)	*Professor Schüth*
Physisorption unit, ASAP 2010C (Micromeritics)	
Physisorption unit, Sorptomatic 1900 (Carlo Erba)	
Pressure gas sorption system PCT Pro 2000 (Hy-Energy)	
Laser system with CCD camera	
Mass spectrometer coupled with TG/DTA unit (Balzers, Netzsch)	
Transmission X-ray diffractometer, STADI P (Stoe)	
Reflection X-ray diffractometer, STADI P (Stoe)	
High temperature X-ray chamber HDK60/S 1500 (Johanna Otto GmbH)	
FTIR Spectrometer Magna 560 E.S.P. (Nicolet)	
FTIR Spectrometer Equinox IFS 55 (Bruker)	
FTIR Spectrometer AVATAR 370 (Thermo Nicolet)	
FTIR Spectrometer AVATAR 370 (Thermo Nicolet)	
GC System HP6890 with Chem Station (Hewlett-Packard)	
GC System HP6890 (Hewlett-Packard)	
GC System HP6890 N (Agilent)	
XPS Spectrometer Axis Hsi (Kratos)	
Particle size and zeta potential analyzer (Brookhaven)	
Glovebox Labmaster 130 (Braun)	
Pressure DSC device (Mettler Toledo)	
Micro DSC VII with high pressure cell (Setaram)	
48-Fold parallel reactor (hte AG)	
Micro Berti reactor Hastelloy C 276	
Particle size analyzer Zetasizer Nano Zs (Malvern)	
HPLC Diode array system (Perkin Elmer)	

Control Unit FT-NMR Avance III 300 WB (Bruker)	
UV/Vis Microscope photo spectrometer MPV (Leitz)	
UV-VIS-NIR Spectrophotometer Cary 5G (Varian)	*Dr. Marlow*
Goniometer (AmKo)	
Atomic force microscope (Topmetrix)	
Confocal Microscope (Olympus)	
Climate Chamber WK 340 (Weiss)	
Elemental Analyser Vario Micro Cube (Elementar)	*Dr. Rinaldi*
	Synthetic Organic Chemistry
Gas chromatograph system (3 GCs, 3 autosampler, PC, software)	*Professor Reetz*
2 Automatic dispenser Genesis RSP 150/8 (Tecan), hotel for micro plates, Te-MO 96-fold pipetting system, photometer, robot arm, incubator, software	
Qpix Colony Picker (Genetix) with software	
Fermenter, 10 L volume (Infors)	
Shaking incubators with 3 levels (Infors)	
TOF-mass spectrometer (Waters), with auto sampler, LC-pump, etc.	
High volume centrifuge (Sorvall)	
Synthesis robot “Accelerator” (Chemspeed) pipetting system, pressure reactors, etc.	
HPLC System “Äkta” for protein purification (GE Healthcare)	
CD Spectrometer J-810-S (Jasco)	
	Organometallic Chemistry
LC/MS System 2010 (Shimadzu)	*Professor Fürstner*
2 HPLC Systems (Shimadzu)	
Glovebox (Braun)	

3 Gas chromatographs 6890 + Mass spectrometer 5973 (Agilent)	
IR-Thermocamera (FLIR-System)	
Microwave reactor (Biotage)	
FTIR Spectrometer with ATR unit (Perkin-Elmer)	
6 Combi-Flash Companions (Isco)	
	Theory
Compute server: Linux cluster of 20 AMD Opteron 2-node systems with a total of 40 cpus and 4 GB of memory per node	*Professor Thiel*
Compute server: Linux cluster of 21 HP DL585 AMD Opteron 4-node systems with a total of 84 cpus and 12 GB of memory per node	
Compute server: Linux cluster of 3 HP DL585 AMD Opteron 4-node systems with a total of 12 dual core cpus and 16 GB of memory per node	
Compute server: Linux cluster of 36 AMD Opteron 2-node systems with a total of 72 dual core cpus and 32 GB of memory per node	
Compute server: Linux cluster of 24 HP DL385 AMD Opteron 4-node systems with a total of 96 dual core cpus and 32 GB of memory per node	
Compute server: 2 HP ProLiant DL785 AMD Opteron 8-node systems with quad core cpus and 256 GB of memory per node	
Compute server: Linux cluster of 30 HP DL380 Intel Xeon 2-node systems with a total of 60 quad core cpus and 48 GB of memory per node	
Compute server: Linux cluster of 32 HP BL460c Intel Xeon 2-node systems with a total of 64 quad core cpus and 24 GB of memory per node	
Compute server: Linux cluster of 16 Dell M610 Intel Xeon 2-node systems with a total of 32 quad core cpus and 24 GB of memory per node	

Compute server: Linux cluster of 20 HP DL380 Intel Xeon 2-node systems with a total of 40 hex core cpus and 48 GB of memory per node	
File server: EMC Celerra NS80 network attached storage system, 2 storage processors, 29 TB of disk storage	
Application server: 3 HP ProLiant DL585 systems with 4 cpus and 16 GB of memory per node	
Graphic workstations: 27 Fujitsu Siemens Linux workstations	
	Computer Group
Alpha-Server 1200 (Compaq)	*Peter Fischer*
Alpha Server ES 40 (Compaq)	
HP ProLiant DL385 Backup-System	
HP ESL 712e LTO-Tapelibrary for Backup	
	Electron Microscopy and Chemical Crystallography
Transmission electron microscope (TEM): Hitachi, HF 2000, equipped with EDX system (Thermo Electron), bottom CCD-camera (SIS)	*Professor Lehmann*
Transmission electron microscope (TEM): Hitachi, H 7500, equipped with EDX system (Oxford), cryo-specimen holder, side-entry CCD camera (SIS), bottom CCD-camera (SIS)	
Scanning electron microscope (SEM): Hitachi, S-3500N, equipped with a high/low-vacuum chamber and EDX system (Qxford)	
2 Evaporation systems: in-house construction (FHI)	
Equipment for solid state sample preparation (Gatan)	
Sputter-evaporation system: Balzers, MED 010	
Image processing: AnalySIS System Five (Soft Image Systems, SIS)	
Preparative light microscope (LM): Olympus, equipped with CCD-camera (SIS)	

Ultra-high resolution scanning electron microscope (SEM), Hitachi S-5500, equipped with STEM and EDX system	
Ion Milling System, Hitachi E-3500	
Transmission electron microscope (TEM), Hitachi H-7100 equipped with side-entry CCD camera (SIS)	
2 Nonius KappaCCD single crystal diffractometers	
2 FR591 rotating anode generators	
Bruker AXS Proteum X8 CCD single crystal diffractometer	
Bruker AXS GADDS micro-diffractometer	
2 STOE STADI P powder diffractometers (one with oven)	
PANalytical X'Pert powder diffractometer (plus reaction chamber)	
EagleII X-ray fluorescence spectrometer	
ComRay laser crystal growth system	
Zinsser Sophas liquid handling system	
	NMR Spectroscopy
Bruker AMX 300 NMR Spectrometer	*Dr. Farès*
Bruker Avance DPX 300 NMR Spectrometer	
Bruker Avance AV 400 NMR Spectrometer	
Bruker Avance AV 400 NMR Spectrometer	
Bruker Avance AVIII 300 Solid State NMR Spectrometer	
Bruker Avance AV 500 Solid State NMR Spectrometer	
Bruker Avance AVIII NMR Spectrometer with triple-resonance Cryoprobe	
Nicolet Magna 750 FT-IR Spectrometer	
	Mass Spectrometry
Thermo Scientific high resolution MS/MS mass spectrometer LTQ-FT with 12 T actively shielded super conducting magnet	*Dr. Schrader*

Bruker APEX III Fourier transform ion cyclotron resonance mass spectrometer (FTICR MS) with a 7 T actively shielded super conducting magnet	
Finnigan MAT 95 double focusing sector field mass spectrometer with EI/CI-, FAB- and ESI/APCI-Ion sources	
Finnigan MAT 8200 double focusing sector field mass spectrometer with EI/CI-Ion source and AUDEVAP automatic sample introduction system	
Finnigan MAT 8400 double focusing sector field mass spectrometer with EI/CI-Ion source and AUDEVAP automatic sample introduction system	
GC/MS system with Finnigan MAT SSQ 7000 quadrupole mass spectrometer and Hewlett Packard 5890 gas chromatograph	
Bruker Esquire 3000 ion trap mass spectrometer with ESI ion source	
Micromass single quadrupole mass spectrometer with ESI-Ion source, gradient liquid pump and automatic injection system	
GPC-System with autosampler, differential-refractometer and fraction collector	
Thermo triple quadrupole mass spectrometer with ESI/APCI- and APPI-Ion source	
TOF-mass spectrometer (Waters), with auto sampler, LC-pump, etc.	
	Chromatography
GC-instrument, type: Agilent 7890A, equipped with automatic injector Gerstel-MPS2L, MSC2, FID and TCD	*Dr. Schulze*
GC-instrument, type: Agilent 7890A, equipped with automatic injector Gerstel-MPS2L, FID/FID	
GC-instrument, type: Agilent 7890A, equipped with automatic injector Gerstel-MPS2L, FID	
GC-instrument, type: HP 6890, equipped with automatic injector HP 7683, FID/FID	

2 GC-instruments, type: HP 6890, equipped with automatic injector HP 7683, FID	
GC-instrument, type: Agilent 6890N, equipped with automatic injector Agilent 7683, FID	
GC-instrument, type: Agilent 6890N, equipped with automatic injector Agilent 7683, FID/NPD	
GC-instrument, type: HP 6890, equipped with automatic injector Gerstel-MPS2L, FID	
GC-instrument, type: Agilent 7890A, equipped with automatic injector Gerstel-MPS2L, PFC, FID/FID	
4 GC-instruments, type: Agilent 6890N, equipped with automatic injector Gerstel-MPS2L, FID	
GC-instrument, type: Agilent 6890, equipped with automatic injector Gerstel-MPS2, automated headspace device (Gerstel), CIS, FID, TCD	
GC instrument, type: MCS2/HP 6890 (Gerstel), double-oven, CIS, cold trapping device and FID/FID	
GC-instrument, type: Agilent 7890A, equipped with automatic injector Gerstel-MPS2L, DHS, TDU, CIS and FID	
GC/MS, type: MSD HP 5973	
A/D-converter; central data acquisition	
HPLC/MS-System: Shimadzu LC 2010; automated binary gradient system equipped with ESI- and APCI-interface	
HPLC/MS-IT-TOF-System: Shimadzu; automated binary gradient system equipped with ESI- and APCI-interface	
UHPLC-System: Agilent RRLC 1200; automated binary gradient system equipped with DAD-detector	
UHPLC-System: Shimadzu LC 20 prominenceXR; automated binary gradient system equipped with DAD-detector	
HPLC-System: Shimadzu LC 20A prominence; automated binary gradient system equipped with DAD-detector	

HPLC-System: Shimadzu LC 20A prominence; automated binary gradient system equipped with DAD-, RI- and ELSD-detector	
HPLC-System: Shimadzu LC 10A; automated binary gradient system equipped with DAD-Detector	
HPLC-System: Shimadzu LC 10A with chiralyser, IBZ instrumentation; automated binary gradient system equipped with DAD-, RI and Polarimetric-Detector	
HPLC-System: Shimadzu LC 10A; automated system for column-switching equipped with UV- and RI-Detector	
HPLC-System: Shimadzu LC 10Avp; automated binary gradient system equipped with UV-Detector	
HPLC-System: Shimadzu LC 2010C; quaternary gradient system with UV-detector	
HPLC-System: Shimadzu LC 2010CHT; quaternary gradient system with UV-detector	
HPLC-System: Shimadzu LC 10Ai; inert quaternary gradient system with UV-detector	
HPLC-System: Shimadzu LC 10A ion chromatograph; automated binary gradient system equipped with UV- and conductivity- and amperiometric detector	
HPLC-System: Shimadzu LC 8A/10A; semipreparative binary gradient system	
HPLC-System: Shimadzu LC 8A/10A; preparative binary gradient system	
HPLC-System: Shimadzu LC 8A/20A; preparative binary gradient system	
CE-System: Hewlett-Packard 3D CE; capillary electrophoresis system	
CE-System: Agilent 7100; capillary electrophoresis system	
Fluorescence detector: Picometrics Zetalif Laser induced fluorescence detector for capillary electrophoresis and liquid chromatography	

	Technical Laboratory
Reaction calorimeter (Mettler Toledo)	*Dr. Theyssen*
SFC-System (Carlo Erba)	
Glove-box (Fa. Braun)	
Hydrogen compressor (Hofer)	
High pressure reactor for reaction calorimeter	
High pressure gas-line system	
Supercritical fluid chromatograph	
Syringe pump for supercritical fluid chromatography	
Glass equipment for technical scale	
High pressure React-IR for online reaction control	
Hydrogen compressor (Maximator)	
Rectification plant for the purification of MTBE	
Automatic control engineering for small- and medium-sized high-pressure boxes	
Rectification plant for the purification of the used hexane isomer mixture	
Synthesis robot “Accelerator” (Chemspeed) pipetting system, pressure reactors etc.	(take-over from Reetz group)
	Glassblowing
Glass working lathe	*Jürgen Lutz*
	Precision Engineering
3 Computer numeric control lathe	*Wolfgang Kersten*
Computer numeric control milling	
Milling and drilling machine	
Milling machine	
Eroding machine	

7.10 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) 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 to Mülheim an der Ruhr Hauptbahnhof.

HOW TO REACH

THE INSTITUTE

Main entrance:
Lembkestraße 7