Max-Planck-Institut für Kohlenforschung

Report for the Period of

January 2005 – December 2007

Printed January 2008

Max-Planck-Institut für Kohlenforschung

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

Dr. Wolfgang Schmidt (since August 2003)

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

Professor Dr. Günther Wilke
Professor Dr. Roland Köster

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CHAPTER 1

The Max-Planck-Institut für Kohlenforschung

1.1 History of the Max-Planck-Institut für Kohlenforschung

The Kaiser-Wilhelm-Institut für Kohlenforschung (coal research) in Mülheim/Ruhr was founded 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 to be the first Director of the Institut für Kohlenforschung.

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 and in Malaysia. In 1939 Franz Fischer instigated a change in the status of the Institute and 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 in the Institute 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 and which could be converted into the corresponding α-olefins or primary alcohols, the latter being 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 and, 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 stereo-chemistry 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.

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 enantioselective homogeneous catalysts involving chiral ligands. The Institute also pursued research in electrochemistry, contributing an efficient electrochemical synthesis of iron(II) ethanolate which became industrially important for the continuous production of ferrocene. The on-going investigation of the use of supercritical gases to separate substances, which was first discovered 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 enantioselective 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 heads (Directors) of the Departments. In 1995 Andreas Pfaltz joined the Institute as the Director of the

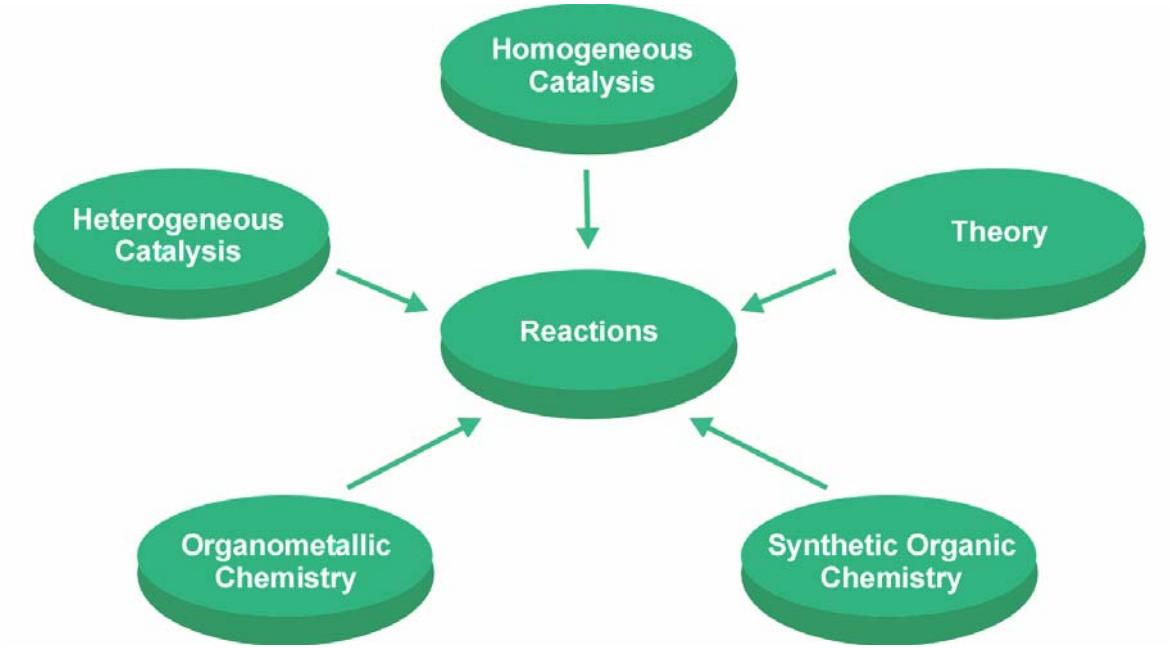
Department of Homogeneous Catalysis, while Manfred T. Reetz headed the Department of Synthetic Organic Chemistry. Thereafter the appointments of Ferdi Schüth (Heterogeneous Catalysis), Alois Fürstner (Organometallic Chemistry) and Walter Thiel (Theory) followed. Thus, the scientific activities of the 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 prominent pioneer in the emerging field of organocatalysis, and he was hired on a C3-position (associate professor) in 2003, with the intention of later promoting him to become the Director of the Department. This has been accomplished in 2005.

The re-organization of the Institute that had been initiated in the 1990s has thus been completed. The Directors of the Departments form the Board of Directors which is responsible for all decisions. The affairs of the Institute are managed by a Managing Director elected from the Board of Directors. As successor to Manfred Reetz, Ferdi Schüth served as Managing Director from 2003-2005, followed by Walter Thiel (2006-2008).

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.



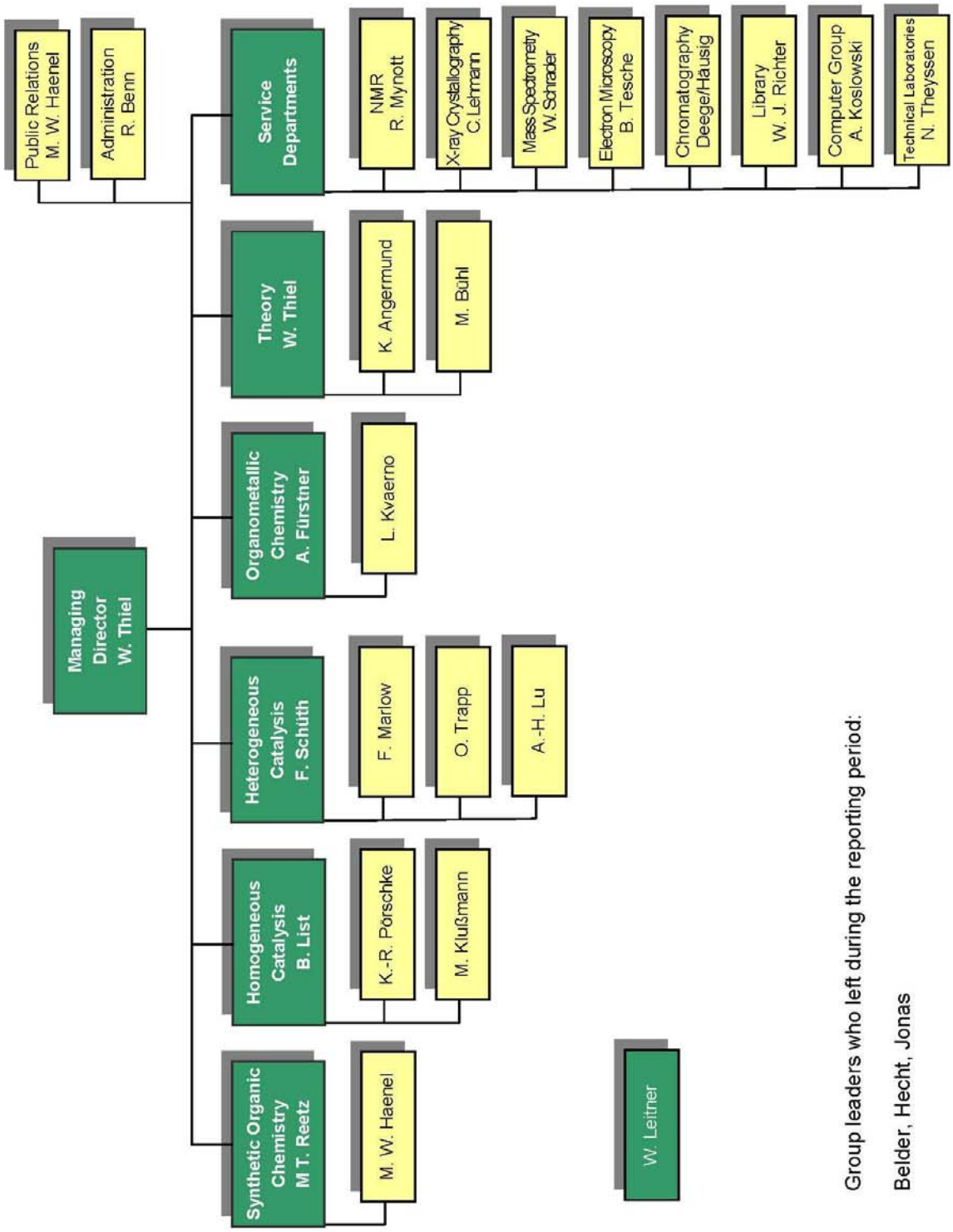
Catalysis is viewed world-wide as the key technology in the establishment of economically and ecologically sound chemical processes of the future. However, the efficiency of numerous catalytic systems is far from ideal, and for many important chemical transformations appropriate catalysts have not even 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 and theory. By necessity this requires the appropriate laboratories, equipment and instrumentation all in one unit. The idea of assembling five research departments encompassing homogeneous and heterogeneous catalysis, organic synthesis, organometallic chemistry and theory under one roof therefore ensures the "critical mass" and the diversity necessary for

meeting the scientific challenges in the field of catalysis. 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 instruments. Finally, a four-semester cycle of lectures for the doctoral students and post-docs of the Institute has been initiated which covers homogeneous and heterogeneous catalysis, organocatalysis, biocatalysis, theory, and aspects of chemical engineering, thereby contributing to the unique nature of the Institute.

Specific projects in the experimentally oriented Departments include unusual kinds of achiral and chiral ligands, novel solid materials displaying specific functional properties, catalytic reactions using small organic molecules, such as proline, as catalysts, and directed evolution of selective enzymes for use in organic chemistry. Much emphasis is also placed on advancements in methodologies. Examples include 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 establishment of ways to study the details of how solid materials actually form 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 at the End of the Reporting Period (December 2007)



Group leaders who left during the reporting period:

Belder, Hecht, Jonas

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. 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. 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

1.5 Members of the Board of Governors ("Verwaltungsrat")

Members of the Board of Governors 2005 and 2006

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

Ralf Blauth (2006)

Dr. Barbara Bludau

Dr. Jürgen Engelhard

Prof. Dr. Fred Robert Heiker

Prof. Dr. Karl Friedrich Jakob (2005)

Dr. Ulrich Knips

Dagmar Mühlenfeld, Oberbürgermeisterin der Stadt Mülheim an der Ruhr

Dr. Jörn Rüter

Dr. Werner Schwilling

Prof. Dr. Günther Wilke, Honorary Member

Members of the Board of Governors 2007

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

Ralf Blauth

Dr. Barbara Bludau

Michael Dettmann

Prof. Dr. Michael Dröscher

Prof. Dr. Dieter Jahn

Dagmar Mühlenfeld, Oberbürgermeisterin der Stadt Mülheim an der Ruhr

Dr. Jörn Rüter

Prof. 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: 14, 17, 36, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 162, 216, 228, 247, 252, 327, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 377, 427, 455, 460, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 531

Further group leaders:

Gerhard Fink (born 1939)
retired from the Institute in June 2004
Publications: 16, 39, 40, 80, 130, 149, 182, 196, 197, 254, 256, 257, 258, 279, 436, 464

Matthias W. Haenel (born 1944)
Publications: 282, 283, 284, 396

Walter Leitner (born 1963)
left the Institute in February 2002, now associated as external scientific member of the Institute
Publications: 18, 19, 29, 30, 53, 77, 172, 217, 276, 320, 372, 378, 432, 461, 472, 486, 487, 502, 503, 522, 525

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 (SIOC)
1980-2007	>150 Plenary Lectures and Name Lectureships

Special Activities

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", Springer
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 and Catalysis, Wiley
2001-2005	Member of Scientific Advisory Board for the School of Engineering and Science, International University Bremen
2002-	Member of Editorial Board, Angewandte Chemie, Wiley-VCH
2003-	Member of International Advisory Board, QSAR & Combinatorial Science, Wiley-VCH
2003-	Member of the Kuratorium der Alfried Krupp von Bohlen und Halbach-Stiftung
2003-	Member of the International Advisory Board "QSAR & Combinatorial Science", Wiley-VCH
2005-	Member of the Editorial Advisory Board "Bulletin of the Chemical Society of Japan"

2006-	Member of the Advisory Board "Topics in Stereochemistry", John Wiley & Sons
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
since 1980	Member of Advisory Committee of numerous scientific conferences

Research in the Department of Synthetic Organic Chemistry

The primary goal of this Department is methodology development in homogeneous transition metal catalysis and in biocatalysis. This entails the creation of new catalytic systems for efficient and ecologically viable transformations in synthetic organic chemistry. Since the departure of Lukas Goossen in 2004 (now professor in Kaiserslautern) and the retirement of Gerhard Fink (also in 2004), the Department of Synthetic Organic Chemistry is composed of the groups of M. T. Reetz and M. Haenel, while W. Leitner continues to contribute as an External Scientific Member of the Institute. The Department has abstained from recruiting new (young) members in view of the fact that M. T. Reetz (born 1943) is scheduled to retire in 2011.

Research activities in the Reetz group concentrate on the development of new catalyst systems in 1) homogeneous transition metal chemistry, and 2) in biocatalysis. Recently the group has devised a novel concept in combinatorial transition metal catalysis, the underlying idea being the use of mixtures of chiral and/or achiral monodentate ligands. Such a combinatorial approach can be applied in the quest to control the enantio-, diastereo- and regioselectivity of transition metal catalyzed reactions. Examples are enantioselective hydrogenation and regioselective hydroformylation. During the next three years, however, the primary focus will be on biocatalysis, as outlined below.

In the 1990s the Reetz group introduced a fundamentally new approach to asymmetric catalysis, namely the directed evolution of enantioselective enzymes for use in synthetic organic chemistry. Following successful projects regarding enantioselective lipases, epoxide hydrolases and monooxygenases using known methodologies of gene mutagenesis, the primary current focus is on the development of new methods and strategies for probing protein sequence space more efficiently than in the past. Fast directed evolution is one of the hottest current endeavors in this emerging field. Questions of selectivity and thermostability under operating conditions, as for example in partial oxidation, are also being addressed by the Reetz group. Another facet is the directed evolution of enantioselective hybrid catalysts in which synthetic transition metal entities are anchored to protein scaffolds. Finally, the development of high-throughput *ee*-screening and selection systems is continuing, including efforts in collaboration with O. Trapp (Department of Heterogeneous Catalysis).

The objectives of the Haenel group concern the development of 1) hyperstable ligands for transition metal catalysis under extreme conditions, and of 2) homogeneous catalysis in coal degradation. In 2005 the group announced a sensational result emerging from its efforts in coal research, namely the first example of a homogeneous catalyst for coal

hydrogenation. The catalysts are boron-based compounds. This discovery not only aroused the interest of the academic community, it was also featured in national and international newspapers.

As an External Scientific Member of the Institute with a special contract, W. Leitner continues to run a small group in Mülheim, specifically in the "Versuchsanlage" where research regarding the use of environmentally benign solvents such as supercritical CO_2 and ionic liquids is being conducted. Dr. Theyssen is responsible for the "daily" research, in addition to providing service for the whole Institute (which goes beyond the question of solvents). Since the beginning of the contract with W. Leitner almost six years ago, this group comprising 2-3 persons has published around 20 papers from Mülheim. Collaborations with M. T. Reetz and other groups proved to be fruitful.

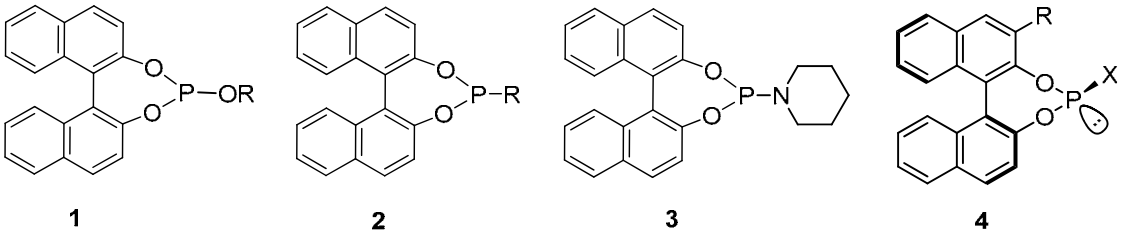
The close ties between the Department of Synthetic Organic Chemistry and the Theory Department are continuing to provide new mechanistic insights in various catalytic systems of current interest. For example, several ongoing Reetz/Thiel collaborations have produced significant results in 1) the mechanism of asymmetric Rh-catalyzed olefin-hydrogenation using chiral monodentate P-ligands, and 2) the source of enhanced enantioselectivity of lipase mutants created by directed evolution. The lessons learned from these theoretical analyses have led to new experiments in the laboratory.

2.1.1 Research Area "Transition Metal Catalyzed Reactions" (M. T. Reetz)

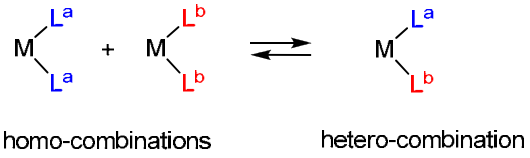
Involved: S. Alfs, S. G. Baca, O. G. Bondarev, Y. Fu, R. Goddard, H. Guo, X. Li, J.-A. Ma, G. Mehler, A. Meiswinkel, P. Scholz, K. Sommer, M. Surowiec, C.-S. Yang

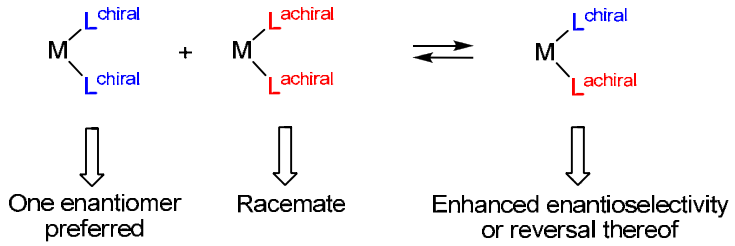
Objective: The objective of this research area is to design and test new types of ligands for enantio-, diastereo- and regioselective transition metal catalysis, and at the same time to develop novel concepts in catalysis. The challenge is to restrict the search for new catalyst systems to those ligands which are accessible in 2-3 simple steps from cheap starting materials, the specific goals being: 1) To understand the source of the previously observed high enantioselectivity of BINOL-derived monophosphites and monophosphonites as ligands in Rh-catalyzed olefin-hydrogenation. 2) To develop a new strategy in combinatorial transition metal catalysis based on the use of mixtures of chiral or achiral monodentate ligands. 3) To design readily available BINOL-derived chelating diphosphites and diphosphonites and to compare them to the respective monodentate counterparts in catalysis.

Results: In the last Report (2002-2004) we presented data showing that BINOL-derived monophosphites **1** and phosphonites **2** are surprisingly efficient ligands in Rh-catalyzed asymmetric olefin-hydrogenation, in many cases the *ee* being > 95%. Since BINOL is one of the cheapest chiral auxiliaries commercially available, this discovery, taken together with the work of B. Feringa/J. G. de Vries (DSM) regarding the use of the analogous phosphoramidites, has opened a new chapter in asymmetric transition metal catalysis. In the Mülheim lab and in many other groups new derivatives have been prepared and tested successfully during the last three years, including our discovery that the phosphoramidite piperidine-derivative **3** is considerably more active and enantioselective than all other ligands previously reported by the Dutch groups. We have also prepared mono-substituted P-ligands **4** which have an additional stereogenic center at phosphorus, and which often lead to even higher enantioselectivities than the simple ones (99% *ee*). These and other results show that the long-standing dogma regarding the necessity of using chelating diphosphines for obtaining high enantioselectivity no longer holds. In collaboration with W. Thiel and D. Blackmond a thorough mechanistic study regarding the source of high enantioselectivity was initiated, which includes kinetics, non-linear effects (NLEs), NMR studies and QM/MM calculations. The results show that an anti-Halpern system is operating, i. e., the major Rh-olefin intermediate is the more reactive one which leads to the product.

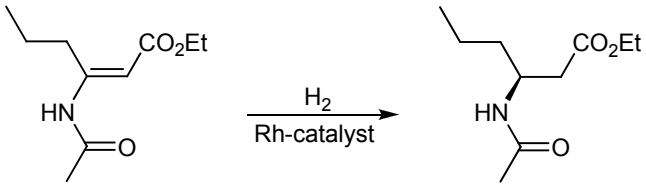


The Report 2002-2004 describes the initial the results of putting a new concept in combinatorial transition metal catalysis into practice, namely the use of mixtures of two chiral monodentate ligands or of mixtures comprising a chiral and an achiral monodentate P-ligand.



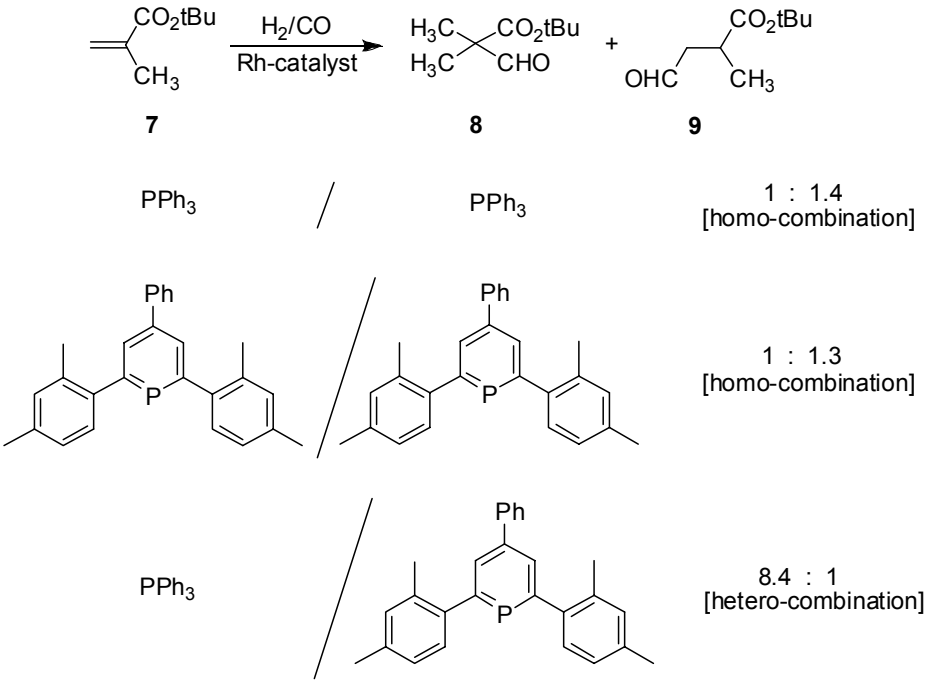


We have generalized this combinatorial approach to include the control of enantio-, diastereo- and regioselectivity. Two of many examples are shown here:

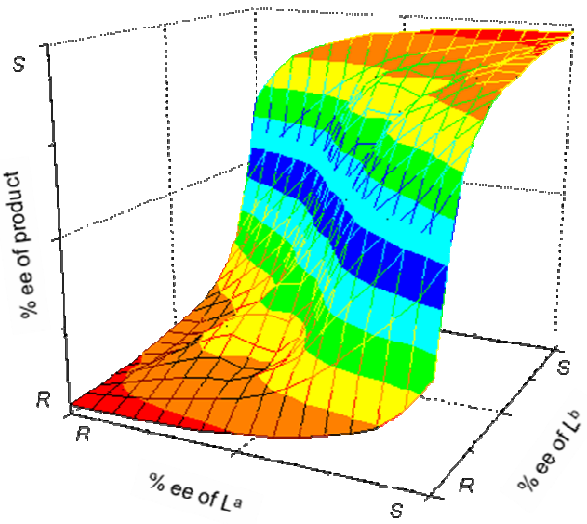


5 **6**

(*R*)-**1** (R=CH_3)/(*R*)-**1** (R=CH_3): 85% *ee* [homo-combination]
(*R*)-**2** (R=$C(CH_3)_3$/(*R*)-**2** (R=$C(CH_3)_3$: 31% *ee* [homo-combination]
(*R*)-**1** (R=CH_3)/(*R*)-**2** (R=$C(CH_3)_3$: 98% *ee* [hetero-combination]

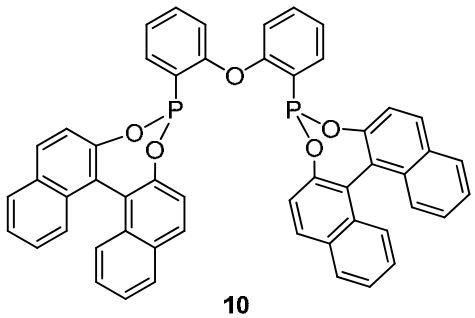


Mechanistic work regarding the mixture concept has also been initiated. In addition to NMR studies, novel non-linear effects were observed when using two different chiral P-ligands in a mixture, L^a and L^b, the enantiopurity of both ligands being varied simultaneously. These effects are strong evidence that in the transition state of hydrogenation two different ligands are bound to rhodium.

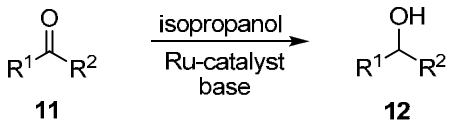


In earlier work we had observed that monodentate ligands such as **1**-**4** are not well suited for asymmetric transfer hydrogenation of prochiral ketones. We therefore studied

various diphosphonites in Ru-catalyzed transfer hydrogenation of prochiral ketones, especially with respect to the difficult class of alkyl/alkyl-ketones **11** which show poor enantioselectivity in the best literature systems. The xanthene-derived ligand **10** turned out to provide unprecedented degrees of enantioselectivity, e. g.:



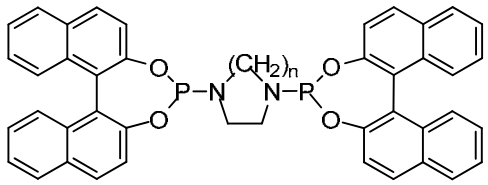
10



11 **12**

R^1 = *c*-C_6H_{11}; R^2 = CH_3 : 99% *ee*
R^1 = $CH(CH_3)_2$; R^2 = CH_3 : 99% *ee*
R^1 = *n*-C_6H_{13}; R^2 = CH_3 : 90% *ee*
R^1 = *n*-C_4H_9; R^2 = CH_3 : 90% *ee*

Finally, we discovered that certain diphosphonites such as **10** are excellent ligands in the asymmetric Ir-catalyzed hydrogenation of quinolines (*ee* = 92-94%), and that diphosphoramidites such as **13a-b** constitute surprisingly efficient ligands in Rh-catalyzed olefin-hydrogenation (*ee* > 95%).



13 a n = 2
b n = 3

Publications resulting from this research area: 14, 138, 139, 141, 142, 143, 144, 145, 146, 216, 347, 348, 350, 351, 352, 353, 355, 455, 508

External funding: Fonds der Chemischen Industrie

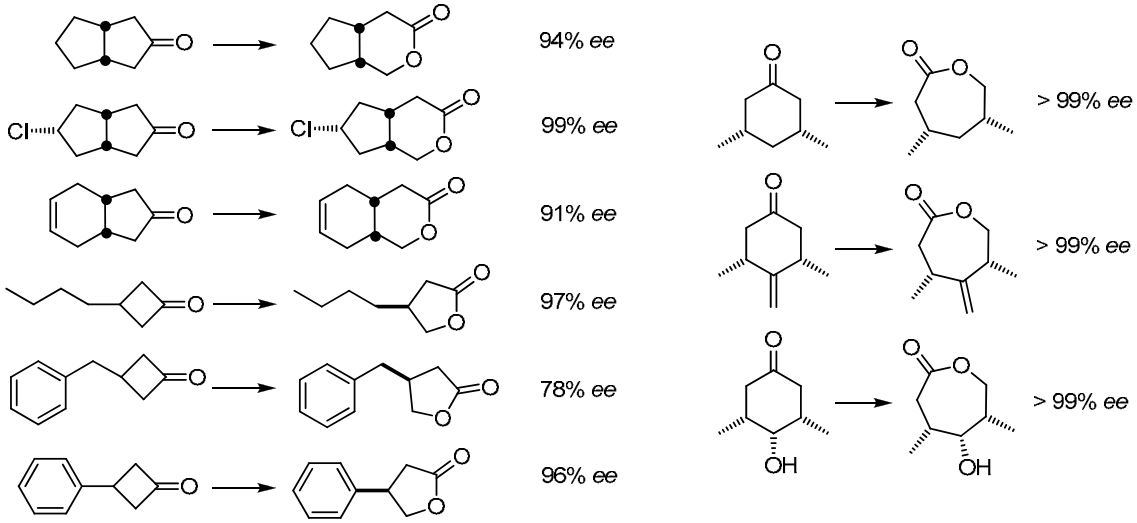
Cooperations: D. G. Blackmond (Imperial College, London, UK); K. Angermund, W. Thiel (Mülheim/Ruhr, DE); J. G. de Vries (DSM, Amsterdam, NL); B. L. Feringa (Groningen University, NL); K. N. Gavrilov (Ryazan State University, RU)

2.1.2 Research Area "Directed Evolution as a Means to Create Enantioselective Enzymes" (M. T. Reetz)

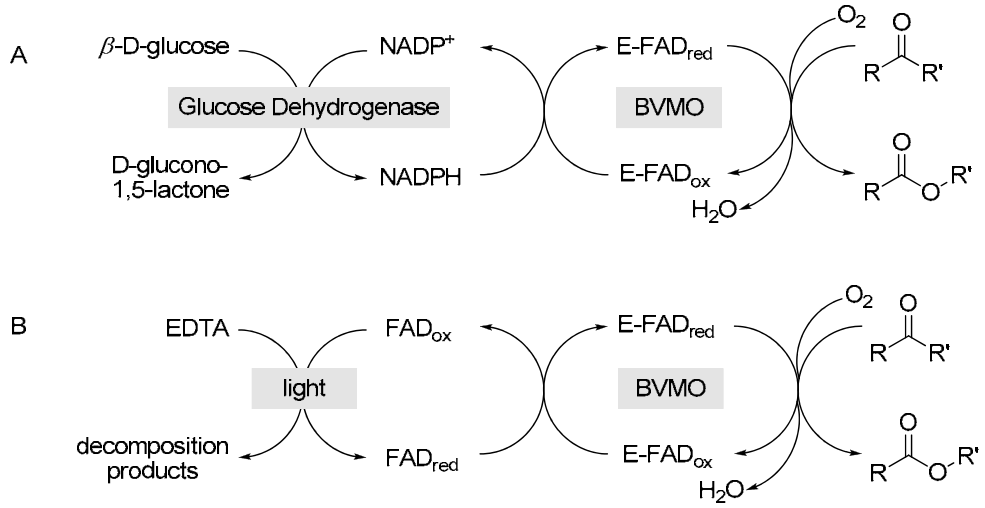
Involved: M. Bocola, J. D. Carballeira, C. M. Clouthier, M. Hermes, H. Höbenreich, F. Hollmann, F. Leca, M. Maichele, J. Peyralans, A. Taglieber, A. Vogel, S. Wu

Objective: During the last three years our long-term project regarding the directed evolution of functional enzymes as enantioselective and thermostable catalysts in organic chemistry has split into two parts. The first part is summarized here, the goals being 1) to explore how well certain mutants of monooxygenases and lipases, previously evolved by our earlier strategies based on error-prone PCR and DNA shuffling, perform when testing them as catalysts in the selective transformation of other substrates; 2) to develop new co-factor regeneration systems for the mono-oxygenases; 3) to understand the source of enhanced enantioselectivity of the evolved mutant enzymes; 4) to develop further high-throughput screening systems. The second part (Section 2.1.3) concerns methodology development in directed evolution.

Results: In a 2004 paper we reported the directed evolution of enantioselective Cyclohexanone Monooxygenase (CHMO) mutants as Baeyer-Villiger catalysts in the O_2-mediated desymmetrization of 4-hydroxycyclohexanone. The WT delivers an *ee* of only 9%. *R*- and *S*-selective mutants were evolved on an optional basis (*ee* = 90%). Based on structural considerations, certain mutants were expected to be good catalysts for other substrates. Since selective partial oxidation is certainly one of the major challenges in current organic chemistry, one of the mutants was tested as a catalyst in the following transformations. None of the presently known synthetic chiral transition metal catalysts using peroxides as oxidants are capable of such performance.

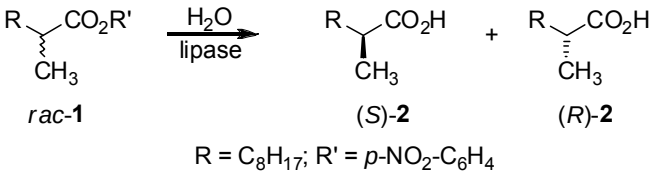


In 2004 the first X-ray structure of a Baeyer-Villiger, Monooxygenase (BVMO), namely Phenylacetone Monooxygenase (PAMO) was published by M. W. Fraaije, with whom we now collaborate. It is thermostable, but hardly accepts any substrates of synthetic interest. We therefore generated PAMO mutants P1, P2 and P3 which show a considerably broadened substrate scope and high enantioselectivity. Mechanistically, the oxidized flavin is reduced by the co-factor NADPH, which is traditionally regenerated by glucose dehydrogenase. In another project we have simplified the overall system considerably by replacing the regeneration-enzyme by light (sunlight or light-bulb), EDTA being the source of electrons. This is the first light-driven BVMO to be reported in the literature, and it is highly enantioselective in relevant cases (*ee* > 95%).



An intriguing facet of directed evolution concerns the source of enhanced enantioselectivity. In the case of the on-going project regarding the directed evolution of enantioselective mutants of the lipase from *Pseudomonas aeruginosa* as catalysts in the hydrolytic kinetic resolution of rac-**1**, the theoretical analysis has proved to be illuminating. The best mutant leads to a selectivity factor of $E = 51$ and is characterized by six mutations, only one of them being near the active site. Thus, for the first time remote effects were shown to influence the enantioselectivity of an enzyme. The QM/MM study uncovered an unusual relay mechanism (see report by W. Thiel). Moreover, it predicted that only two of the mutations are mainly responsible for enhanced enantioselectivity. We went back to the lab and prepared several of these "reduced" mutants. Indeed, the predicted double mutant is highly enantioselective in the model reaction ($E = 64$!). This is a triumph of theory, but it also indicates that in our original directed evolution study using repeating rounds of epPCR and DNA shuffling, superfluous mutations had accumulated. This "disturbing" observation is a clear sign

that our original strategies are successful, but certainly not as efficient as they could be (see Section 2.1.3).

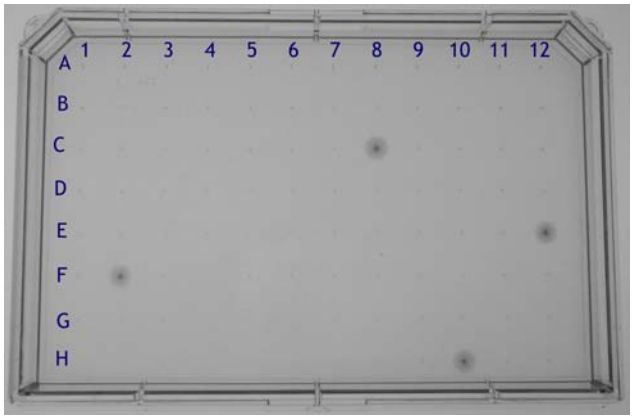


rac-**1** (*S*)-**2** (*R*)-**2**

R = C_8H_{17}; R' = *p*-NO_2-C_6H_4

Another challenge in directed evolution concerns the development of high-throughput assays needed in evaluating thousands of mutants, as for example when evolving enantioselectivity. We have previously devised several such screens, including the Mülheim MS-based *ee*-assay for kinetic resolution and desymmetrization. Nevertheless, we are continuing, two long-term goals being: 1) Enantioselective reactions and *ee*-analysis on a single chip (lab-on-a-chip), and 2) Selection systems on the basis of a growth advantage of the host microorganism, rather than screening. In collaboration with D. Belder (see his report for details), a device was designed and implemented which constitutes for the first time a lab-on-a-chip in which both the biocatalytic enantioselective reaction and the *ee*-analysis can be performed. Parallelization of the micro-channels in order to achieve high-throughput is the next goal. With regard to selection systems in the directed evolution of enantioselective enzymes, we have considered several approaches, some of which are beginning to be successful in this truly difficult endeavor: 1) Phage display (in collaboration with W. Quax/Groningen); 2) Cell sorting using FACS (in collaboration with H. Kolmar/Darmstadt); 3) Pre-selection test for evaluating the activity of epoxide hydrolases (EHs).

Pre-screens or pre-selection assays are ideal in directed evolution, because most libraries contain numerous non-active clones, which can be sorted out prior to elaborate *ee*-analysis. Since epoxides, but not the diols of a kinetic resolution thereof, are toxic to organisms, we devised an efficient pre-selection system. Accordingly, we showed that bacterial growth (*E. coli*) on agar plates relates directly to the presence of active EH mutants because they catalyze the detoxicating hydrolysis of the epoxide substrates. The photograph below features an agar plate harboring 96 *E. coli* colonies containing an epoxide and an EH, the four spots correctly signaling the presence of active enzyme mutants.



Preliminary work on promiscuity in enzyme catalysis has been initiated with the perspective of exploiting our methods of directed evolution in the quest to entice enzymes to catalyze certain classes of reaction types which are not possible with the respective wild-type. Among the early results is the finding that some lipases catalyze the Morita-Baylis-Hillman reaction. Our other discovery that the enzyme tHisF, which is instrumental in the biosynthesis of histidine, shows promiscuous behavior toward esters (esterase-like hydrolysis) is perhaps not so astonishing. What is really intriguing, however, is our surprising finding that this promiscuous catalysis does not occur in the active site where the natural reaction is known to take place. We call this unusual phenomenon "alternate-site promiscuity". Our discoverys appears to be the first known exception to the accepted dogma in the theory of evolution that natural and promiscuous reactions occur in one and the same binding pocket!

Publications resulting from this research area: 17, 36, 136, 140, 162, 228, 252, 327, 342, 343, 344, 356, 460, 505, 506, 507, 510, 511, 512, 531

External funding: Idecat (EU); DFG (Schwerpunkt "Gerichtete Evolution"); Fonds der Chemischen Industrie

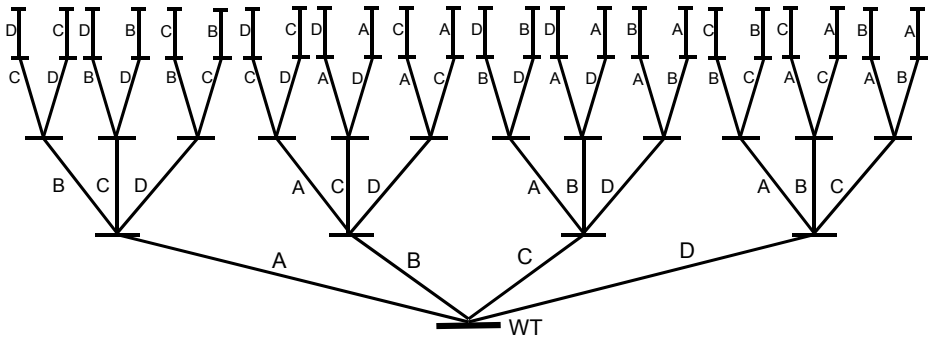
Cooperations: W. Thiel (Mülheim/Ruhr, DE); D. Belder (Mülheim/Ruhr, now Regensburg, DE); K.-E. Jaeger (Düsseldorf/Jülich, DE); J. E. Bäckvall (Stockholm, SE); M. M. Kayser (St. John, CA); J. Baratti and R. Furstoss (Marseilles, FR); B. W. Dijkstra and W. Quax (Groningen, NE); H. Kolmar (Darmstadt, DE)

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

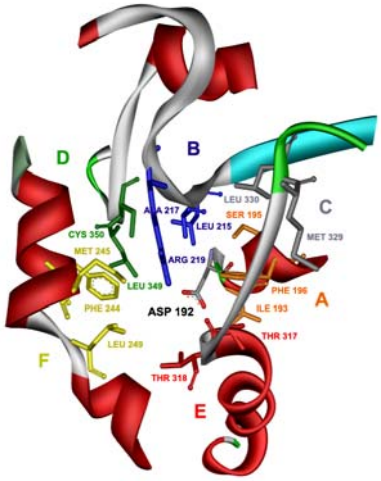
Involved: Y. An, S. Bastian, M. Bocola, J. D. Carballeira, C. M. Clouthier, J. Drone, L. Fernandez, Y. Gumulya, H. Höbenreich, D. Kahakeaw, S. Kille, R. Lohmer, L. Oliveira, S. Prasad, J. Sanchis, F. Schulz, P. Soni, A. Taglieber, L.-W. Wang, S. Wu, F. Zilly

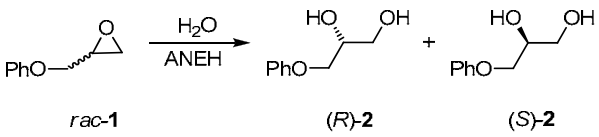
Objective: All previous papers on directed evolution emerging from our laboratory or from other groups describe successful experiments using such gene mutagenesis methods as epPCR (which is used most often), saturation mutagenesis, DNA shuffling and/or other molecular biological techniques. However, one current challenge revolves around the question of how to design and maximize the *quality* of mutant libraries, enabling "fast" directed evolution. Our goal was to find a method which ensures the generation of "smart" libraries in order to solve problems of 1) substrate scope of enzymes; 2) enantioselectivity; and 3) thermostability.

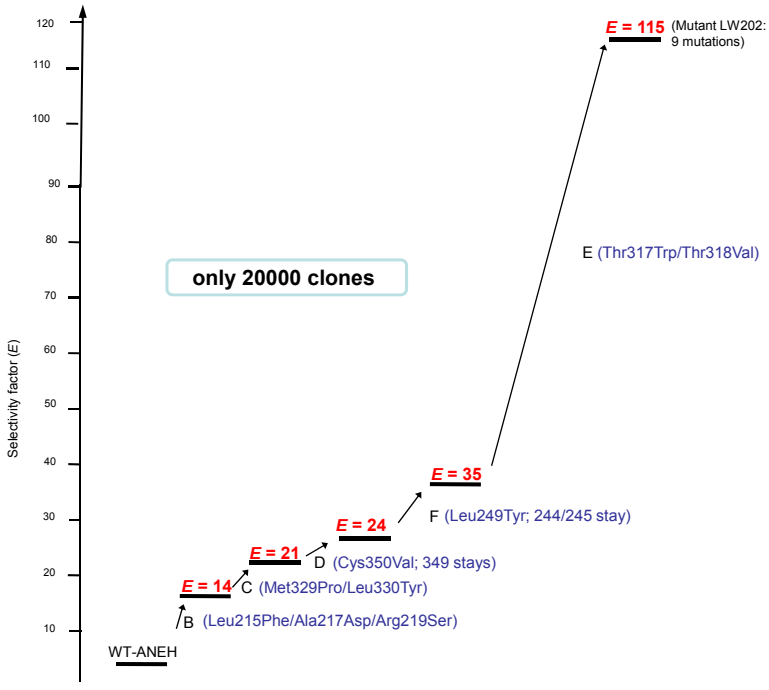
Results: Our contribution to the development of "fast" directed evolution is Iterative Saturation Mutagenesis (ISM). The first step requires a decision as to the appropriate sites A, B, C, D, etc. where saturation mutagenesis is to be performed, which means random introduction of all 20 proteinogenic amino acids. A given site can be comprised of one, two, three (or more) amino acid positions in the enzyme. This decision depends upon the nature of the property to be engineered. In the case of substrate acceptance and/or enantioselectivity, the choice is made on the basis of the Combinatorial Active-Site Saturation Test (CAST). When enhancing thermostability using ISM, the criterion is based on B-factors. Then the respective sites are each randomized with formation of focused libraries, and the mutant genes of the respective hits are used to perform further saturation mutagenesis at the other sites. ISM is illustrated here for the case of four sites A, B, C, and D:



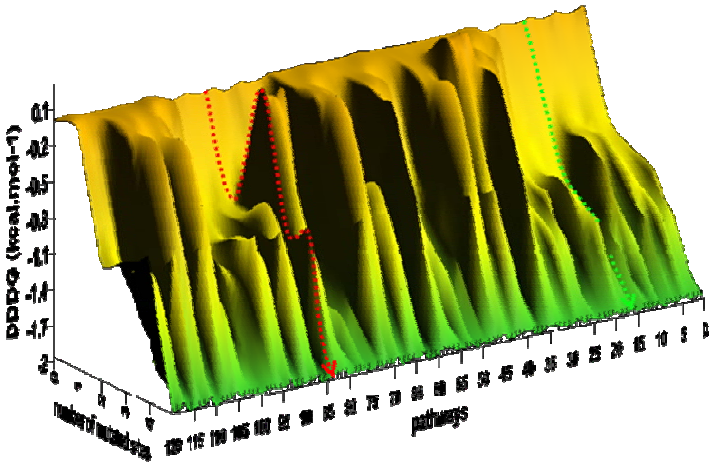
CASTing means the systematic generation of focused libraries by saturation mutagenesis at sites around the complete binding pocket. We have applied CASTing successfully in broadening the substrate scope of lipases and in enhancing the enantioselectivity of a Baeyer-Villigerase and of the epoxide hydrolase from *Aspergillus niger* (ANEH). The latter is illustrated here. It can be seen that the selectivity factor of the kinetic resolution increases from E = 4.6 (WT) to E = 115. The number of clones that were screened amounts to only 20000, which happens to be the same number required in our earlier study using the conventional approach based on epPCR, but which led to only E = 11. Thus, ISM *appears to be far superior to conventional ways of probing protein sequence space*.



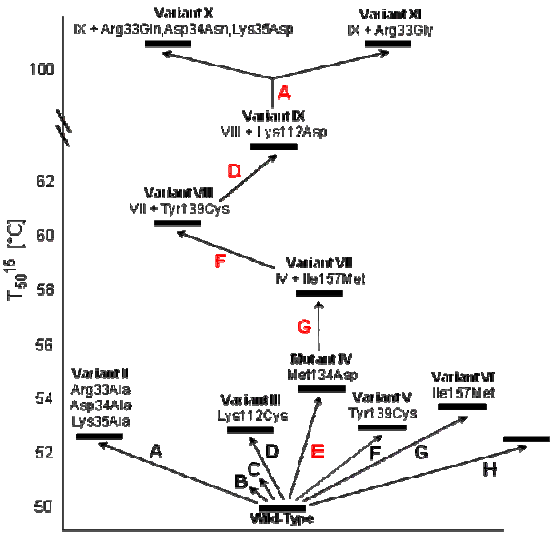




Other upward pathways have not yet been explored. However, the deconvolution of the five *sets* of observed mutations shows that numerous other feasible pathways leading to mutant LW202 exist. The energy site-mutation landscape of all of the theoretically possible 120 pathways to this *specific* mutant has been mapped, two different types becoming visible: Favored (green), less feasible (red):



The criterion for choosing the appropriate sites when attempting to increase the thermostability of enzymes is different. Since hyperthermophilic enzymes are known to be more rigid than the mesophilic counterparts, we chose those sites where mutations can be expected to influence rigidity, specifically by considering B-factors from X-ray data which reflect increased smearing of atomic electron densities relative to equilibrium positions. Using what we call the B-FIT method, we were able to increase the thermostability of the lipase from *Bacillus subtilis* by 45 °C. Such dramatic thermostabilization has no precedence in directed evolution. Only 8000 clones were screened in five iterative rounds of saturation mutagenesis, which again illustrates the power of ISM.



Variant X	Variant XI
T_{50}^{60} = 89 °C	T_{50}^{60} = 93 °C
ΔT_{50}^{60} = 41 °C	ΔT_{50}^{60} = 45 °C

Same catalytic profile at room temperature as WT

Only 8000 mutants screened!

We have also used statistical models from the literature to calculate the degree of oversampling that is necessary when going for 95% coverage of the respective protein sequence space in saturation mutagenesis (in our studies thus far such complete coverage was not strived for). A computer aid is available on our homepage. Part of the data is shown below in the table, which raises the crucial question as to the choice of the optimal codon degeneracy. All results so far show that employing NDT, meaning the use of only 12 amino acids as building blocks, is far superior to the conventional NNK degeneracy which encodes all 20 amino acids but which requires dramatically more oversampling. The respective mutant libraries have a much higher *density* as well as enhanced *quality* of hits. If this observation should prove to be general, which we suspect at this point, then ISM will turn out to be an even more powerful tool in directed evolution. The ISM-approach means a symbiosis of "rational design" and randomization at appropriately chosen sites. The unfortunate accumulation of superfluous or deleterious mutations, as observed in older studies using conventional tools such as repeating rounds of epPCR and DNA shuffling, is not likely to occur when using ISM correctly.

Codon usage	No. of codons	No. of AA	No. of stops	AA encoded	95% coverage for 2 pos.	95% coverage for 3 pos.
NNK	32	20	1	All 20	3066	98163
NDT	12	12	0	RNDCGHILFSYV	430	5175
DBK	18	12	0	ARCGILMFSTWV	969	17470
NRT	8	8	0	RNDCGHSY	190	1532

N: adenine / cytosine / guanine / thymine; K: guanine / thymine;
D: adenine / guanine / thymine; T: thymine

Publications resulting from this research area: 136, 137, 247, 344, 345, 346, 505, 506, 509, 514

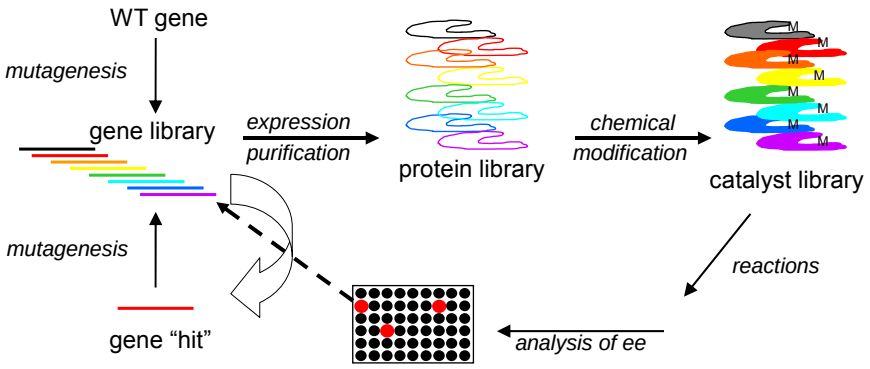
External funding: DFG (Schwerpunkt "Directed Evolution"); Fonds der Chemischen Industrie

Cooperations: none

2.1.4 Research Area "Directed Evolution of Hybrid Catalysts" (M. T. Reetz)

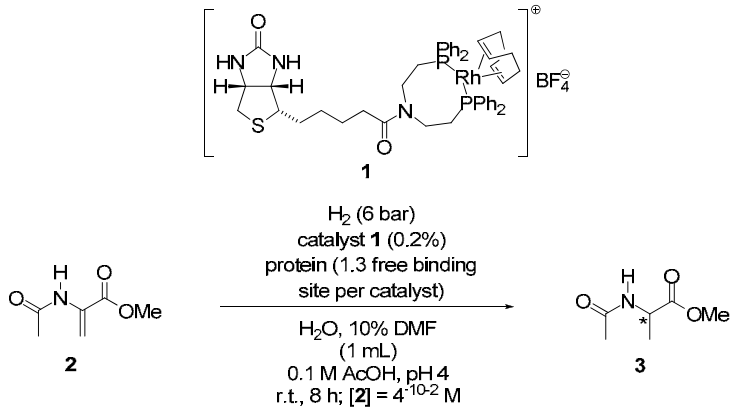
Involved: Y. Fu, F. Hollmann, N. Jiao, A. Maichele, P. Maiwald, M. Maywald, R. Mondiere, J.-P. Peyralans, A. Pletsch, J. Podtetenieff, B. Rasmussen, M. Rentzsch, A. Taglieber

Objective: Enzymes are capable of catalyzing a wide variety of selective bond-forming reactions of interest in synthetic organic chemistry, but they cannot catalyze the majority of reactions in organic chemistry mediated by synthetic transition metal catalysts incorporating such metals as Pd, Pt, Rh, Ru, Au, etc., transformations that are often known to work even in aqueous medium. On the other hand, it has been known for a long time that a ligand/metal entity can be anchored to proteins covalently or non-covalently, providing a hybrid catalyst. Since there is no reason to believe that the particular environment around the newly introduced transition metal provided by the WT protein should already be ideal for the purpose at hand, e. g., high enantio- or regioselectivity of a given reaction of interest, we proposed in 2002 the idea of *directed evolution of hybrid catalysts*:

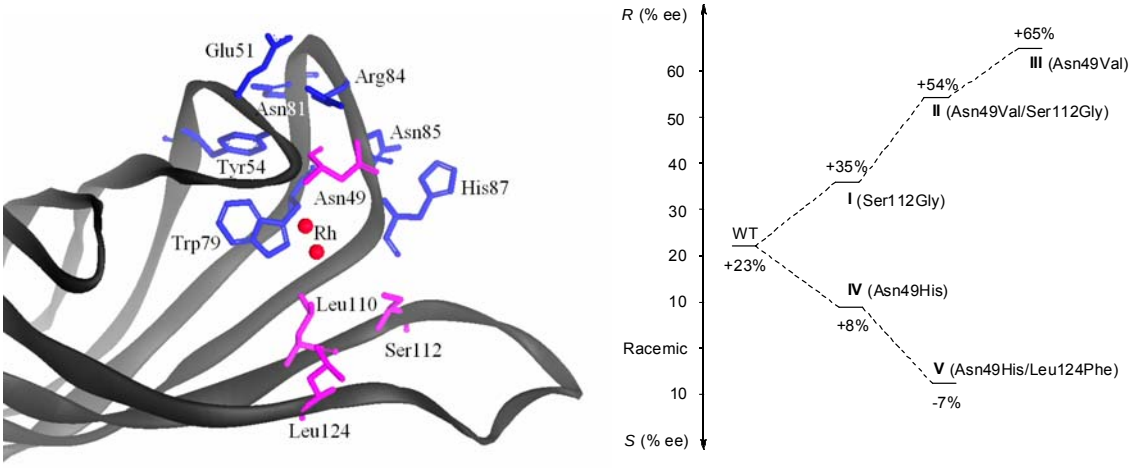


In the last Report 2002-2004 we outlined the technological problems in putting this concept into practice, which includes the necessity of *en masse* purification following the expression of thousands of mutant proteins (which is not necessary in normal directed evolution!). It also requires an excellent expression system which can be miniaturized and parallelized, producing enough protein for *en masse* bioconjugation and catalysis. This is a particularly sensitive issue, because synthetic catalysts are generally several orders of magnitude less active than enzymes. Finally, the host protein needs to be robust. During the last three years in this long-term project we followed two objectives: 1) To provide for the first time proof-of-principle of this novel way to tune a transition metal catalyst; and 2) To continue to develop platforms upon which the concept can be implemented in a practical manner.

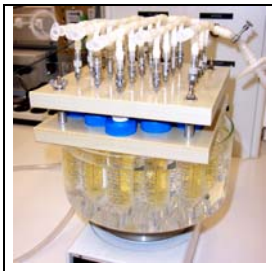
Results: Early on we opted for the Whitesides system, who had shown in 1978 that the biotinylated Rh/diphosphine complex **1** binds strongly in a non-covalent manner to avidin, as expected, providing a bioconjugate (hybrid catalyst) which catalyzes the asymmetric hydrogenation of *N*-acylamino acrylic acid (*ee* = 33-44%). We reasoned that since an efficient expression for avidin was not known, streptavidin should be the better choice for the host protein. Indeed, several expression systems for this protein had been reported, one of them being particularly efficient and providing enough material calculated to be necessary in each deep-well of appropriate microtiter plates. We also chose the ester **2** as the substrate (not the acid) because it can be extracted in a continuous manner.



Unfortunately, it was not possible to reproduce the published expression system for streptavidin production, which threatened the whole project. A molecular biologist in the group spent almost two years trying to develop a new expression system, but only a moderately improved version of a different known system could be implemented in the lab. This forced us to generate only very small mutant libraries, each fermentation being carried out in a 500 ml flask (instead of the planned 2-ml deep-wells!). This tedious procedure in combination with a ChemSpeed Accelerator SLT 100 Synthesizer allowed us to screen about 200 mutants per library. We modeled the Rh into the streptavidin cavity (two major conformations), and designed appropriate CAST libraries. In this way proof-of-principle was achieved after three iterative rounds of CASTing. In this "mini" directed evolution, work was terminated after reaching 65% *ee* in the product **3**:



Should a highly efficient and reproducible expression system for streptavidin be reported in the future, it will be logical to return to this platform for other reaction types such as hydroformylation (regio- and enantioselectivity!). In the meantime we have concentrated our efforts on alternative systems. One of them is tHisF as the host protein, a thermostable enzyme active in the biosynthesis of histidine. The development of a platform for the directed evolution based on this protein is almost finished. One of the crucial steps is *en masse* purification in parallized form on microtiter plates, which we have achieved by a simple heating procedure in a PCR instrument, a process which leads to the denaturization and precipitation of all protein material in the supernatant except that of the robust tHisF. Covalent bioconjugation is proceeding well.



19-fold fermentation unit

- 19 × 40 mL sterile LB-medium
- Inoculation with 0.5 mL preculture, incubation at 37 °C
- Induction with 40 µL 1 M IPTG at OD_{600} = 0.4 - 0.7
- Centrifugation after 6 h at 5000 rpm/10 min/4 °C in rotor for30 tubes
- Rinsing of cell pellet with 1 mL phosphate buffer (100 mM, pH = 7.8)
- *Resuspension in 400 µL phosphate buffer (10 mM, pH = 7.8 containing 2 mM DTT and 12.5 units/mL benzonase)*

24-deep-well plate

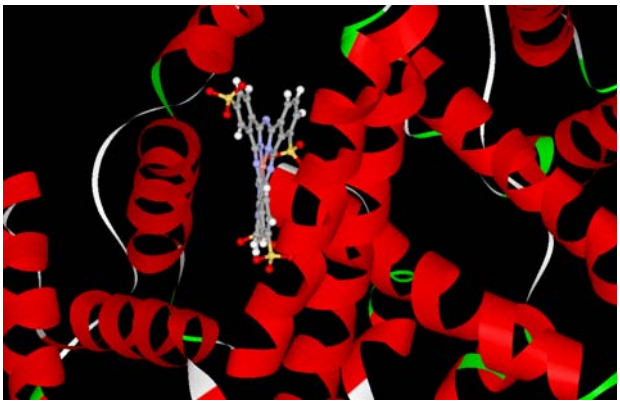
- 24 × 5 mL sterile LB-medium
- Corresponds to 576 cultures per incubator
- Inoculation with 0.1 mL preculture, incubation at 37 °C
- Induction with 5 µL 1 M IPTG at OD_{600} = 0.4 - 0.7
- Centrifugation after 6 h at 4000 rpm/40 min/4 °C using rotor for 4 plates
- Rinsing of cell pellet with 200 µL phosphate buffer (100 mM, pH = 7.8)
- Resuspension in 100 µL phosphate buffer (10 mM, pH = 7.8 containing 2 mM DTT and 12.5 units/mL benzonase)

↓

- Transfer into 96-well plates suitable for PCR-block
- 30 min heat-treatment at 72 °C in PCR-block (combined cell lysis and thermoprecipitation of *E. coli* host proteins)
- Centrifugation at 4000 rpm/120 min/4 °C in rotor for plates
- Collecting supernatant and freezing at –78 °C for storage

- Yield: approx. 3 mg in 200 µL Buffer
- Yield: approx. 0.3 mg in 40 µL Buffer
- Immediately before chemical modification: precipitation with 400 / 80 µL sat. ammonium sulfate, centrifugation, 2 × rinsing with 200 / 40 µL ammonium sulfate, resuspension of protein precipitate in phosphate buffer (10 mM, pH = 7.0).

We have also considered serum albumins such as BSA and HSA to which we have anchored site-selectively water-soluble sulfonylated Cu(II)-phthalocyanine complexes. The WT biojunjugate catalyzes some Diels-Alder reactions with amazingly high enantioselectivity (85-98% *ee*). In other cases the *ee*s are poor, which is not surprising. Since a good expression system is known for HSA, this may constitute another platform, although *en masse* protein purification still needs to be achieved.



Publications resulting from this research area: 349, 354, 513

External funding: EU

Cooperations: R. Sterner (Regensburg, DE)

2.1.5 Research Area "Homogeneous Hydrogenation/Hydrogenolysis of Coals" (M. W. Haenel)

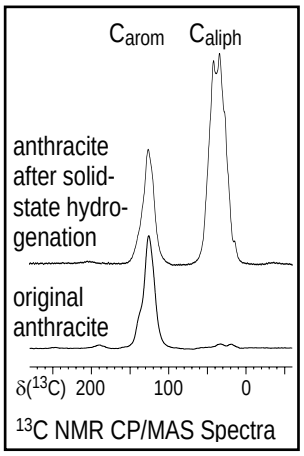
Involved: U.-B. Richter, A. Rufińska

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 catalyst. 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 plays major roles (solvent-mediated hydrogenolysis of strong C_{aryl}–C_{alkyl} bonds, hydrogen donation, 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. On the other hand, we previously have studied boranes and iodine as homogeneous catalysts and have found a first case of an extensive homogeneous hydrogenation of coal. Since the iodoboranes and molecular iodine used as catalysts vaporize at the reaction temperature at 350°C, even solid-state hydrogenation of high-rank coals with gaseous catalysts becomes possible. This opens new perspectives for coal liquefaction and the production of coke and tar.

Results: High-rank bituminous coals such as low-volatile bituminous coals (lvb coals, Ess- and Magerkohlen) and even anthracite were hydrogenated as fine powders suspended in toluene by using dialkyliodoboranes, iodohydroboranes, boron triiodide or iodine as catalysts (25 MPa hydrogen, 350°C, 12-24 h). Iododihydroborane simply could be generated *in situ* from sodium tetrahydridoborate and iodine ($NaBH_4 + I_2 \rightarrow NaI + H_2BI + H_2$). The most active catalyst so far was BI_3 forming presumably diiodohydroborane ($BI_3 + H_2 \rightarrow HBI_2 + HI$). The solid products obtained by hydrogenation were highly soluble in pyridine (up to 90%), which on the basis of studies of model

compounds is attributed to partial hydrogenation of polycyclic aromatic units and hydrogenolytic cleavages of C–C bonds. As shown by ^{13}C CP/MAS NMR solid state spectra, the hydrogenation resulted in a strong increase of aliphatic carbon atoms on the expense of the aromatic carbon atoms originally present in the coals. For instance the ratio C_{aliph}**:**C_{arom} increased up to 60**:**40 from 11**:**89 in the original Magerkohle or from 5**:**95 in the original anthracite, respectively. The strong increase of the aliphatic structure by homogeneous coal hydrogenation for the first time enabled high-rank bituminous coals (lvb coals such as Magerkohle) to be liquefied in subsequent conventional hydrocracking processes.

The swelling of coal by a solvent like toluene has been considered to be crucial that a dissolved catalyst is imbibed inside the coal particle together with the solvent. However, against all expectations lvb coals (Magerkohle) and anthracite were found to be hydrogenated extensively as powdered solids (particle diameters <0.08 mm) in the presence of catalytic BI_3. Under the reaction conditions BI_3 (b.p. 210°C) is gaseous and apparently can penetrate the coal particles without a solvent. The ratio C_{aliph}**:**C_{arom} 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 (compare the ^{13}C CP/MAS NMR solid state spectra). Hydrogenation with gaseous catalysts provides the possibility for manipulating the chemical properties of high-rank bituminous in the solid state in order to enhance their suitability to subsequent liquefaction or pyrolysis in coke ovens. Similarly as in the case of liquefaction, the coal rank is also a main parameter which determines the coal quality required for metallurgical coke-making. Coals having a content of volatile matter (loss in weight resulting from heating a coal sample to 900°C under specified conditions) less than 20% do not form a lumpy and strong coke needed for steel production in blast furnaces. The low content of volatile matter in anthracite (7.4%) and Magerkohle (11.2%) increased in the hydrogenated products up to 46 and 61%, respectively. This means that the volatile matter of such coals can be adjusted in a broad range by solid-state hydrogenation with gaseous catalysts. Hence lvb coals and anthracite, which have a poor baking ability and therefore form only a powdery coke, might be convertible into products similar to medium-volatile bituminous coals, i.e. valuable coking coals.



^{13}C NMR CP/MAS Spectra

The solid-state hydrogenation of anthracite with BI_3 was found to be dependent on the particle size. In the case of particle diameters 0.2–0.4 or 0.4–1 mm, the yield of the solid products decreased from 95 to 75% and 79% and the ratio C_{aliph}**:**C_{arom} from 65**:**35 to

26**:**74 and 30**:**70. This was compensated by the formation of gas (C_1–C_4) and some liquid. Obviously the hydrogenation is progressing from the periphery to the interior of the coal particle, and in the case of larger particles the periphery begins already to be degraded into gas and liquids before the interior is extensively hydrogenated. Applying less severe reaction conditions, it should be possible to hydrogenate just the periphery of larger coal particles, in order to generate an outer shell of hydroaromatic structures. On pyrolysis, the hydrogenated shell might be able to cake the particles forming a solid lumpy coke (compare the Scheme). Expensive hydrogen is saved, if one does not need to hydrogenate the whole coal particles.

Future directions: Worldwide 500 x 10^6 t a^{-1} coal are pyrolysed to produce 350 x 10^6 t a^{-1} metallurgical coke. In view of the limited supply of high-quality coking coals, solid-state hydrogenation of non-coking coals such as lvb coals and anthracites with gaseous catalysts appears to become a promising chemical tool, by which the caking and coking ability of these coal might be enhanced. Such a chemical manipulation of an important property in solid coals is a “dream reaction” in coal chemistry and therefore its further investigation, the improvement of the catalyst activity and mechanistic studies on model compounds shall be main topics of our future research.

Publications resulting from this research area: 282, 283, 284, 396

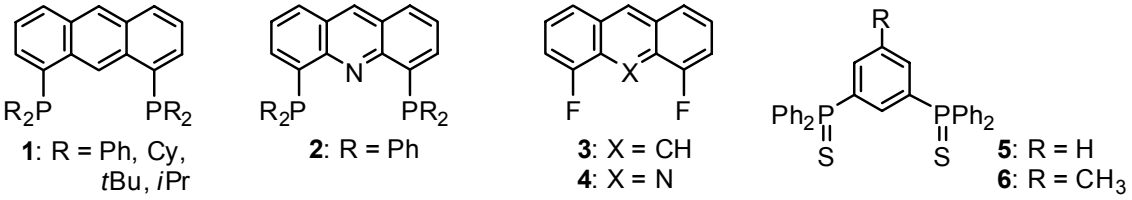
External funding: none

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

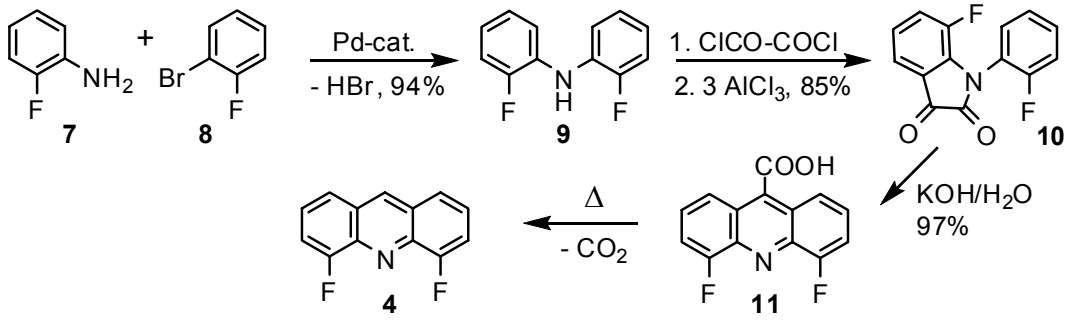
2.1.6 Research Area "Development of Thermostable Homogeneous Catalysts" (M. W. Haenel)

Involved: E. Wöstefeld, F. Sedlatzek, C. Wirtz (NMR), B. Gabor (NMR), B. Spliethoff (electron microscopy)

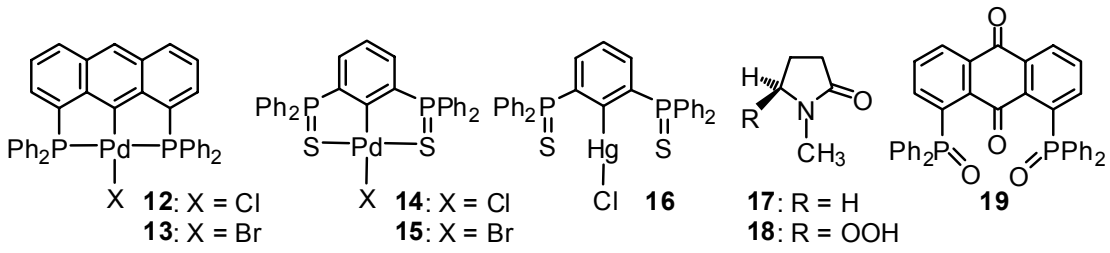
Objective: Thermally robust homogeneous catalysts have 3 major advantages: 1) catalytic conversion of less reactive substrates, for which the kinetics require high temperatures; 2) extension of homogeneous catalysis to endothermic processes, for which the thermodynamics require high temperatures; 3) facile catalyst separation by distillation of educts 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** and recently we investigated also the SCS-pincer ligand **5** (the methyl compound **6** has been reported by a Japanese group in 2003). Ligands **1** and **2** are accessible in high yields from 1,8-difluoroanthracene **3** and 4,5-difluoroacridine **4** by nucleophilic substitution with alkali metal phosphides and similarly **5** was prepared from commercial 1,3-fluorobenzene with potassium diphenylphosphide and treatment with sulphur.



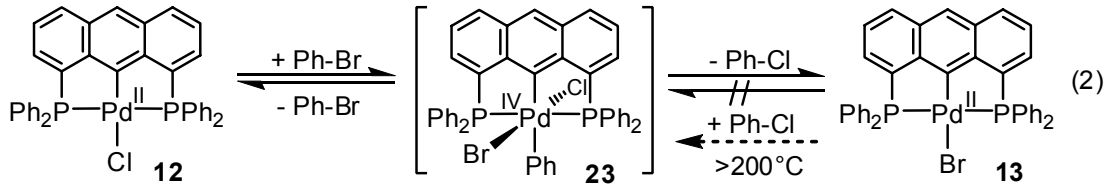
Results: Whereas 1,8-difluoroanthracene **3** could be prepared by an efficient three-step synthesis from commercial 1,8-dichloro-9,10-anthraquinone, our previous seven-step synthesis of 4,5-difluoroacridine **4** was laborious and not very efficient in one step. By using modern Pd-catalyzed C–N coupling 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 all 4 steps. We are trying to replace the use of 3 equivalents $AlCl_3$ in the conversion of **9** into **10** by a catalytic alternative. The new synthesis makes studies on acriphos complexes a lot easier.



After we previously had investigated mainly anthraphos iridium and rhodium complexes with regard to C–H activation, our research of the past 2 years was concerned mainly with the anthraphos and SCS pincer PdCl complexes **12** and **14** and their roles as catalysts in C–C coupling reactions. Both **12** and **14** are catalysts for the *Mizoroki-Heck* reaction of bromobenzene **20** and *n*-butyl acrylate **21** to form *n*-butyl *E*-cinnamate **22** in high yields [NaOAc or Na_2CO_3 as base, NMP **17** or DMA, 140°C, TON up to 76000, eq. (1)], but no reaction occurred with chlorobenzene. The reaction solutions maintained their yellow colour of the palladium complexes or changed just to brownish-yellow. At the end of the reactions, the anthraphos and SCS pincer PdBr complexes **13** and **15** have been formed, as was shown by MS spectrometry.



In solution of NMP **17** the PdCl complex **12** and bromobenzene were slowly converted at 140°C into the PdBr complex **13** and chlorobenzene, but the back reaction was observed only above 200°C (eq. 2). This suggested that an octahedral Pd(IV) intermediate **23** might be involved. For a possible role of **23** in the catalytic cycle of reaction (1), one of the two halides has to dissociate in order to create a free site for the coordination of olefin **21**. The observation, that **12** and **14** showed catalytic activity only in highly polar solvents such as Pd(0)/R_3P, seemed to agree with the required dissociation of a halide.



On the other hand, the kinetics, which showed varying results in repeated experiments with sigmoid conversion-time curves or induction periods in some cases, and the mercury test seemed to support a mechanism via Pd(0) colloids. Addition of Hg(0) blocked of the activity of **12** and **14** and generally it is assumed that Hg(0) leads to poisoning of heterogeneous metal particles by amalgamation, but does not affect homogeneous cata-

lysts. To our surprise, the SCS pincer PdCl complex **14** was quickly converted by mercury at 140°C into the phenyl-HgCl compound **16** (see Fig.1), whereas the anthraphos PdCl complex **12** was stable against mercury even at 220°C. Studies by electron microscopy revealed that the anthraphos PdCl complex **12** contained traces of Pd(0) colloids

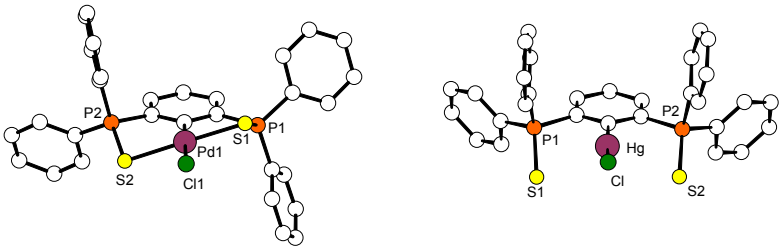
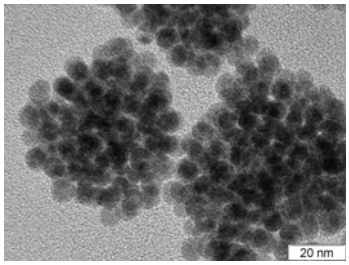


Fig. 1: X-ray structures of **14** (Pd–S1/S2: 2.32/2.33 Å) and **16** (Hg–S1/S2: 3.04/3.09 Å).

already from the synthesis, which were not removed by filtration through cellite and recrystallization, and in addition new Pd(0) nanoparticles were formed also under the conditions of reaction (1). The latter were remarkably small and uniform in size (3–10 nm, see the photograph) and both their formation from **12** and their stabilization at the stage of nanoparticles might be favored particularly by the amidic solvent NMP **17**. We suspect traces of the known NMP peroxide **18** being responsible for oxidative decomposition of the thermostable complex **12**, which via an anthracene-9,10-endoperoxide structure might form anthraquinone **19**, Pd(0) and HCl. On the other hand, stirring the solution of **12** in NMP with mercury at 25°C was found to be an efficient method to remove Pd(0) colloids. This solution of **12**, after being separated from mercury, did not catalyze reaction (1), but the halogen exchange (2) with bromobenzene occurred in this solution already at 25°C. If mercury was still present in the solution of **12** in NMP, neither reaction (1) nor (2) were observed at 140°C. Hence oxidative addition of bromobenzene to **12** appears to be possible already at 25°C, but is blocked or impeded in the presence of Hg(0) or Pd(0). The latter might be explained by the reduction potential of Hg(0) and Pd(0), preventing the formation of a Pd(IV) species. The *Mizoroki-Heck* reaction (1), however, is catalyzed solely by Pd(0) nanoparticles delivered in traces by very slow decomposition of **12** and **14**. A mechanism via a Pd(II)/Pd(IV) cycle involving an intermediate such as **23** must be ruled out.



Publications resulting from this research area: none

External funding: none

Cooperations: C. W. Lehmann (Mülheim/Ruhr, DE), R. Mynott (Mülheim/Ruhr, DE), B. Tesche (Mülheim/Ruhr, DE)

2.1.7 Research Area „Supercritical Carbon Dioxide as a Reaction Medium for Catalysis“ (W. Leitner, N. Theyssen)

Involved: A. Brinkmann, Z. Hou, C. Maul, T. Scholl, B. Spliethoff, C. Weidenthaler

Objective: We focus on the use of carbon dioxide as a reaction medium for catalytic reactions, whereby aerobic oxidations of alcohols using nano-structured palladium catalysts for fixed bed technology were investigated in particular.

Results: Recently, we have developed an efficient catalyst system for continuous-flow aerobic alcohol oxidation using palladium nanoclusters (range 2-3 nm) that were stabilized and immobilized in a liquid poly(ethylenglycol) (PEG) matrix in combination with supercritical carbon dioxide ($scCO_2$) as the mobile phase. In two successive studies we synthesized two entirely different kinds of stable Pd-nanoscale catalysts based on solid organic/inorganic hybrid materials as supports which allowed the use of simple and highly efficient fixed bed technology (Figure 1 and 2).

a) Silicates containing covalently anchored PEG-units (System A). The aforementioned palladium nanoclusters were deposited on the surfaces of i) pure silica, ii) silica with a non-covalently bound PEG film and iii) silica modified with covalently attached PEG chains of moderate length (average molecular weight = 750 g/mol). Significant differences were observed especially for the long term stability of the tested catalysts. The catalyst, which contains only adsorbed Pd clusters without any stabilizing matrix, shows the lowest initial activity, and a continuous and fairly rapid deactivation occurs leading to only 30% single pass conversion after 30 h on stream. The non-covalently bound PEG film leads to a slightly higher activity, but deactivation is still significant within the investigated time frame. In contrast, the covalently bound PEG chains lead to an excellent activity and stabilization of the Pd cluster: After 30 h a total turnover number of 1750 corresponding to an average turnover frequency of 58 h^{-1} was reached based on the total Pd-loading as the most conservative basis. Therefore PEG-modified silica are proven to effectively stabilize and immobilize palladium nanoparticles for their use as selective oxidation catalysts in combination with $scCO_2$ as reaction medium under mild conditions. This concept is expected to be of general utility for catalysis with supported metal nanoparticles.

b) Mesoporous silicates with 2,2’-dipyridylamine as a linker (System B). Pd-Nano-catalysts were also synthesized in situ by reduction of palladium acetate which was impregnated on 2,2'-dipyridylamine linker of mesoporous silica (pore diameter ~ 4 nm).

Such an arrangement should allow a uniform incorporation of the metal inside the pores and sufficiently hinder the unwanted agglomeration of the primary nanocrystals. It was found that the chosen reduction method (benzyl alcohol vs. hydrogen) controls the texture of the obtained palladium species resulting in significant differences in the catalytic activity. The hydrogen reduction yields medium-sized primary particles (ca 6 nm) of very regular shape together with a second highly dispersed Pd(0) phase. In contrast, the alcoholic reduction leads to a texture containing small primary crystallites (ca 2 nm) which conglomerate to larger units of about 25 nm size. A reasonable explanation for the much higher catalytic activity of the latter system might be the many different crystalline orientations in such ensembles. The resulting high number of accessible edges and corners provide many potential sites for catalytically active Pd(0)-centers. This concept might be of more general validity for nanoscale oxidation methods.

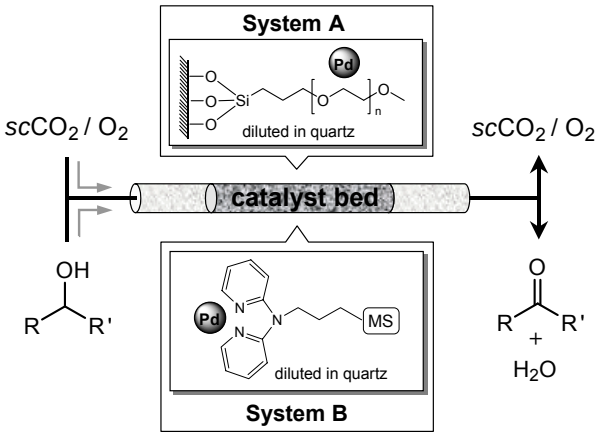


Figure 1. Continuous oxidation of alcohols with nano-structured Palladium fixed bed catalysts

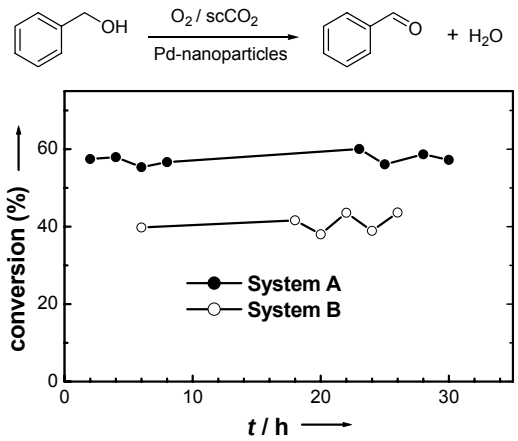


Figure 2. Continuous oxidation of benzyl alcohol with the systems **A** and **B**

Publications resulting from this research area: 77, 378, 461, 486, 487, 525

External Funding: BMBF joint project "NanoSelOx" (via RWTH Aachen)

Cooperations: M. Bühl (Mülheim/Ruhr, DE); W. Grünert (Bochum, DE); K. V. Klementiev (Hamburg, DE); W. Schmidt (Mülheim/Ruhr, DE); B. Tesche (Mülheim/Ruhr, DE).

2.1.8 Research area: "Novel Ruthenium Dihydrogen Complexes and their Application in Catalysis" (W. Leitner, N. Theyssen)

Involved: M. H. G. Prechtl, D. Stelmaszyk, W. Wisniewski, K. Wobser

Objektive: As a part of our ongoing research project in the field of nonclassical ruthenium hydride complexes we are interested in catalytic applications of this fascinating compound class. Ruthenium dihydrogen complexes have a great potential as catalysts for CH-activation, especially for H/D-exchange and (de)hydrogenation.

Results: We synthesized the novel dihydrogen complexes [$RuH_2(H_2)$(*dtbpmp)*] **1** and [$RuH_2(H_2)$(*dtbpoet)*] **2** and characterized them by NMR and FT-IR analysis. The H-H-distances were calculated from T_1 relaxation time measurements. They are clearly different from classical polyhydride complexes (1.8 - 2.5 Å, free H_2: 0.74 Å) and lie in the range of typical (0.8 - 1.0 Å) and elongated (1.1 - 1.5 Å) dihydrogen complexes. DFT-calculations (B3LYP / DZP) are in agreement with the experimental data (Figure 1).

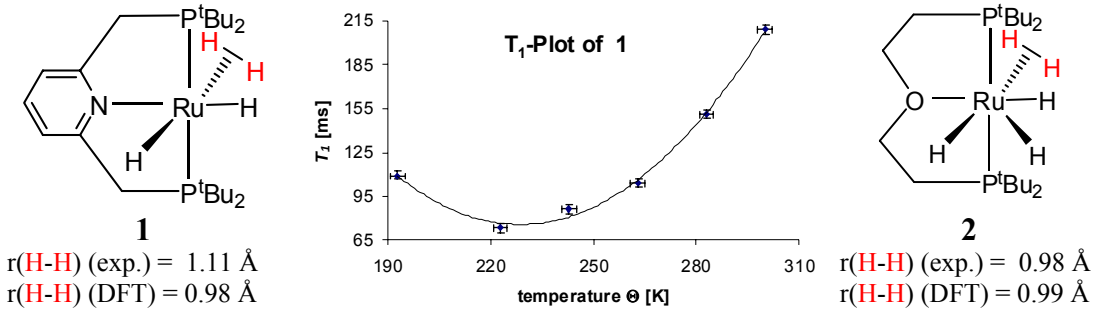


Figure 1. Characterization of r(H-H) in complexes **1** and **2** by T_1(min)-measurements and DFT-calculations

The nonclassical ruthenium hydride complex **1** is an effective catalyst precursor for the H/D exchange reaction between aromatic substrates and D_2O as the cheapest deuterium source at unprecedented mild conditions. The incorporation occurs with aromatic and heteroaromatic substrates and shows significant chemo- and regioselectivity in certain cases (Figure 2).

Other applications showed the potential of complex **1** as an effective catalyst precursor for the dehydrogenation of aliphatic and benzyl alcohols resulting in the corresponding homoesters (Figure 3). Likewise secondary alcohols are transformed into the corresponding ketones without the need for a stoichiometric hydrogen acceptor molecule.

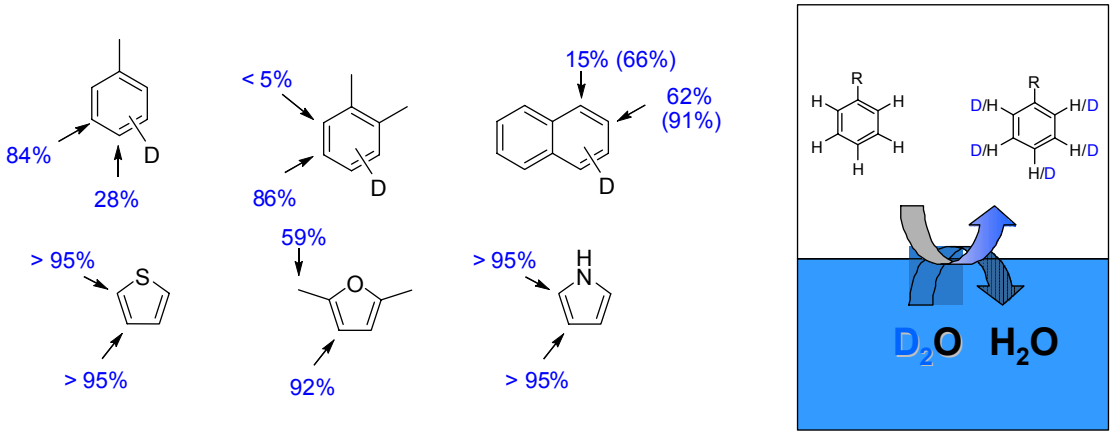


Figure 2. H/D-Exchange: Ruthenium complex **1** (1 mol-%) catalyzes deuteration of arenes and heterocycles with D_2O at 50 °C (75 °C) within 3 days. Conversions are assigned for each position in the figure.

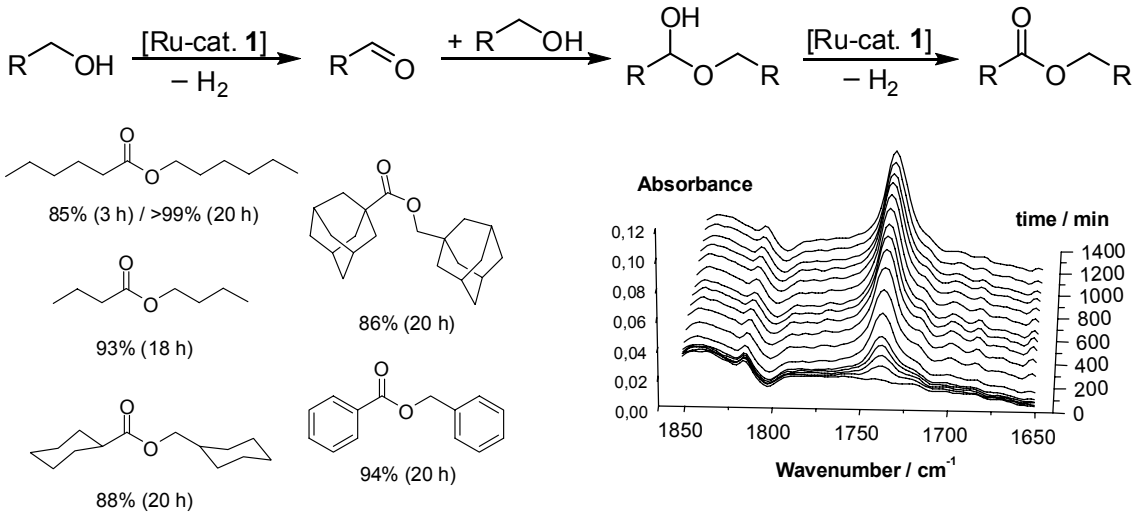


Figure 3. Dehydrogenation of alcohols: Ruthenium complex **1** (1 mol-%) catalyzes the conversion of primary alcohols into esters and molecular dihydrogen under an flow of argon in toluene under reflux. The ester formation can be monitored by IR-Operando analysis of the increasing ν(C=O) band at 1740 cm^{-1} (here: formation of hexyl hexanoate).

Publications resulting from this research area: 502, 503

External Funding: Fonds der Chemischen Industrie, German-Israeli Project Cooperation (DIP G7.1)

Cooperations: Y. Ben-David (Rehovot, IL); M. Hölscher (Aachen, DE); D. Milstein (Rehovot, IL); C. Minnich (Aachen, DE); R. J. Mynott (Mülheim/Ruhr, DE).

2.2 Department of Homogeneous Catalysis

Director: Benjamin List (born 1968)
Publications: 74, 110, 166, 200, 201, 261, 288, 297, 312, 313, 314, 325, 326, 332, 373, 398, 473, 475, 479, 484, 485, 491, 492, 493, 549, 550, 554, 555

Further group leaders:

Martin Klußmann (born 1974)
joined the Institute in January 2007
Publications: 411, 412, 467

Klaus Jonas (born 1941)
retired from the Institute in December 2006
Publication: 413

Klaus-Richard Pörschke (born 1949)
Publications: 2, 35, 359, 379, 413, 428, 429

Curriculum Vitae: Benjamin List

1968	Born in Frankfurt, Germany
1993	Chemistry Diplom, Free University Berlin
1997	PhD, University 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 University of Cologne
2005	Director at the Max-Planck-Institut für Kohlenforschung

Awards and Honors

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
2007	OBC Lecture Award
2007	AstraZeneca Research Award in Organic Chemistry
1999-2007	ca. 50 Plenary and Name Lectureships

Special Activities

2005-	Co-Editor of *Synfacts* (Thieme)
2005-2011	Coordination of the DFG Priority Program (SPP1179) “Organocatalysis”
2007-	Member of the editorial advisory board of the Beilstein Journal of Organic Chemistry

Research in the Department of Homogeneous Catalysis

The department primarily focuses on the development of new catalysis concepts within the areas of organocatalysis, transition metal catalysis, and, to some extent, biocatalysis. We explore new catalysts, expand the substrate scope of certain catalytic reactions, apply asymmetric catalysis in natural product synthesis and pharmaceuticals synthesis, and study mechanisms of homogeneous catalytic reactions (B. List, K. R. Pörschke, M. Klußmann).

After several years without leader, Professor Benjamin List became the director of the Department of Homogeneous Catalysis in 2005. Since then the department has grown significantly from ca. 15 members to currently more than 40 members overall. In 2006 Professor Klaus Jonas retired from the Institute, and in 2007 Dr. Martin Klußmann has joined the department as a junior group leader.

The group of Professor List continues to develop organocatalysis as a new methodology complementing the already more advanced fields of biocatalysis and transition metal catalysis as a third approach to asymmetric catalysis. The catalysis with small organic molecules, where an inorganic element is not part of the active principle, has become a highly dynamic area in chemical research. The field is still rather young and currently undergoes a massive growth (Figure 1). The List group 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. Although to a much lesser extent, the group also develops new concepts in the areas of transition metal catalysis and biocatalysis.

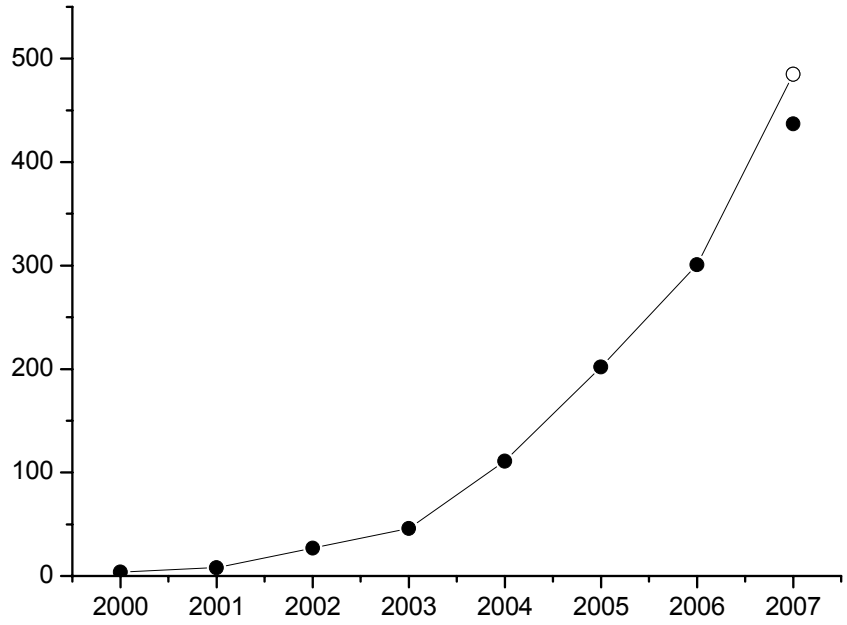


Figure 1. Number of publications using the term „organocatalysis“ in the title or abstract since the year 2000 ([●] from SciFinder as of November 21st; second value in 2007 [○] has been predicted).

Research in the laboratory of Professor Pörschke aims at a deeper mechanistic understanding of transition metal catalyzed reactions. Priority is given to the investigation of the structure and reactivity of organometallic compounds relevant to catalytic cycles. A further interdisciplinary project is directed at the investigation of the solid state phase properties of organometallic compounds.

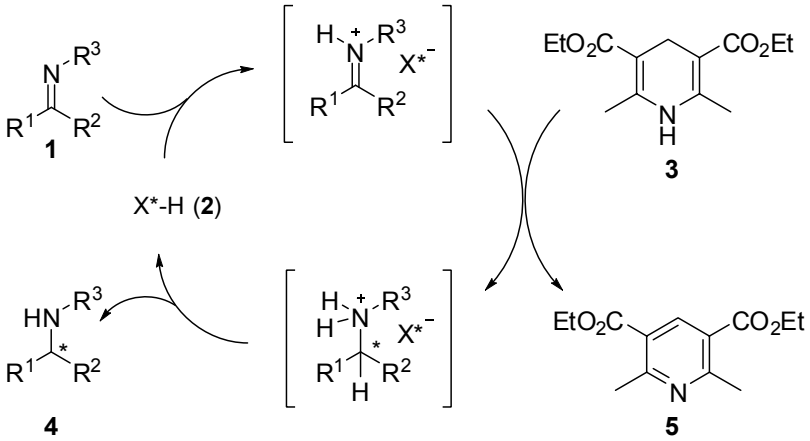
The group of Dr. Klußmann develops new atom economic catalytic reactions and studies the evolution of biological homochirality from a presumably racemic primordial earth.

2.2.1 Research Area „Organocatalytic Reduction of Imines / Reductive Amination" (B. List)

Involved: S. Hoffmann, A. Majeed Seayad, M. Nicoletti

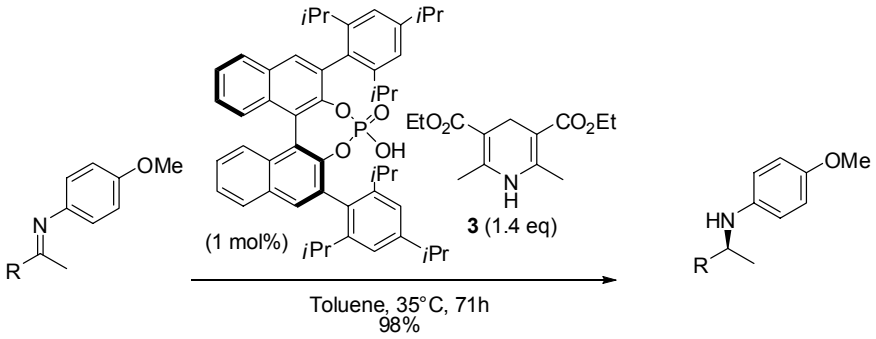
Objective: Hydrogenation is arguably the most important catalytic reaction for the synthesis of enantiomerically pure compounds and is crucial for all living organisms.
While effective and industrially relevant catalytic asymmetric hydrogenations and transfer hydrogenations of olefins and ketones have been developed, the corresponding imine reductions although potentially highly useful for the synthesis of enantiomerically pure amines, are less advanced. Asymmetric versions have been realized that require metal-catalysts or the stoichiometric use of metal hydrides. However, the removal of metal-impurities from the reaction product can be difficult but is required in the production of pharmaceuticals because of toxicity concerns.
The aim of this project is the development of a metal-free highly enantioselective transfer hydrogenation of imines. Further, this methodology should be expanded to a reductive amination including a dynamic kinetic resolution of α-branched aldehydes.

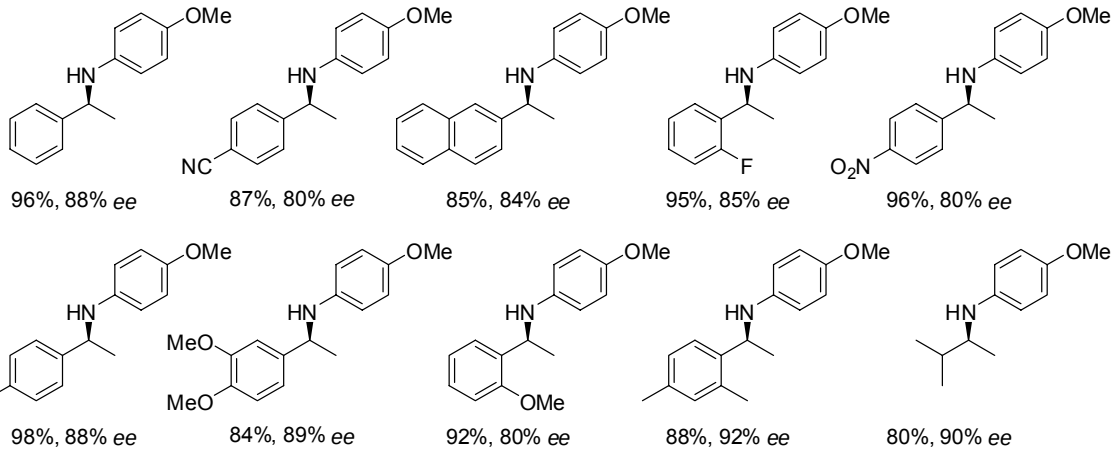
Results: Relatively strong chiral phosphoric acids were recently introduced by Akiyama et al. and Terada et al. in pioneering studies as new small organic molecule catalysts for asymmetric addition reactions to aldimines. Inspired by these studies and the observation that imines are reduced with Hantzsch esters in the presence of achiral Lewis- or Brønsted acid catalysts we envisioned a catalytic cycle which is initiated via ketimine (**1**) protonation from a chiral Brønsted acid (**2**) catalyst.



The resulting iminium ion pair, which may be stabilized via hydrogen bonding, is chiral and its reaction with the Hantzsch dihydropyridine **3** could give an enantiomerically enriched amine **4** and pyridine **5**.

As a proof of principle, a commercially available phosphoric acid catalyst clearly showed turnover, giving the product with low enantioselectivity (6% *ee*). Encouraged by these results we synthesized and screened a variety of chiral phosphoric acid catalysts and studied different reaction conditions in the presence of Hantzsch ester **3**. The highest enantioselectivities (up to 93% *ee*) were achieved with only 1 mol% of the new sterically congested phosphoric acid catalyst TRIP. The optimized conditions have been applied to several substituted aromatic ketimines and one aliphatic imine with good to excellent results.

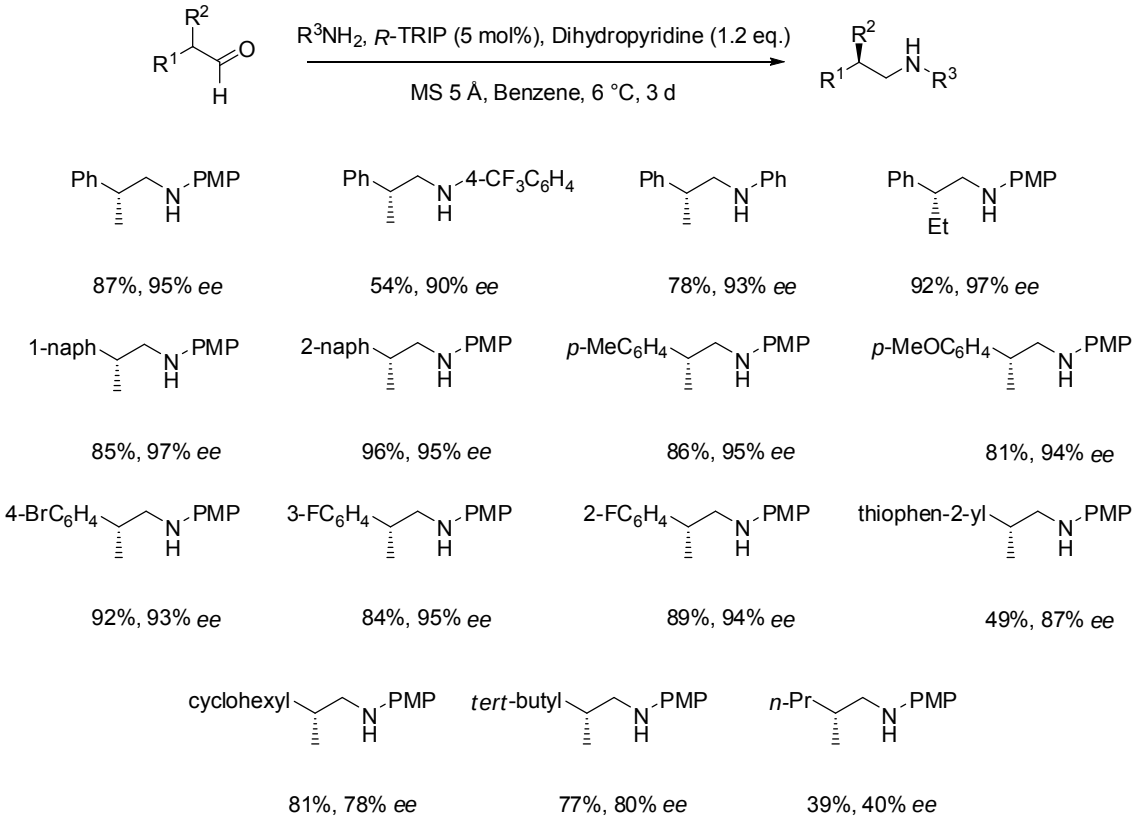




During the preparation of this manuscript a similar study by the group of Rueping using Akiyama's phosphoric acid catalyst appeared.

We hypothesized that under our reductive amination conditions a α-branched aldehyde substrate would undergo a fast racemization in the presence of the amine and acid catalyst via an imine/enamine tautomerization. The reductive amination of one of the two imine enantiomers would then have to be faster than that of the other, resulting in an enantiomerically enriched product via a dynamic kinetic resolution. Although selected asymmetric reductive aminations of ketones to give chiral, α-branched amines

in an enantioface-differentiating process have been reported, the corresponding reactions of α-branched aldehydes to give enriched β-branched amines were unknown. Our optimized protocol was used for the direct reductive amination of both aromatic as well as aliphatic α-branched aldehydes giving good to excellent results.



In summary we have developed an efficient organocatalytic asymmetric ketimine reduction using the chiral phosphoric acid derivative TRIP in the presence of a commercially available dihydropyridine. Additionally, we have reported an efficient enantioselective reductive amination of α-branched aldehydes via dynamic kinetic resolution. Our processes are broad in scope and both aromatic and aliphatic aldehydes can be used.

Publications resulting from this research area: 74, 288

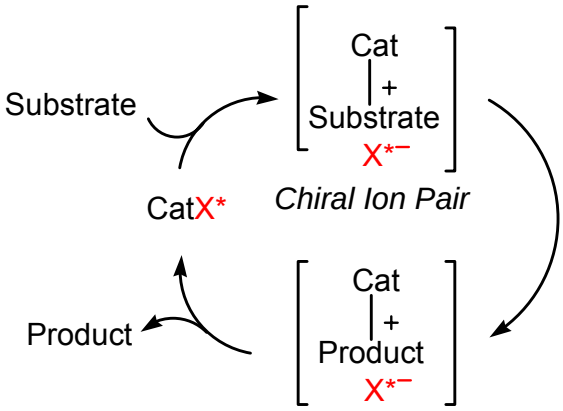
External funding: DFG SPP 1179

Cooperations: none

2.2.2 Research Area „Asymmetric Counteranion-Directed Catalysis (ACDC)" (B. List)

Involved: S. Mayer, N. Martin, X. Wang

Objective: Most chemical reactions proceed via charged intermediates or transitions states. Such "polar reactions" can be influenced by the counterion. Although efficient asymmetric catalytic transformations involving anionic intermediates with chiral, cationic catalyst have been realized, analogous versions of *inverse* polarity with reasonable enantioselectivity have been elusive, despite several attempts. The aim of this project was to develop a catalytic salts consisting of an achiral but catalytic cation and a chiral phosphate anion for highly enantioselective transformations.

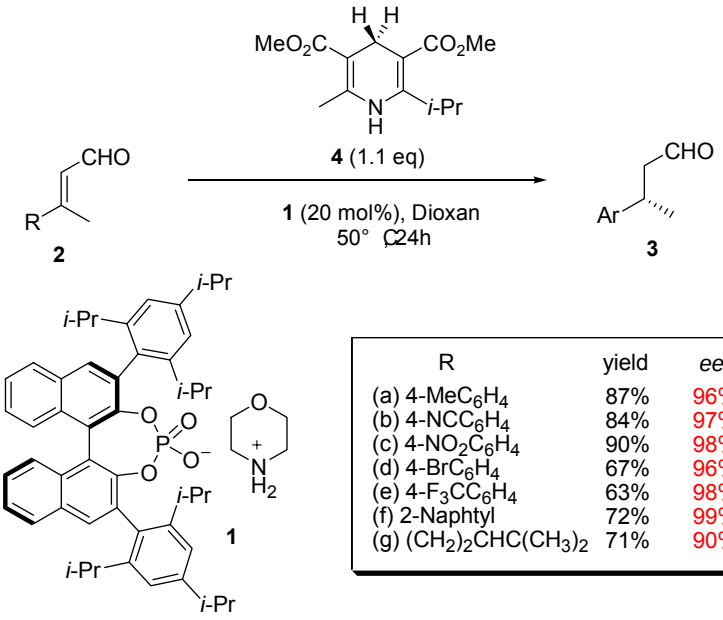


Asymmetric, Counteranion-Directed Catalysis (ACDC)

Results: Recently, a metal-free biomimetic transfer hydrogenation of α,β–unsaturated aldehyds was discovered in our research group and independently by MacMillan and coworkers. The reaction is catalyzed by salts of chiral amines and proceeds via iminium ions intermediates in the presence of Hantzsch ester as hydrogen source. Intrigued by the observation of a strong counteranion effect on the yield and enantioselectivity and inspired by the recent introduction of chiral phosphates as asymmetric Brønsted acid catalysts, we hypothesized that catalytic salts of achiral amines and chiral phosphoric acids could induce asymmetry in the process.

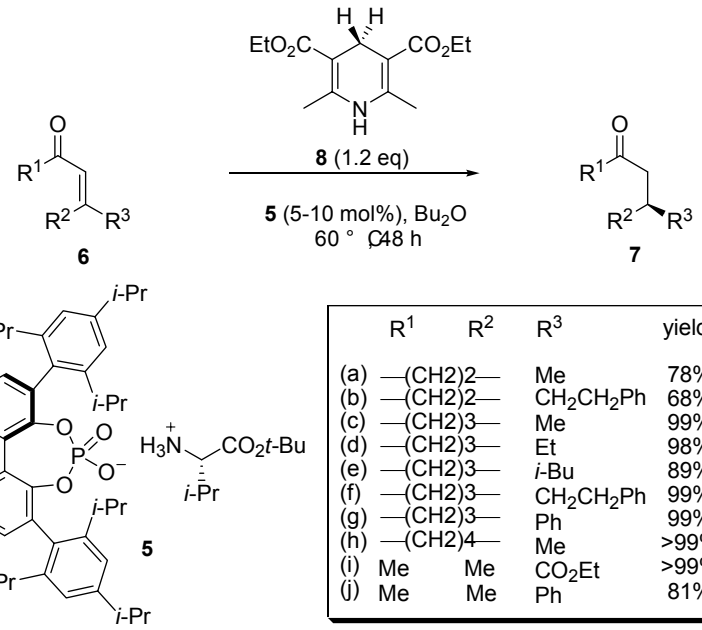
After an extensive screening of several organic salts made of commercially available primary and secondary amines with chiral binaphthol-derived phosphoric acids we found that upon treating trisubstituted α,β-unsaturated aldehydes **2** with a catalytic

amount of morpholine salt **1** and dihydropyridine **4**, the corresponding saturated aldehydes **3** were obtained in high yields and enantioselectivities.



R	yield	*ee*
(a) 4-MeC_6H_4	87%	96%
(b) 4-NCC_6H_4	84%	97%
(c) 4-$NO_2C_6H_4$	90%	98%
(d) 4-BrC_6H_4	67%	96%
(e) 4-$F_3CC_6H_4$	63%	98%
(f) 2-Naphtyl	72%	99%
(g) $(CH_2)_2CHC(CH_3)_2$	71%	90%

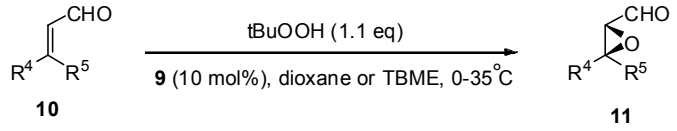
Next, the concept was extended to the transfer hydrogenation of α,β-unsaturated ketones **6** in the presence of a catalytic amount of primary amine salt **5** and dihydropyridine **8** to form the corresponding saturated ketones **7** in high yields and enantioselectivities.

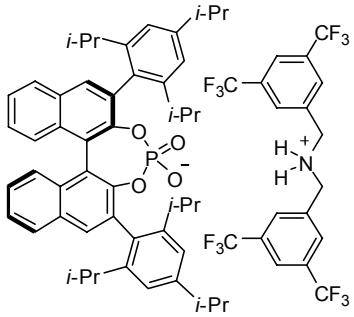


	R^1	R^2	R^3	yield	*ee*
(a)	—(CH2)2—		Me	78%	98%
(b)	—(CH2)2—		CH_2CH_2Ph	68%	96%
(c)	—(CH2)3—		Me	99%	94%
(d)	—(CH2)3—		Et	98%	96%
(e)	—(CH2)3—		*i*-Bu	89%	95%
(f)	—(CH2)3—		CH_2CH_2Ph	99%	96%
(g)	—(CH2)3—		Ph	99%	84%
(h)	—(CH2)4—		Me	>99%	97%
(i)	Me	Me	CO_2Et	>99%	83%
(j)	Me	Me	Ph	81%	69%

Catalytic enantioselective epoxidations of olefins have traditionally defined the state of the art in asymmetric catalysis. Very recently, equally elegant and useful

organocatalytic asymmetric epoxidations of α,β-unsaturated aldehydes via iminium catalysis have been developed by Jørgensen et al. We have now identified a new salt (**9**) formed from an achiral ammonium ion and a chiral phosphate anion that catalyzes the highly enantioselective epoxidation of disubstituted aromatic α,β-unsaturated aldehydes (**10a-m**) and also gives excellent enantioselectivities with trisubstituted α,β-unsaturated aldehydes (**10n-q**), which previously have been illusive substrates for any type of highly enantioselective epoxidation.





9

	R^4	R^5	yield	*dr*	*ee*
(a)	Ph	H	75%	>99 : 1	91%
(b)	2-naphthyl	H	76%	>99 : 1	95%
(c)	1-naphthyl	H	70%	98 : 2	91%
(d)	4-Ph-C_6H_4	H	78%	>99 : 1	91%
(e)	4-Me-C_6H_4	H	65%	>99 : 1	92%
(f)	3-Me-C_6H_4	H	68%	>99 : 1	92%
(g)	2-Me-C_6H_4	H	62%	97 : 3	90%
(h)	4-Cy-C_6H_4	H	60%	>99 : 1	90%
(i)	4-F-C_6H_4	H	78%	>99 : 1	93%
(j)	3-F-C_6H_4	H	82%	>99 : 1	84%
(k)	2-F-C_6H_4	H	69%	98 : 2	91%
(l)	4-Cl-C_6H_4	H	84%	>99 : 1	87%
(m)	4-Br-C_6H_4	H	80%	>99 : 1	87%
(n)	Me	Me	83%	95 : 5	94%
(o)	Et	Et	85%	--	94%
(p)	--$(CH_2)_5$--	Me	75%	--	90%
(q)	$(CH_2)_2CHC(CH_3)_2$		95%	72 : 28	76%(*trans*) 92%(*cis*)

In summary, our ACDC concept has been successfully applied to enantioselective organocatalytic conjugate reductions and epoxidations of α,β-unsaturated carbonyl compounds. We are currently extending the concepts to other areas, including transition metal catalysis.

Publications resulting from this research area: 325, 326

External Funding: DFG SPP 1179

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

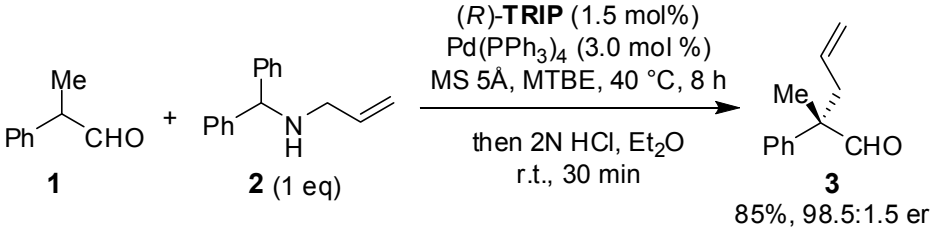
2.2.3 Research Area "Asymmetric Direct α-Allylation of Aldehydes" (B. List)

Involved: S. Mukherjee

Objective: The enantioselective construction of all-carbon quaternary stereogenic centers is a challenging task in organic synthesis. Asymmetric alkylations of α-branched carbonyl compounds constitute an attractive solution to this problem and the palladium-catalyzed asymmetric allylic alkylation has proven particularly useful. However, the asymmetric α-allylation of α-branched aldehydes still remains a considerable challenge. Although recently a few methods have been described for the direct catalytic asymmetric α-allylation of aldehydes, none of these methods allow for the formation of quaternary stereogenic centers. The aim of this project was to develop an efficient and highly enantioselective direct α-allylation of α-branched aldehydes.

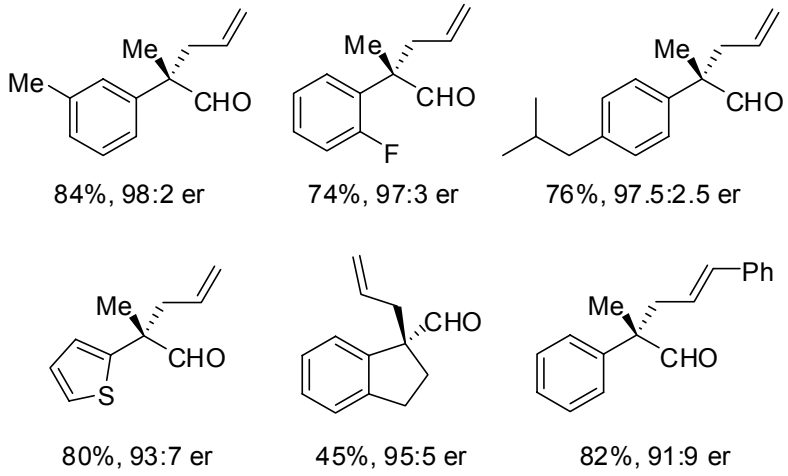
Results: We have recently introduced the concept of asymmetric counteranion direct catalysis (*ACDC*) as a new tool in asymmetric catalysis and demonstrated its potential in the enantioselective transfer hydrogenation and the asymmetric epoxydation of enals. However, the application of *ACDC* was so far limited in the domain of organocatalysis. We reasoned that this concept could be applied to organometallic systems as well. To prove this principle we studied the enantioselective direct α-allylation of α-branched aldehydes.

We found that when 2-phenyl propionaldehyde **1** was treated with *N*-benzhydryl allyl amine **2** as the allylating agent in the presence of $Pd(PPh_3)_4$ (3 mol%) and the phosphoric acid co-catalyst **TRIP** (1.5 mol%) under optimized reaction conditions (MS 5 Å, MTBE, 40 °C, 8 h), α-allylated aldehyde **3** was obtained in 85% yield with 98.5:1.5 er after hydrolysis.



We also studied the scope of this enantioselective direct aldehyde α-allylation reaction. A number of differently substituted phenyl and other 2-aryl propionaldehydes were employed as substrates and the products were obtained in good yields (71-89%) and er (93:7 to >98:2). The allylated product of 2,3-dihydro-1-indanone derived aldehyde was

obtained in high er but in moderate yield. Substitution at the 3-position of the allyl group has also been investigated with good results. Currently we are working on to extend the scope of *ACDC* to other metal-catalyzed reactions.



84%, 98:2 er 74%, 97:3 er 76%, 97.5:2.5 er

80%, 93:7 er 45%, 95:5 er 82%, 91:9 er

Publications resulting from this research area: 485

External Funding: none

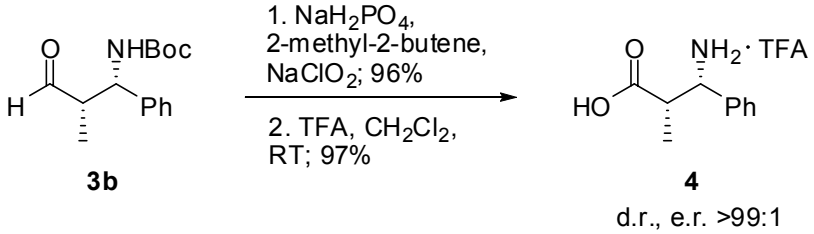
Cooperations: none

2.2.4 Research Area „Proline-Catalyzed Mannich Reaction of Aldehydes with *N*-Boc Imines" (B. List)

Involved: J. W. Yang, M. Stadler

Objective: The catalytic asymmetric Mannich reaction is arguably the most useful approach to synthesize chiral β-amino carbonyl compounds. We discovered a proline-catalyzed version of this powerful reaction. Originally, the proline-catalyzed Mannich reaction required the use of anilines as the amine component. Since the N-substituent is usually employed as protecting group, it should be easily removable after the reaction has taken place. However, the removal of the most commonly used *p*-methoxyphenyl (PMP) group from nitrogen often requires drastic oxidative conditions involving harmful reagents such as ceric ammonium nitrate (CAN) that are not compatible with all substrates. We have now employed the *tert*-butoxycarbonyl (Boc)-group as an easily removable protecting group in order to overcome this drawback. The aim of this project has been to develop the efficient, practical, and highly stereoselective Mannich reaction of *N*-Boc imines.

Results: We found the reaction of unmodified aldehydes and ketones with simple preformed aromatic *N*-Boc-imines including electron-poor and electron-rich imines to give chiral β-amino aldehydes and ketones in high levels of diastereo- and enantioselectivities. For instance, when the benzaldehyde-derived *N*-Boc-imine **2a** (R_3 = Ph) was treated with a two-fold excess of *n*-hexanal in the presence of 20 mol% (*S*)-proline in CH_3CN at 0 °C, the desired product **3a** precipitated and could be collected by filtration (**Fig. 1**) in 84% yield with extremely high diastereoselectivity (>99:1 *dr*) and enantioselectivity (>99:1 *er*). Similarly with most other substrate combinations, the products of the reaction either precipitate from the reaction mixture and can be collected *via* filtration, or are obtained by an aqueous workup/organic extraction process as stable, crystalline solids. Purification of the products can be achieved by trituration with cool hexanes. The *N*-Boc-imine derived Mannich products **3a-g** can readily be converted into the corresponding α,β-branched-β-amino acids **4** ($\beta^{2,3}$-amino acids).



3b **4**

d.r., e.r. >99:1

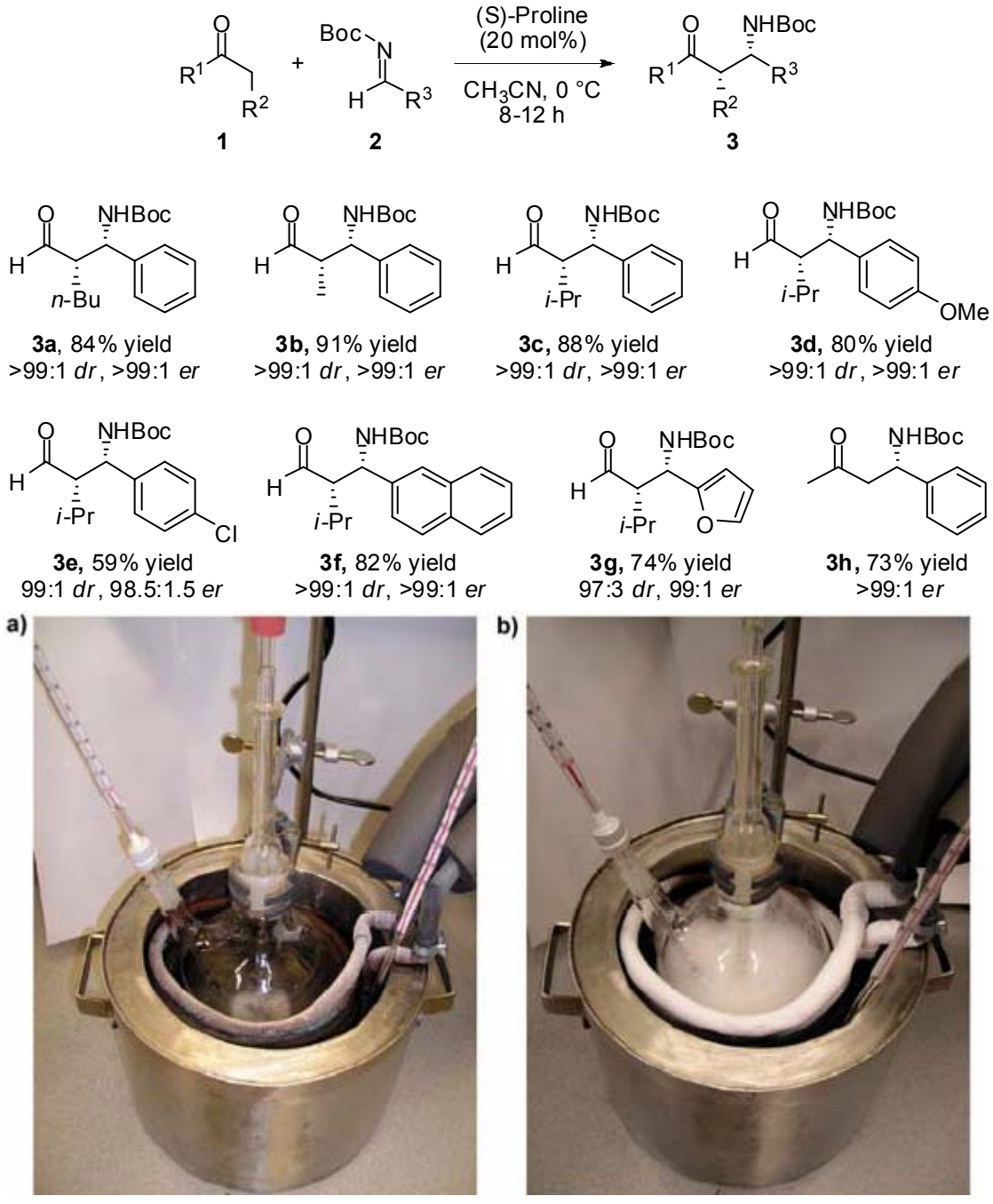


Fig. 1: a) Reaction vessel after mixing all compounds; b) Precipitated product after reaction

In summary, we have developed a remarkably efficient and enantioselective variant of the proline-catalyzed Mannich reaction. In our new procedure, aldehydes react with preformed *N*-Boc-imines in the presence of proline to give the corresponding β-amino aldehydes in excellent diastereoselectivities and enantioselectivites.

Publications resulting from this research area: 549, 550

External Funding: none

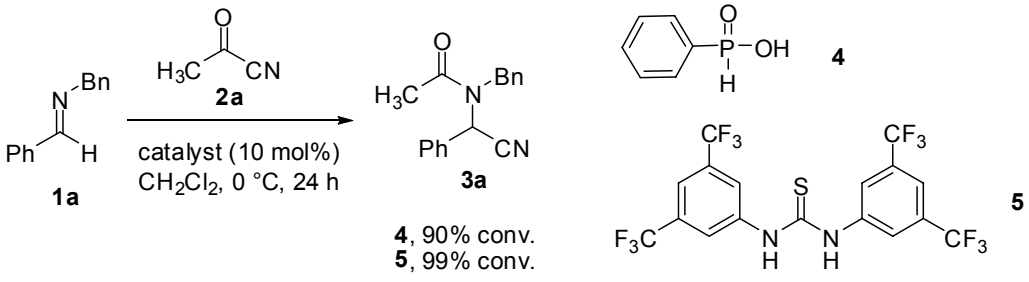
Cooperations: none

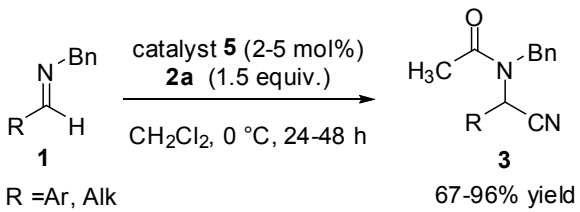
2.2.5. Research Area „Catalytic Acylcyanation of Imines" (B. List)

Involved: S. C. Pan, J. Zhou

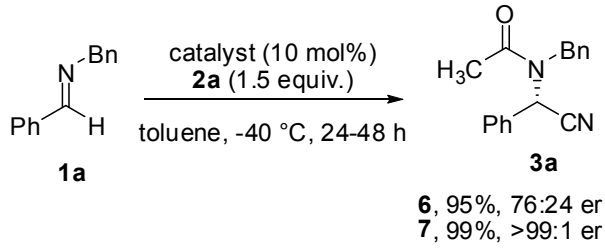
Objective: Discovered in 1850, the Strecker reaction has been identified as one of the most efficient methods for the preparation of α-amino nitriles, which are useful intermediates in the synthesis of α-amino acids. In recent years, considerable effort has been devoted toward the development of asymmetric Strecker reactions. Despite rapid progress in this field, volatile and highly toxic HCN has been used in most Strecker variants. On the other hand, acyl cyanides are less toxic and have already been used for the acylcyanation of carbonyl compounds. Surprisingly however, the reaction of acyl cyanides with imines has been significantly less investigated. The aim of this project was to develop a catalytic asymmetric and non-asymmetric acylcyanation of imines. We also intended to develop a three-component variant of the acylcyanation reaction.

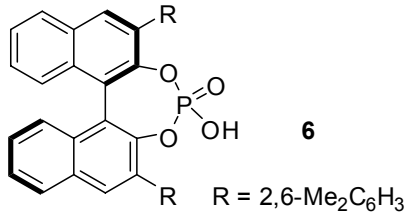
Results: Building upon the observations of Dornow and Lüpfert, we initially investigated triethyl amine as catalyst for the reaction of benzaldehyde derived imine **1a** with acetyl cyanide **2a**, however only 4% conversion to the product **3a** was obtained using dichloromethane as the solvent. Reasoning that in addition to base-catalysis, an acid catalyzed pathway should be possible as well, we next investigated different Brønsted acid catalysts to promote the reaction. In fact, moderately acidic phenyl phosphinic acid **4** gave good conversion at 0°C. Finally, hydrogen-bonding-type Schreiner thiourea catalyst **5** was identified to be the best catalyst for the reaction. Decreasing the catalyst loading from 10 mol% to 2 mol% essentially preserved the conversion (98%). With 2-5 mol% of catalyst **5**, the scope of this reaction was studied and 67-96% yield was obtained for different aliphatic and aromatic aldimines.

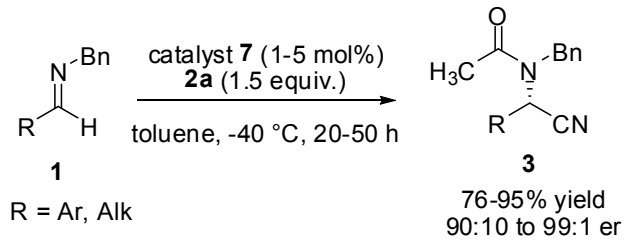


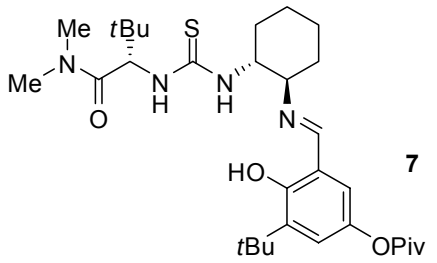


To develop an asymmetric version of this reaction, we initially prepared several chiral binol-derived phosphoric acid catalysts. However, while these catalysts gave *N*-acetylated amino nitrile product **3a** in high yields, enantioselectivities were only moderate. In the best case, the use of catalyst **6** led to **3a** with 79:21 er. We then prepared a range of chiral thiourea catalysts. Remarkably, catalyst **7** gave the product in essentially enantiomerically pure form. In the further optimization, we tried to lower the catalyst loading and found that 1 mol% of catalyst **7** is sufficient to give the product in high yield as well as with excellent enantioselectivity.

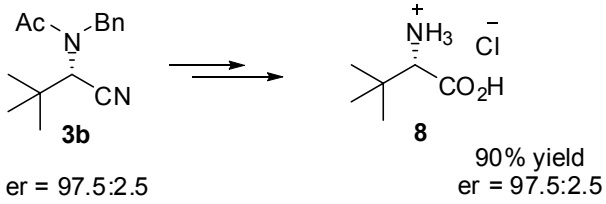






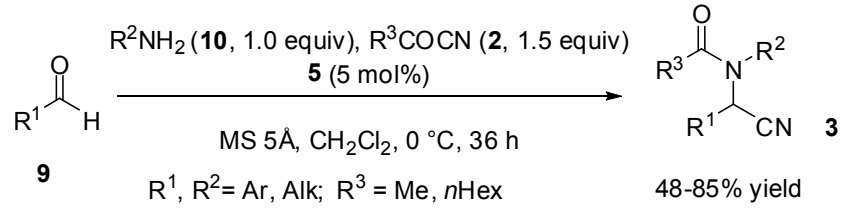


Then, this catalyst has been investigated with a number of different imines and it was found that the reaction gives products in very high enantioselectivities with different aromatic, heteroaromatic, aliphatic and unsaturated aldimines. Noteworthy, high enantioselectivity (98:2 er) have been obtained for the important pivalaldehyde derived imine **1b**. *N*-acylated α-amino nitrile **3b** was converted into *t*-leucine salt **8** via acid mediated hydrolysis and hydrogenolysis without racemisation.

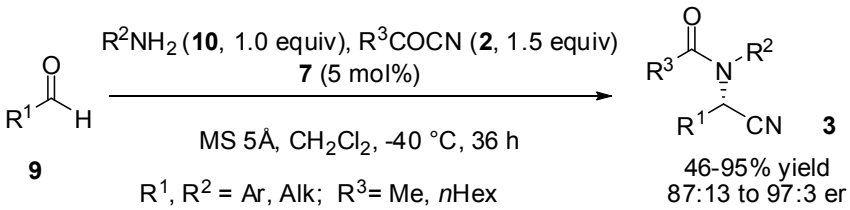


We then started to develop a three-component variant of the acylcyanation reaction. Initially we found that stirring benzaldehyde (**9a**), benzyl amine (**10a**), $MgSO_4$, catalyst **5**, and acetyl cyanide (**2a**) at 0 °C for 24 h in dichloromethane resulted in poor yield of the desired product **3a** and considerable side product formation. In this case, a considerable amount of *N*-benzyl acetamide was formed resulting from the direct reaction of benzyl amine with acetyl cyanide. We envisioned that in order to suppress

this side reaction, the order of reagent mixing may be crucial. Thus, when acetyl cyanide was added last, significant conversion to the desired product could be realized. The best result (99% conv.) was obtained when the mixture of aldehyde, amine, MS 5Å, and catalyst **5** were stirred together at room temperature for 2 h before the addition of acetyl cyanide at 0 °C. After establishing suitable reaction conditions, we decided to explore the scope of this new three-component reaction. Different aldehydes (both aryl and alkyl) and different amines (both benzyl and alkyl) gave the products in moderate to high yields. The third component of our reaction can also be varied. For example, commercially available heptanoyl cyanide gave the product in 72% yield.



We reasoned that extending our acylcyanation methodology to an attractive one-pot three-component catalytic asymmetric acyl-Strecker reaction could be possible. We decided to explore our three-component variant using Jacobsen's thiourea catalyst **7** which gave high enantioselectivities in the analogous preformed imine variant. According to our findings in the non-asymmetric three-component version, we added acetyl cyanide at last to realize efficient conversion to the desired product. Finally, we identified that the best result (98% yield, 97:3 e.r.) was obtained if the aldehyde was first mixed with the amine and MS 5Å for 2 h at r.t. before the catalyst and acetyl cyanide were added subsequently at -40 °C. Under this optimized condition, different aldehydes, amines and acylcyanides were studied and good results were obtained.



Our processes represent the first catalytic asymmetric acylcyanation of imines and the first organocatalytic asymmetric three-component acyl-Strecker reaction.

Publications resulting from this research area: 332, 491, 492, 493

External Funding: none

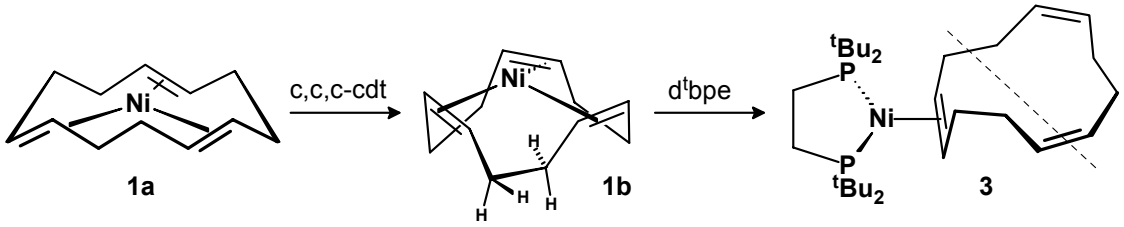
Cooperations: none

2.2.6 Research area "Coordination Chemistry of Nickel and Palladium" (K.-R. Pörschke)

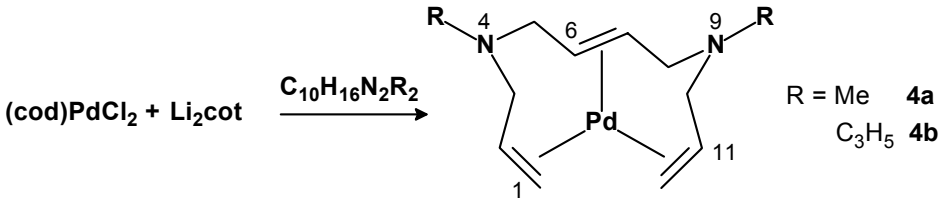
Involved: E. Chernyshova, X. Tian, R. Goddard

Objective: While many reactions are catalyzed by Ni and Pd compounds, the exact nature of the catalyst is often not clear. (a) We were intrigued to learn more about the properties of "naked nickel" complexes and whether "naked palladium" can also be provided. (b) Furthermore, the species developed from the reaction of $(\eta^3\text{-}C_3H_5)M(L)X$ (M = Ni, Pd; L = phosphane or NHC; X = halide) with AgY (Y = noncoordinating anion) is still under discussion (NHC = *N*-heterocyclic carbene). (c) While *β*-diketiminato ("nacnac") has emerged as an interesting ligand conferring unusual properties to many metals (e.g., Ni), relatively little is known about its coordination chemistry with palladium. The research reported here is intended to shed more light in these areas.

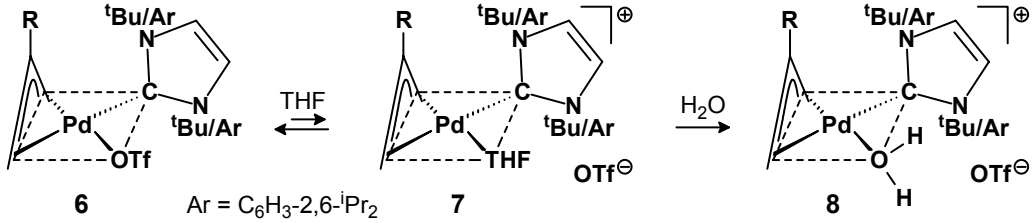
Results: (a) As compared to Wilke's famous (t,t,t-cdt)Ni (**1a**) (cdt = 1,5,9-cyclododecatriene) having the three C=C bonds twisted out of the coordination plane, the isomeric (c,c,c-cdt) (**1b**) was suggested to show an in-plane arrangement of the C=C bonds and consequently an improved backbonding. However, although **1b** is formed from **1a**, it is thermally less stable and considerably more reactive with respect to oxidation, aspects which called for a closer inspection of the bonding. A general investigation of the ligand properties of c,c,c-cdt showed that it coordinates to a circumferentially positioned metal in a C_2 symmetrical ("helical") conformation and to a central metal in a C_3 symmetrical ("ratchet") mode. Rather stable complexes are obtained for a central Cu(I), (c,c,c-cdt)CuX (**2**). While in the latter complexes the three C=C bonds are indeed approximately coplanar, their individual coordination to the metal center is asymmetric, and furthermore, the metal is displaced out of the plane of the C=C bonds. Thus, c,c,c-cdt does apparently not accommodate an ideally trigonally planar coordinated metal atom, and the coordination geometry of a central metal is perforce distorted toward trigonal pyramidal. This explains why backbonding in **1b** is not optimal, and it also explains the observed reactivity of **1b**. According to an X-ray structure analysis, **1b** crystallizes in the trigonal space group $R\bar{3}m$, with one (c,c,c-cdt)Ni moiety in the unit cell. The molecules are disordered and stacked vertically above one another, and the molecules of adjacent columns are close-packed to each other. Reaction of **1b** with a bidentate phosphine leads to displacement of two of the three C=C bonds and formation of complex **3**, in which the c,c,c-cdt ligand has now assumed the helical conformation.



While in t,t,t,-cdt and c,c,c-cdt the three C=C bonds are in a 1,5,9-sequence, it was shown in a further investigation that 1,6,11-trienes are even better suited to coordinate to a d^{10} metal, and here acyclic ligands already confer sufficient stability to the complexes. Thus, while the Pd(0) homologues to **1a,b** are unknown, **4a,b** bearing 4,9-diazadodeca-1,trans-6,11-triene ligands are stable. These Pd(0) complexes, which readily sublime above 50 °C, both represent viable sources for "naked palladium" in solution and also appear suited for vapor deposition techniques.

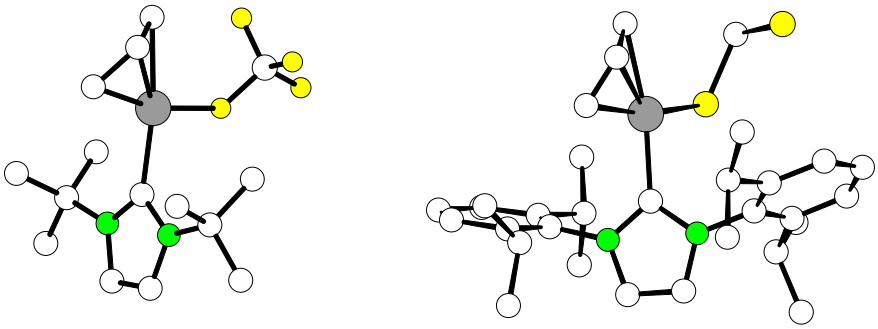


(b) $\{(\eta^3\text{-}2\text{-}RC_3H_4)Pd(\mu\text{-}Cl)\}_2$ (R = H, Me) react with AgOTf to give the polymeric $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}OTf)\}_n$ (**5a**), forming close-packed helical chains in the crystal, and the dimeric $\{(\eta^3\text{-}MeC_3H_4)Pd(\mu\text{-}OTf)\}_2$ (**5b**). Reaction of **5** with NHC (NHC = $C(N(^t\text{Bu})CH)_2$, $C(N(C_6H_3\text{-}2,6\text{-}^i\text{Pr}_2)CH)_2$) affords the so far elusive triflates $(\eta^3\text{-}2\text{-}RC_3H_4)Pd(NHC)(OTf)$ (**6**). These were shown to reversibly dissociate in THF to generate the ionic solvates $[(\eta^3\text{-}2\text{-}RC_3H_4)Pd(NHC)(THF)]OTf$ (**7**); both **6** and **7** react irreversibly with water to give the hydrates $[(\eta^3\text{-}2\text{-}RC_3H_4)Pd(NHC)(H_2O)]OTf$ (**8**). These studies show that THF and the anionic OTf are about equally weakly nucleophilic toward Pd(II), whereas water is stronger.



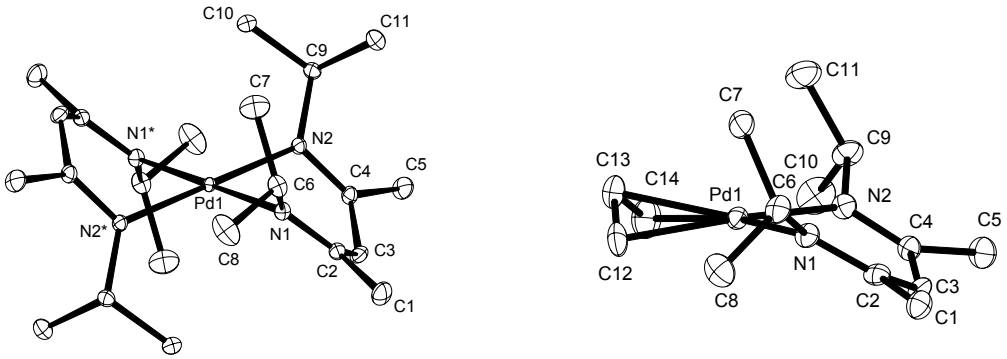
For the synthesis of complexes $(\eta^3\text{-}2\text{-}RC_3H_4)Pd(NHC)Y$ with even weaker nucleophiles Y than OTf the chlorides $(\eta^3\text{-}C_3H_5)Pd(NHC)Cl$ have been reacted with AgY (Y = BF_4, PF_6, $Al\{OC(CF_3)_3\}_4$) in CH_2Cl_2. For Y = BF_4 the undissociated adducts $(\eta^3\text{-}C_3H_5)Pd(NHC)(BF_4)$ (**9**) are isolated, whereas for Y = PF_6 and $Al\{OC(CF_3)_3\}_4$ the ionic CH_2Cl_2-solvates $[(\eta^3\text{-}C_3H_5)Pd(NHC)(CH_2Cl_2)]Y$ (**10**) separate. Examples of **9** and **10** have been characterized, inter alia, by X-ray structure analysis. When the

CH_2Cl_2-solvates **10** are subjected to a vacuum at ambient temperature, the CH_2Cl_2 evaporates and the solvent-free complexes $[(\eta^3\text{-}C_3H_5)Pd(NHC)]Y$ (Y = PF_6, $Al\{OC(CF_3)_3\}_4$) (**11**) remain; these await presently further characterization.



Molecular structures of $(\eta^3\text{-}C_3H_5)Pd(C\{N(^tBu)CH\}_2)(BF_4)$ (**9**) and $[(\eta^3\text{-}C_3H_5)Pd(C\{N(C_6H_3\text{-}2,6\text{-}^iPr_2)CH\}_2)(CH_2Cl_2)]PF_6$ (**10**) (cation only)

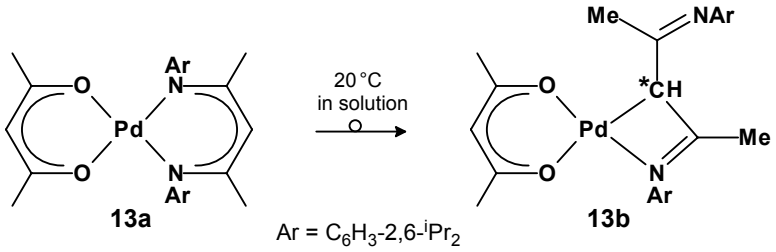
(c) We have performed a systematic study on the properties of *β*-diketiminate ligands at Pd(II), as exemplified for the *N*-isopropyl substituted $^iPr_2$-nacnac and the *N*-C_6H_3-2,6-$^iPr_2$ substituted Ar_2-nacnac ligands. $Pd(acac)_2$ reacts with Li($^iPr_2$-nacnac) via the isolatable intermediate (acac)Pd($^iPr_2$-nacnac) (**12a**) to afford the homoleptic Pd($^iPr_2$-nacnac)$_2$ (**12b**). The reaction is complicated by oxidative coupling of two $^iPr_2$-nacnac anions, concomitant with reduction of Pd, in an so far inevitable side reaction. Complex **12b** shows a rigid 2-fold envelope conformation with 12 close-packed methyl groups completely shielding the core of the complex. By reacting $\{(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}Cl)\}_2$ with Li($^iPr_2$-nacnac) we have also prepared the mixed allyl/nacnac complex **12c**, likewise characterized by single crystal structure analysis.



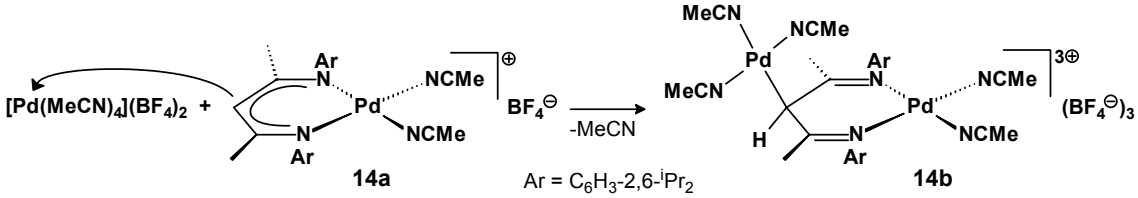
Molecular structures of Pd($^iPr_2$-nacnac)$_2$ (**12b**) and $(\eta^3\text{-}C_3H_5)Pd(^iPr_2\text{-nacnac})$ (**12c**)

The Ar_2-nacnac ligand is more bulky and the reaction of $Pd(acac)_2$ with Li(Ar_2-nacnac) halts at the stage of the mixed ligand complex (acac)Pd(Ar_2-nacnac) (**13a**). While the isolated **13a** is thermally stable at ambient temperature, it slowly isomerizes in solution

to give **13b**, bearing a novel chiral κ^2*C,N*-nacnac ligand. The latter represents a formal azaallyl, in which the electrons are localized in an enyl structure. The four-membered chelate ring is explained by a strong coordination of the central anionic carbon at Pd in the form of a Pd–C single bond and a weaker coordination of one imine nitrogen atom to complete the 4-fold coordination around Pd(II).



The retained high nucleophilicity of the central methine group in the "normal" Pd–κ^2*N,N*-nacnac complexes is also illustrated by the reaction of **14a** – obtained from $[Pd(NCMe)_4](BF_4)_2$ and $Li(Ar_2\text{-nacnac})$ – with a further 1 equiv of $[Pd(NCMe)_4](BF_4)_2$ to afford the dinuclear **14b**. In the course of this reaction the methine group displaces one acetonitrile ligand and undergoes a bridging coordination to another Pd(II) center. The electron distribution of the κ^2*N,N*-nacnac-dienyl system becomes localized in a 2,4-diimin-3-yl structure. To conclude, the R_2-nacnac ligands are quite versatile in their coordination modes toward the Pd(II) center. Unfortunately, the Pd(II)–R_2-nacnac combination, as long as acetonitrile is absent, is prone to undergo internal redox reactions resulting in decomposition, but acetonitrile significantly stabilizes the system.



Publications resulting from this research area: 2, 35, 379, 413, 428, 429

External funding: Industrial

Cooperation: none

2.2.7 Research area "Dynamically Disordered Mesophases (Plastic Crystals) of Pentacoordinate (π-Allyl)ML_3-type Complexes (M = Ni, Co, Rh, Ir)"

(K.-R. Pörschke)

Involved: W. Ben Mustapha, C. Creusen, R. Goddard, A. Rufinska, C. Weidenthaler

Objective: Following up on our discovery of the ionic $[(\pi\text{-}C_3H_5)NiL_3]Y$ (L = $P(OMe)_3$; Y = OTf (**2a**), PF_6 (**2b**)) complexes having plastically crystalline (PC) properties (see previous report, **2.2.6**), we have extended the range of such mesogens (a) for further anions, (b) for L = PMe_3, (c) for substituted π-allyl ligands, and (d) for M = Co–Ir. While plastically crystalline mesogens are still very rare in organometallic chemistry, we are now in a position to describe the properties of about 40 complexes of this type.

Results: We have extended the previous set of pentacoordinate, *ionic* 18e d^8 complexes $[(\eta^3\text{-}C_3H_5)Ni(PMe_3)_3]Y$ (**1**) and $[(\eta^3\text{-}C_3H_5)Ni\{P(OMe)_3\}_3]Y$ (**2**) (Y = OTf, PF_6, Br, I (**a**–**d**)) for Y = BF_4 (**e**), $B(C_6F_5)_4$ (**f**), $Al\{OC(CF_3)_3\}_4$ (**g**), and the "plasticizing anion" NTf_2 (**h**). In these complexes the occurrence of a PC mesophase results from the combined entropic contributions of the disorder in cations and anions. While $[(\eta^3\text{-allyl})NiL_3]Y$ complexes appear to withstand the formation of a mesophase for Y = halide and BF_4 due to the absent (halide) or low (BF_4) entropic contribution from the anions, the complexes $[(\eta^3\text{-}C_3H_5)Ni\{P(OMe)_3\}_3]Y$ (**2f–h**) show mesogenic properties, with **2g**,**h** displaying particulary low phase transition temperatures because of the many facile rotations of the OMe, CF_3, and SO_2CF_3 substituents in both the cation and the anions. In contrast, only one example of a $[(\eta^3\text{-}C_3H_5)Ni(PMe_3)_3]Y$ complex having PC properties has so far been realized, namely **1h** with Y = NTf_2. Here, the low entropic contribution from the cation is complemented by the extra high contribution from the anion. Similar results are observed for 2-methyl or syn,syn-1,3-dimethyl substitution at the allyl group. In the dynamically disordered mesophase the molecules or ions appear to rotate on their site in the lattice, giving rise to solution-type properties (e. g., in solid state NMR), although they in fact represent solids.

The results from the ionic Ni complexes directed our interest toward the known *neutral* 18e d^8 complexes $(\eta^3\text{-}C_3H_5)ML_3$ (M = Co (**3**, **4**), Rh (**5**, **6**), Ir (**7**, **8**); L = PMe_3, $P(OMe)_3$), lacking the entropic contribution of an anion. Moreover, these complexes comprise in the lattice no longer the quite strong electrostatic cation–anion interactions, but rather the much weaker van-der-Waals and dipol-dipol interactions between neutral molecules. Muetterties et al. studied the solution properties of these complexes in the 1980ies and noted already their high fluxionality, along with "waxy" solid state

properties. These were eluding the complexes from single crystal X-ray analysis at that time. We have extended the known set of complexes by the 2-methallyl derivatives, so that we were able to study the solid state phase properties of a total of 12 complexes $(\eta^3\text{-}2\text{-}RC_3H_4)ML_3$ (R = H, Me) by means of DSC (Differential Scanning Calorimetry), solid state NMR, and single crystal and powder X-ray crystallography. For the parent $(\eta^3\text{-}C_3H_5)M(PMe_3)_3$ (M = Co (**3**), Rh (**5**), Ir (**7**)) complexes we have verified the anticipated *SPY*-5 structure by single crystal X-ray analysis. All complexes form a plastically crystalline mesophase, with the phase transition temperature being highest for $(\eta^3\text{-}C_3H_5)Ir(PMe_3)_3$ (323 K) and lowest for $(\eta^3\text{-}2\text{-}MeC_3H_4)Ir\{P(OMe)_3\}_3$ (195 K), all others falling in that range. Generally, the transition temperatures are found to be (expectedly) lower for the $P(OMe)_3$ than for the PMe_3 complexes and (unexpectedly) much lower for the methallyl than for the parent allyl complexes. As a further noteworthy feature of these complexes, the enthalpies and entropies of the crystalline→PC phase transition as low as $\Delta H = 0.4$ kJ mol^{-1} and $\Delta S = 1.5$ J mol^{-1} K^{-1} are unprecedented small for PC mesogens (typical values are at least 10 times as large). Also of interest, the PC Ni complexes **1**–**2** display a relatively low barrier of turnstile rotation of the three phosphorus ligands and a higher barrier for π-allyl motion (with respect to the rest of the solid). There, the additional π-allyl dynamics (Ni being now completely structural fluxional) appear to cause the occurrence of the crystalline→PC phase transition. In contrast, for the Muetterties complexes **3**–**8** in the PC phase the barrier of the π-allyl dynamics may be lower than that of the phosphorus turnstile rotation; that is, the phosphorus ligand dynamics may already be "frozen out", while the allyl group is still in motion (apparently, π-allyl motion necessarily accompanies the formation of a PC phase). Here, structurally rigid *SPY*-5 molecules appear to rotate on their sites in the lattice.

Publication resulting from this research area: 359

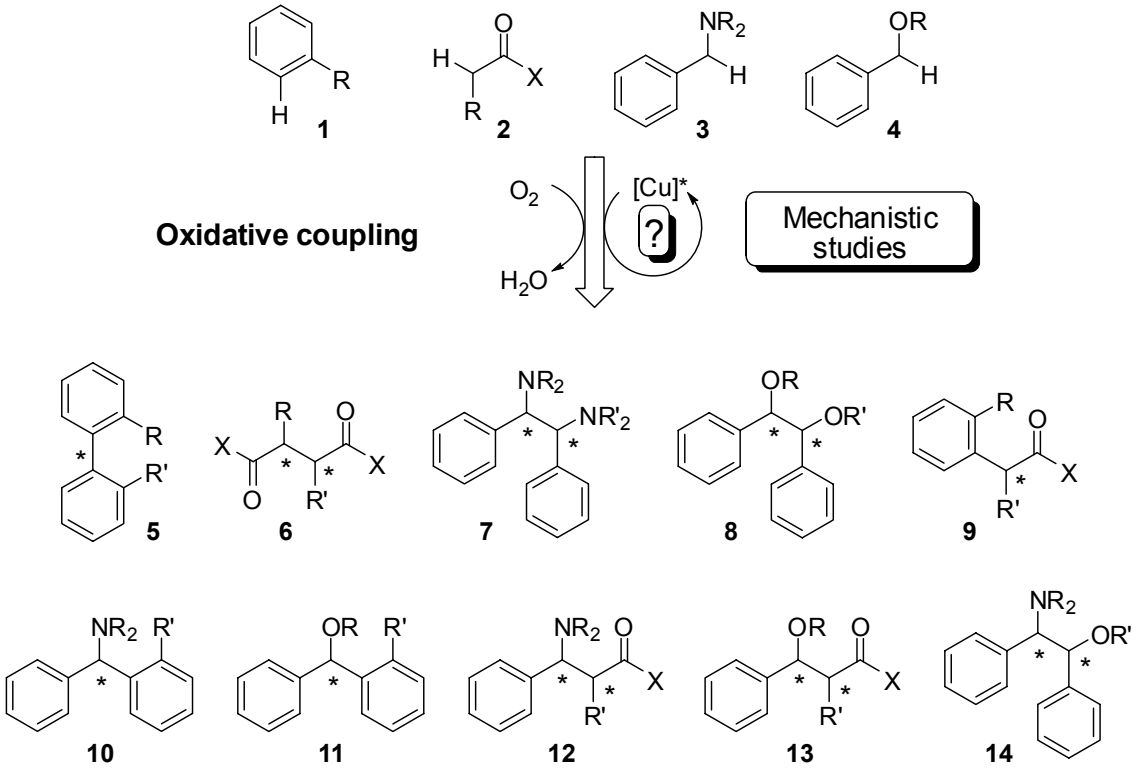
External funding: DAAD

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

2.2.8 Research Area „Copper-Catalyzed Asymmetric Oxidative Coupling Reactions for the Formation of Carbon-Carbon Bonds" (M. Klußmann)

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

Objective: Oxidative coupling allows for the direct CC-coupling of two fragments with cleavage of a carbon-hydrogen (CH) bond each, resulting in a net oxidation of the fragments. The reaction can be catalyzed by metal compounds with the use of atmospheric oxygen with water as the side product. Examples for this type of reaction are long known, yet many of these still suffer from low activity or selectivity or are performed with stoichiometric amounts of metal compounds as oxidant. Furthermore, there is to date no satisfying understanding of the reaction mechanism(s) and contradictory models occasionally serve as the basis for reaction development.
This gap in understanding is planned to be filled by the present research project. Therefore, mechanistic studies will go hand in hand with reaction development. The substrate scope for oxidative coupling reactions is large, e.g. **1**-**4**, and as both homo- and heterocoupling is possible, a large variety of products **5**-**14** is possible, as shown below.



Eventually, this project will lead to the development of catalytic systems to couple a whole variety of substrates in new ways to a plethora of potentially chiral products,

many of which still pose a challenge today. Additionally, these reactions will satisfy modern requirements as they will only utilize catalytic amounts of a relatively cheap metal compound (Cu), will not require preactivated substrates (simply CH-bonds next to a directing group), use an environmentally benign oxidation agent (O_2) and will be basically waste-free (water as the only by-product).

Publications resulting from this research area: none

External funding: none

Cooperation: none

2.2.9 Research Area „Asymmetric Amplification by Phase Behaviour with Potential Implications for the Origin of Life" (M. Klußmann)

Involved: E. Böß, A. Sud

Objective: The origin of life is one of the most intriguing puzzles in science, with the evolution of biological homochirality from a presumably racemic primordial earth being a particularly puzzling piece for chemists dealing with chirality. Amongst several different models, phase behaviour has been evoked as a way of amplifying small imbalances in enantiomeric composition to high excesses of one enantiomer. A striking example is the amino acid serine which in solid-solution equilibrium can attain nearly enantiopure solutions. But even for other compounds such strong amplification can be possible if the crystal structure of the solid phase is accordingly altered.
Based on these previous results, I plan to investigate the phase behaviour of one amino acid in the presence of an additional cocrystalizing substance. Any change in crystal structure will lead to a change of solution behaviour and could lead to stronger chiral amplification. Ultimately, more complex systems will be investigated, as aqueous solutions containing several amino acids and other compounds are a much more likely scenario for the prebiotic soup than just a single substance. An amplified solution ee will then provide the basis for chirality transfer to new biologically important products via solution phase reactions. Investigations are planned on the formation of peptides which could themselves be used as catalysts for asymmetric carbohydrate synthesis. Thus, a model might be developed of how homochirality in biological building blocks could have been achieved by an interplay of "prebiotic crystal engineering" and catalysis.
These studies on complex solid-solution systems will have major implications beyond the field of prebiotic chemistry; the study of cocrystals and their phase behaviour, for example, will contribute to the growing field of crystal engineering and holds importance for the pharmaceutical industry.

Publication resulting from this research area: 411, 412, 467

External funding: none

Cooperation: D.G. Blackmond (Imperial College, London, UK)

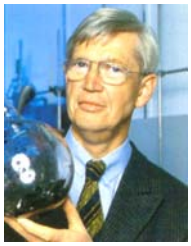
2.3 Department of Heterogeneous Catalysis

Director:

Ferdi Schüth (born 1960)
Publications: 13, 37, 69, 99, 105, 106, 107, 108, 111, 112, 113, 114, 115, 116, 131, 156, 157, 158, 159, 160, 161, 165, 175, 185, 187, 190, 199, 213, 214, 215, 219, 220, 229, 230, 233, 249, 310, 311, 316, 317, 318, 319, 321, 322, 331, 336, 358, 360, 364, 365, 366, 367, 368, 371, 376, 390, 393, 394, 417, 430, 434, 476, 477, 497, 498, 499, 501, 504, 519, 520, 524, 548, 552

Further group leaders:

An-Hui Lu (born 1972)
Publications: 105, 106, 108, 111, 112, 113, 114, 115, 116, 117, 315, 316, 317, 318, 319, 393, 476, 477, 501



Helmut Bönnemann (born 1939)
retired from the Institute in November 2004
Publications: 20, 21, 22, 23, 76, 90, 111, 123, 124, 133, 192, 193, 194, 195, 223, 224, 232, 248, 295, 296, 303, 304, 403, 414, 415, 416, 418, 466, 480, 488, 542

Frank Marlow (born 1960)
Publications: 93, 103, 104, 119, 120, 178, 298, 305, 309, 323, 324, 380, 433, 468, 478, 524, 528, 529, 530, 544

Oliver Trapp (born 1973)
Publications: 89, 179, 180, 185, 285, 381, 382, 383, 384, 385, 386, 397, 535, 536, 537

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

Special Activities

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-	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-	Chairman of the Selection Committee, Humboldt Award
2003-	Member of the Editorial Board "QSAR-Combinatorial Science"
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
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 DFG

Research in the Department of Heterogeneous Catalysis (F. Schüth)

The department of Heterogeneous Catalysis is now fully in steady state operation, i.e. while the head of the department, F. Schüth, remains in place, group leaders are leaving the Institute to face new challenges at other institutions, and new group leaders start their independent career at the MPI für Kohlenforschung. Continuity is ascertained by very few senior scientists on permanent positions (W. Schmidt, F. Marlow), in addition to the director.

The major focus of the department remains to be the controlled synthesis of solids, which are often complex composites. The target area of application of the solids is predominantly catalysis, but if materials or synthetic pathways are found to be interesting in other areas as well, these will also be explored. Examples for this are mesostructured magnetic solids or photonic materials. Around this main thrust are grouped several supporting research fields, such as understanding the formation of the catalytic materials, where mass spectrometric analysis of crystallizing solutions is one of the most exciting developments of the reporting period, the development of high throughput methodologies, or the development of catalyzed hydrogen storage materials.

Over the reporting period, the department consisted of four groups, Prof. Dr. F. Schüth (director), Dr. A.H. Lu (promoted from post-doc to group leader in 2005), Dr. habil. F. Marlow, and Dr. O. Trapp (presently leader of an Emmy-Noether-group of the DFG). This type of organization has proved to be successful, and it is planned to continue the turnover for two of the group leaders on a time scale of about five years. Dr. Lu is already in late stage discussions with Chinese universities to be appointed full professor in 2008. As a successor, most probably Dr. R. Palkovits, who graduated from the Institute and is now working as a post-doc at Utrecht university in the group of Bert Weckhuysen, will rejoin the department in early 2008 and be integrated in the excellence cluster in cooperation with RWTH Aachen. She had been awarded the Hendrik Casimir - Karl Ziegler award of the Nordrhein-Westfälische Akademie der Wissenschaften in 2006.

In addition to the groups listed above, Prof. B. Bogdanovic is still associated with the department to support the work on hydrogen storage materials. During the reporting period, substantial independent research has also been carried out by other senior scientists of the department who formally do not hold group leader positions, such as Dr. W. Schmidt and Dr. C. Weidenthaler, in areas supplementing the fields of expertise covered by the other groups.

The major focus of the department is the synthesis of novel catalytic materials. In the reporting period, the work has moved more and more towards complex composite catalysts which were obtained by design and spatially controlled modification of the base materials. For this work, partly standard techniques are used, but more often innovative methods have been developed, highlighted in the creation of sinter-stable catalysts by hollow sphere encapsulation. The work on novel catalytic materials was primarily pursued in the groups of A.H. Lu and F. Schüth, who also operate some specific characterization techniques and test units for several different catalytic reactions. Novel instrumental developments are pursued where needed, for example in the characterization of the copper surface area by parallelized N_2O frontal chromatography. O. Trapp had just joined the department at the end of the last reporting period; his group is now fully up to speed. He is developing novel multiplexing techniques for chromatography and on-column catalytic reactions, which serve both for screening purposes and for determination of kinetic data. This activity perfectly complements the more materials oriented work of the other groups of the department. Last but not least, the team of Frank Marlow leverages the expertise of the department in the synthesis of solid materials to applications in optics and photonics. This group also provides valuable expertise in the analysis and exploitation of optical phenomena necessary for the development of novel photocatalytic processes, a project between the Marlow and the Schüth groups which has just been initiated.

The materials-oriented approach of the department entails a rather wide range of different topics covered by the research activities. This is caused by the fact that often materials are discovered as side-products of other projects, which are so interesting that they deserve in-depth study. This occasionally leads to the development of initially not foreseen research directions. However, this is seen rather as a strength than as a weakness, as long as it does not change the overall direction of the department, since the size of the department is sufficiently large and the expertise sufficiently broad that such fortuitous projects can be picked up and brought to completion over a reasonable time frame.

Many of the research fields and projects will be described in more detail in the following. However, not all aspects of the work can be covered on the space available, and thus a substantial fraction of the research done in the department can not be mentioned, so that these citations are missing in the description of the research areas. The readers are therefore referred to the original publications listed at the end of this report for a complete overview. In materials development the research over the

reporting period was dominated by the exploitation of the hard templating pathway to create high surface area materials, but also other interesting composite systems. Inititally, the hard templating was primarily used for the synthesis of high surface area oxides via the activated carbon route and for the synthesis of carbons and carbon-templated oxides. This has now been generalized, and hard templates are employed for replication of different materials on the scale of hundreds of nanometers, such as for the synthesis of photonic crystals and hollow spheres, down to the scale of only a few nanometers for the replication of ordered mesoporous silica. The excellent control of the hard templating pathway allows spatially selective functionalization, which will be detailed in the following reports on the research areas.

The methodological thrust in the development of components for an integrated high throughput approach for the discovery of novel solid catalysts has been reduced during the reporting period. This is due to two reasons: on the one hand, the development is becoming more and more a technological question, which has partly left the realm of basic research. Such developments are thus better pursued by commercial enterprises. On the other hand, high throughput solutions for most of the problems studied in the department have been developed in the past and are now available and in routine use. There are only some components missing. Most notable are the multiplexing chromatography developments in the group of O. Trapp, but also computational support of high throughput experimentation programs by artificial intelligence tools is gaining more and more importance also in the department.

Methodological developments in another field, in ESI mass spectrometry, however, have led to exciting new discoveries in the research area concerning the understanding of catalyst synthesis. Deep insight has been gained in the processes occurring in silicate solutions up to the point of zeolite crystallization, and it is expected that this direction will be pursued more intensively in the future.

The department’s activities in the development of optical materials and materials for hydrogen storage have continued on the same level as in the previous reporting period. There is intensive exchange between these fields and the other activities in the department. The hydrogen storage materials have successfully been used as hydrogenation catalysts, the work on photonic crystals is being expanded to use them in novel photochemical reactors.

The cooperations between the department and the analytical groups have been intensified, especially with the mass spectrometry group. There is a second Ph.D.

student supervised jointly now, and a number of joint publications have appeared as result of this cooperation. Additional close cooperation exists with the TEM group and solid state NMR, the service of the chromatography group is also of very high importance. Finally, part of the XRD work for the department is done by C. Weidenthaler in direct cooperation with the department. There is also a cooperation project with the Thiel group on quantum-chemical calculations on a very stable molecular Pt-catalyst and cooperations with the List group on heterogenization of proline catalysts.

Most of the groups of the department are linked with many other groups worldwide through formal or informal cooperations, including an EU network of excellence (IDECAT), several BMBF grants, and participation of the department in DFG Schwerpunktprogrammen (priority programs) and Sonderforschungsbereichen (centers of excellence). In November 2007 the decision concerning the excellence program of the federal government was made, and RWTH Aachen was awarded an excellence cluster “Tailor-made Fuels from Biomass”. The department is part of this excellence cluster, and this will be especially important for R. Palkovits, who will be tightly integrated into the teaching activities in Aachen via this cluster.

These networking activities are supplemented by bilateral research projects between research groups, and funded cooperation projects with industrial companies. The department is also closely involved in the Max-Planck International Research School SURMAT. The involvement in these cooperations brings in substantial third party funds. In addition, very substantial funding for all projects, which will not be listed separately in the following, was obtained by the Leibniz-award of the DFG.

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

Involved: S. Pelster, F. Kleitz, M. Linden, B. Schaack, S. Vukojevic

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: Electron Spray Ionization Mass Spectrometry (ESI-MS) has been established as almost routine tool by now for the study of processes in pre-nucleating and nucleating solutions. In the last reporting period, the first time-resolved studies of hydrolysis and condensation reactions in silicate solutions had been introduced. These methods have now been extended to investigate dynamics of different silicate species in solution. Spectacular and surprising results have been obtained when studying the interconversion of cage-like oligomers, i.e. the cubic octamer and the prismatic hexamer. The main innovation was the use of fully isotopically labeled ^{29}Si silicate solutions. Using this approach, two identical precursor solutions, which are just different in their isotopic compositions, could be prepared. Upon mixing, the chemical state of the system

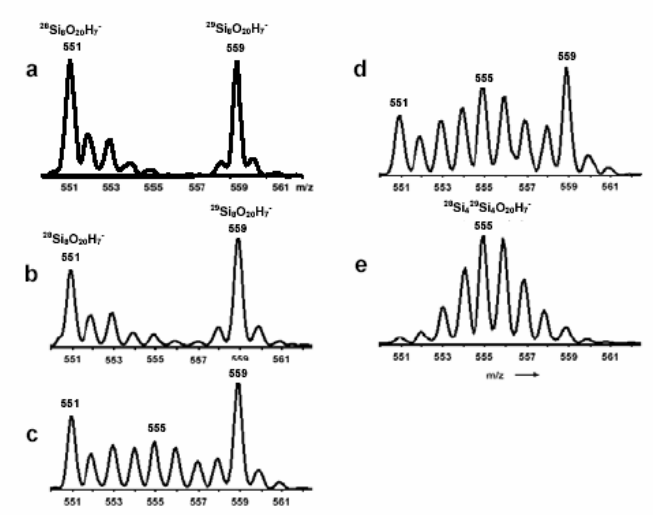


Fig. 1: Development of the signal in the range of the cubic silicate octamer with time after mixing precursor solutions containing the ^{29}Si and the ^{28}Si octamers respectively. (a) superposition of spectra of precursor solutions, (b) after 2 min, (c) after 55 min, (d) after 85 min, (e) after 5h.

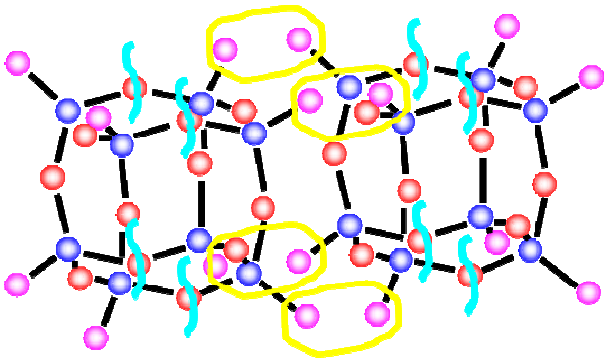


Fig. 2: Proposed model for the exchange reaction between two cubic octamers. It is not suggested that all four corners exchange simultaneously, but cubes may link at one corner, then the other bonds will form stepwise, while the remaining four rings are released to enter the silicate pool.

does not change, but the isotopes in the oligomers start to scramble, and the rate of scrambling allows determination of the kinetics of these exchange reactions and of the stability of the oligomers. Surprisingly, the exchange of silicon atoms between the oligomers did not proceed one by one, but in a concerted fashion (Fig. 1). For a one by one exchange of the cubic octamer (m/z = 551 for the all ^{28}Si cube, m/z = 559 for the all ^{29}Si cube), one would expect scrambled species to develop with time first close to the parent peaks, i.e. first the 552 and the 558, then the 553 and 558 signal, and so on. However, what is observed in all experiments at different temperatures is the growth of the 555 species at the onset of the reaction with highest rate, the other peaks follow with some delay. This can only be explained by a simultaneous exchange of four silicon atoms (Fig. 2), most probably of full faces of the cubes. A model has been formulated for this process, which allows the determination of kinetic parameters for this reaction. Similar experiments have been carried out for the prismatic hexamer, but this reaction is so fast that the system had to be cooled down to 5 °C; at room temperature, the distribution is equilibrated within less than one minute. Also for the hexamer there is a concerted exchange, but here three silicon atoms are exchanged simultaneously instead of four, which can be explained by the exchange of the top and bottom triangular faces of the prism, which are known to be less shielded by the alkylammonium ions present in the systems. This research using isotopically labeled compounds is now being extended to systems in which zeolite crystals are present in order to investigate the exchange of the surface species with the solutions.

In non-labelled systems the studies have already been performed at silicate concentration levels at which zeolite formation takes place. In a first project, the crystallization of MFI and MEL type zeolites has been compared. No single pronounced oligomeric species was found to be present, but a wide range of different species instead is observed during the crystallization. In the early phase, high molecular weight species prevail, while in later stages, when solid has already formed, the distribution shifts to lighter species (Fig.3). This can be explained by the decreased solution concentration of silicon which is known to lead to depolymerization of silicates. No pronounced differences were observed for MFI and MEL type zeolites, with the exception of the time scales,

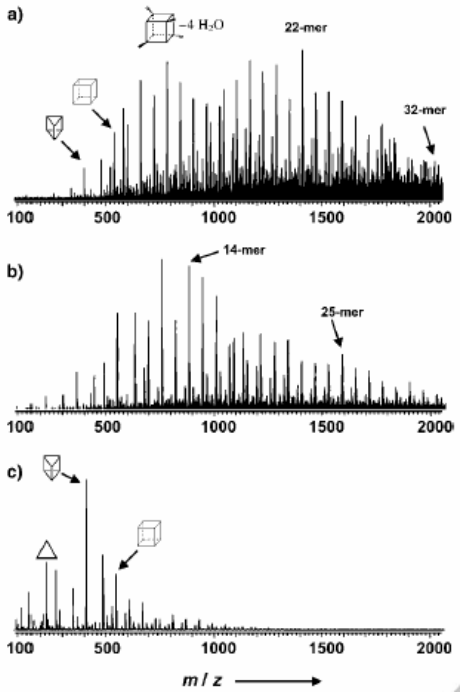


Fig. 3: Species detected in crystallizing zeolite solutions (MFI) by mass spectrometry. (a) after 24 h aging at RT, (b) 6 h after heating to 92°C, (c) 61 h after heating. At the last stage zeolite is already present.

which are substantially longer for MEL crystallization.
This research is now being extended to studies into the incorporation of heteroelements in the zeolite frameworks. Initial results for the incorporation of germanium suggest, that germanium prefers closed-cage species – in agreement with literature data reporting that germanium is found in four rings and stabilizes them. Interestingly, in MFI synthesis at low germanium concentration, the heteroelement seems to be more frequently part of a chain than present as part of rings, while in Ge-FAU synthesis at high germanium concentrations, the germanium is largely incorporated in four rings, which are also abundant in the structure of the final zeolite.
A similar pronounced difference was observed in the comparison of gallium and germanium as heteroatom. While gallium seems to be bridging two all-silica ring species or to be part of chain-like species, germanium again is present in the rings. This may explain why it is difficult to synthesize high gallium zeolites, but relatively straightforward to produce high germanium zeolites. However, the interpretation of the results is still preliminary, the results, though, were reproduced in numerous experiments.
Also EXAFS is used to study the formation of catalytic materials. This is done in cooperation with the group of J.D. Grunwaldt. A special cell has been designed to follow in-situ the generation of metal nanoparticles from solution, and first experiments have been performed at ANKA in Karlsruhe. In these experiments, it could be shown that for Al-stabilized copper nanoparticles reduction takes place directly from Cu^{2+} to Cu^{0} without intermediate Cu^{+} species.

Publications resulting from this research area: 3, 4, 69, 178, 230, 336, 380, 497, 498, 499

External Funding: DFG SFB 558

Cooperations: J.D. Grunwaldt (Zürich, CH); W. Schrader (Mülheim, DE).

2.3.2 Research area "Combinatorial Catalysis and Novel Reactor Concepts" (F. Schüth)

Involved: N. Ardentov, C. Baltes, J.S. Girardon, J. Llamas-Galilea, J. Procelewska, S. Vukojevic, S. Wang

Objective: High throughput technologies have fully entered routine use as a research tool. About half of the catalytic set-ups used in the department are parallelized. Only selected projects were pursued in the reporting period with respect to technology development, since almost all necessary components are in place. Computational approaches, however, have become more important. In addition, a project on the integration of a high throughput approach to obtain more detailed insight into the relevant factors governing the performance of a solid catalyst has been carried out.

Results: A missing piece in the analytical tools for high throughput characterization was parallelized frontal chromatography. Since several projects in the department deal with copper-based catalysts, high throughput N_2O frontal chromatography was urgently needed, since lack of information on copper surface area was a severe limitation in the progress of the projects using copper catalysts. It was decided to base the parallel set-up on IR spectroscopy, using a focal plane array (FPA) detector described in the last report. The detector was coupled with a 16 channel parallel reactor linked to a 16 channel parallel gas cuvette. The cuvette was imaged on the FPA detector, so that integration of the spectra of all pixels belonging to the same channel gave information on the gas phase present in the channel. By adaptation of the software to rapid scan mode, the time resolution could be brought down to about 4 s which is sufficient to follow the breakthrough of N_2O after the surface of the copper catalysts had been oxidized in flowing N_2O, corresponding to a stoichiometry of 2 Cu / 1 O. Surface areas can be determined with a precision of about ± 1 m^2/g, as determined by comparison with the results obtained on a dedicated set-up in the laboratory of M. Muhler.
This parallelized N_2O frontal chromatography was a key component in a project to find the parameters necessary for best performing methanol synthesis catalysts. In this project we used a unique approach, where first catalysts were synthesized under a variety of different conditions, characterized with high throughput characterization methods at the precursor and catalyst stage, and with respect to activity using the high pressure parallel reactor described in the last report. Selected samples which appeared to be interesting with respect to understanding the requirements for a well performing catalyst were then characterized in-depth by non-parallelized methods, such as TEM,

XRD or XPS. Fig.1 shows the comparison of BET surface area, copper surface area and catalytic activity in methanol synthesis for a set of catalysts. The profiles are very similar, with, however, some deviations, especially concerning the correlation between BET surface area and activity. The detailed analysis revealed that the precursors of the well performing catalysts contain hydroxycarbonates of copper and/or zinc. These hydroxycarbonates are temperature stable for the best performing systems, and are still present in the precursors after calcination at 300 °C.

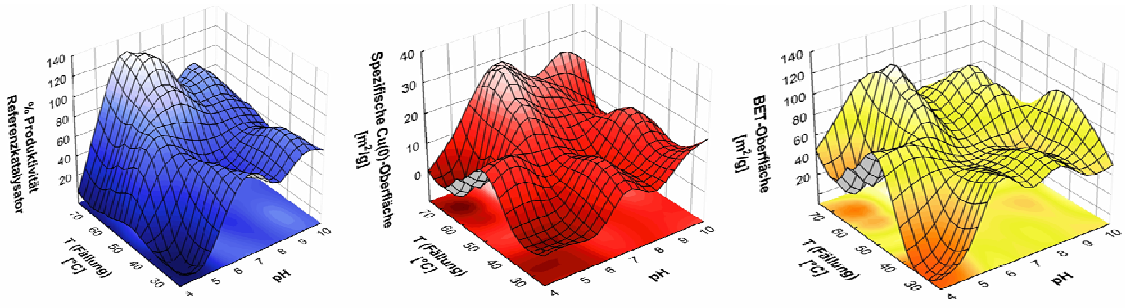


Fig. 1: Activity, copper surface area, and BET surface area of a set of catalysts, for which the precursors were synthesized at different pH and precipitation temperature. The catalytic activity is normalized to a commercial methanol synthesis catalyst.

In addition, the influence of aging of the precursors on catalytic activity was studied. The activity was low after aging up to 20 min, since for such short times the precursors were amorphous. Best performing catalysts were obtained for aging time between 20 min and 1 h, and free development of the pH during aging instead of maintaining it at a fixed value was advantageous.

Although in this study catalysts were found which surpassed the activity of the commercial benchmark by 30%, this is probably no alternative for a commercial catalyst, since the deactivation of these best performing samples in the first hours on stream was significant due to loss of copper surface area.

The development of computational methods was pursued in two directions. The artificial intelligence approach described in the last report was designed for the identification of suitable descriptors that would allow prediction of the catalytic performance of arbitrarily chosen catalysts. Although this approach was successful, it was only the first stage in a truly virtual screening of solid catalysts. In the reporting period it was attempted to also take the second step, i.e. the generation of a vast library in-silico, virtual screening using the identified descriptors, and finally synthesis of a promising subset of catalysts. However, it was found that out of the suggested catalysts, only about 25 % could actually be synthesized, since the software suggested in many cases catalysts, which were outside the synthetically accessible parameter range. Thus,

the software was modified to include "chemical knowledge", i.e. in many iteration cycles rule sets were defined, which would restrict the search space to accessible parameters, but not restrict it more than necessary. This software is almost completed now, and the virtual screening with experimental validation is now being re-started.

In parallel to this project which is very fundamental and will still need years to completion, multi-objective optimization using genetic algorithms was implemented in order to improve the search efficiency for systems, where there is already substantial knowledge available. Since in catalyst development typically more than one target needs to be optimized (such as activity, selectivity, cost, etc.), the screening strategy should allow for such multi-objective optimization. However, this had previously not been done, and therefore several different algorithms and encoding schemes for the catalysts have been tested to develop a suitable concept for the example of the $DeNO_x$ reaction under lean conditions. As two objectives to be reached, activity and low temperature for activity were selected. In a number of generations, the development approached a Pareto-optimal front, which can be estimated as the asymptote of the front of subsequent generations. This estimate is of high value, even if no satisfactory catalyst can be found, since it allows – with reasonable certainty – to predict, how far a development project under a given set of boundary conditions may go. Fig. 2 shows the development of the performance of the catalysts from different generations and the estimated Pareto-optimal front.

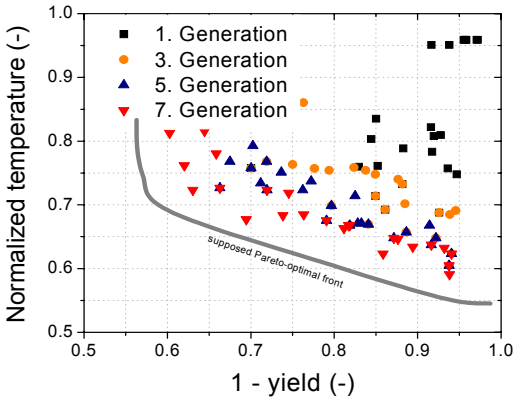


Fig. 2: Performance of subsequent generations of catalysts in lean $DeNO_x$ developed by multi-objective optimization using genetic algorithms. The grey line represents the estimated Pareto-optimal front, i.e. the line which will probably not be exceeded as long as no novel elements or synthetic procedures are used.

Publications resulting from this research area: 37, 99, 128, 159, 160, 164, 219, 221, 281, 366, 368, 370, 394, 395, 504, 518

External Funding: DFG SFB 558, Cognis

Cooperations: D. Farrusseng (Villeurbanne, FR); M. Muhler (Bochum, DE).

2.3.3 Research area "High surface area materials" (F. Schüth)

Involved: N. Ardentov, P. Arnal, P. Bazula, M.J. Benitez, A. Cepak, Y. Ilhan, F. Kleitz, J. Kornatowski, W.C. Li, M. Linden, A.H. Lu, A. Martinez, N. Muratova, S. Olejnik, R. Palkovitz, C. Pavel. R. Rinaldi, I. Ritzkopf, A. Rumplecker, E. Salabas, W. Schmidt, K. Schlichte, M. Schwickardi, H. Tüysüz, C. Weidenthaler, U. Wilczok, C.M. Yang

Objective: In this group of projects we are investigating and developing novel pathways for the synthesis of high surface area materials. These materials are mostly oxides; the carbon materials which had gained increasing importance over the last years are now primarily pursued in the group of A.H. Lu, partly in joint projects. The driving forces for such developments are typically catalytic processes for which an advantageous use of high surface area materials is envisaged. This project group originated in the work on zeolites and ordered mesoporous solids, but recently also other materials were included.

Results: Zeolites were investigated with approximately constant intensity since ramping up the work of the department in 1998. In the reporting period, the creation of MFI type zeolites with large external surface area and tailored mesopore system for the Beckmann rearrangement of cyclohexanoneoxime to ε-caprolactam on the one hand, and the synthesis of ETS-10 with controlled defect concentration on the other hand – the latter independently pursued by W. Schmidt – were in the focus of the attention.

Two pathways were pursued for the creation of a mesopore system for MFI type zeolites: In one route, zeolite nanocrystals were crosslinked via polysiloxanes, and the composites were subsequently calcined. This results in conversion of the polysiloxane to a highly porous silica framework in which the zeolite nanocrystals are embedded and are highly accessible. The catalytic activity of these composites for the Beckmann rearrangement is as high as the best ones reported in literature. Remarkably, crosslinked TS-1 nanocrystals do not show the pronounced deactivation which is typical for MFI type materials in this reaction, but the reason for this behavior is not clear as yet. The nanocasting, using a zeolite synthesis gel in a carbon aerogel hard template, developed in the department, also gives high activity MFI catalysts with a controllable mesopore system. Since the carbon aerogels are directly obtained as pellets, also the nanocasting pathway directly leads to pellet formation, and thus no additional forming operations are necessary.

By careful control of the synthesis parameters, a pronounced mesopore system can also be introduced in ETS-10, a tetrahedral-octahedral titanosilicate. These mesopores are

formed by microwave treatment in hydrogen peroxide, by which part of the titanium and silicon is leached from the crystals. The mesopores were found to be also very beneficial in the Beckmann rearrangement reaction, where the activity correlated well with the mesopore surface area of the crystals.

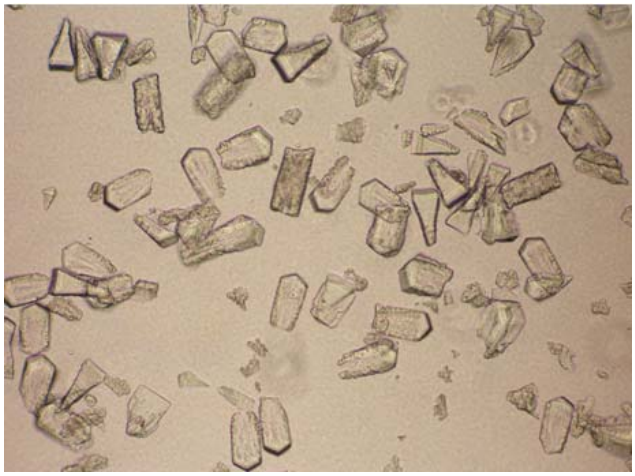


Fig. 1: Optical micrograph of single crystalline segments of silicalite I, obtained by microwave treatment in H_2O_2 followed by ultrasonication.

Microwave treatment of zeolites in hydrogen peroxide proved to be very interesting also in a cooperation project of W. Schmidt with the Kärger-group in Leipzig in which well defined zeolite crystals for diffusion studies are the target of the synthetic work. This treatment, followed by ultrasonication, leads to disintegration of the large, twinned crystals into the segments of which they are composed of (Fig.1). These segments are truly singly crystalline, and this ends a many year long quest for the creation of large MFI type single crystals.

The Beckmann rearrangement of cyclohexanoneoxime was also found to be highly interesting for the study of different types of acid sites in ordered mesoporous silica of the SBA-15 type. By using the method of sequentially removing template from the meso- and the micropores, and selective passivation of the silanols in the mesopores by reaction with functional silanes after template removal from the mesopores, the activity of the different types of silanol groups could be studied separately. The concentration and strength of the acid groups in these two types of pores was analyzed by NMR spectroscopy and FTIR spectroscopy with probe molecules. It was found that both, the silanols in the micro- and the mesopores, are active for the Beckmann rearrangement. However, the activity of the groups in the mesopores was appreciably higher by a factor of about two than that of the silanols in the micropores.

During the reporting period, increased emphasis was placed on the synthesis of oxides via the nanocasting pathway from silica. This had been started already during the last period, but at that time, only one example, Co_3O_4, had been realized, and this needed a special, vinyl-containing mesoporous silica template. By systematically investigating the conditions of the nanocasting process, especially the connectivity of the template silicas and the loading with the oxide to be casted, it was possible to also use regular SBA-15 materials as hard templates and to obtain a detailed picture on the requirements for a successful casting process. Like the previous investigations, these studies were

carried out with Co_3O_4, since the synthesis of this material is rather robust and very well reproducible. Fig. 2 shows the results of a variation of the Co_3O_4 loading of the pore system for the hexagonally ordered material. One can clearly see that at a loading of only 15 % no coherent replica is achieved, but the material remains rather disordered. At 18 % loading larger ordered domains are produced, and at around 20 % loading the replication process is fully satisfactory. Also XRD patterns indicate the higher degree of order with increasing loading. This study incidentally also proved that the material to be nanocasted is collected in domains in the pore system in the hard template instead of being homogeneously distributed. Otherwise it could not be explained, why at a relatively low loading of 20% such well ordered material is produced.

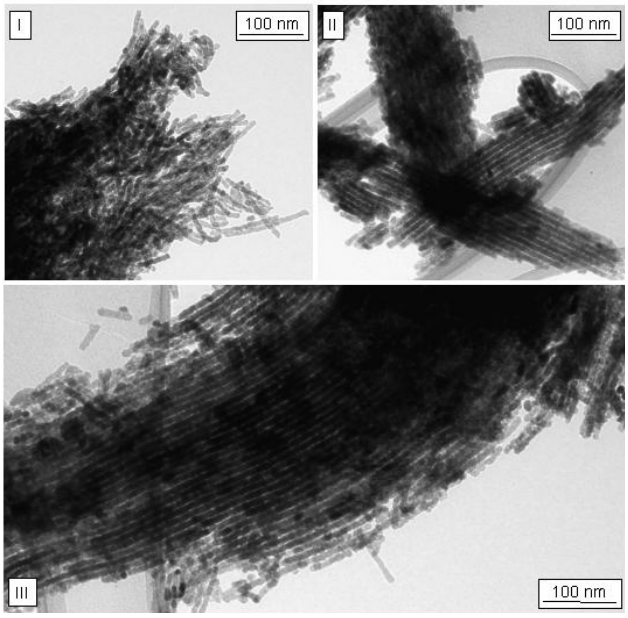


Fig. 2: Effect of the variation of the loading amount in the nanocasting of Co_3O_4 from SBA-15. Upper left 15% loading, upper right 18% loading, bottom 21 % loading.

The Co_3O_4 system was the first one to be studied in detail with magnetic measurements. The material, which is antiferromagnetic, shows weak ferromagnetism at low temperature and a so called exchange bias effect which results from the interaction between a ferromagnet and an antiferromagnet. This was explained by a spin glass behavior of the system, which induces the ferromagnetism due to the large surface to volume ratio in these samples. After the successful synthesis of Co_3O_4 it was attempted to synthesize other materials with interesting magnetic behavior via the nanocasting route. A successful example is ferrihydrite, also an antiferromagnet exhibiting the signatures of an exchange bias system. Synthetically the most interesting system is a nanocast CrO_2, a strong ferromagnet the synthesis of which is rather difficult. It is produced by hydrothermal treatment of Cr_2O_3 under strongly oxidizing conditions, and at present a phase content of CrO_2 of about 80 % has been achieved. These materials are expected to form the basis of magnetic composite materials – 3-D magnetic heterostructures -, in which one magnetic material interpenetrates another magnetic material on the scale of nanometers. This should, for instance, lead to very hard magnets

in case of two ferromagnets being combined, or to systems with more strongly pronounced exchange bias effects, if antiferromagnets and ferromagnets are combined.
Since the syntheses of ordered mesoporous materials are rather complex and expensive, methods to synthesize less ordered solids by cheaper pathways have been pursued as well. Several years ago the activated carbon route had been described by the group for the first time, and the materials basis which can be produced by this pathway has been substantially expanded. Also the role of different additives to increase surface areas has been systematically explored, and for many compositions surface areas of several hundred square meters per gram can routinely be produced by using small amounts of alumina or phosphates as additives. Spherical carbons have proved to be especially suitable for the production of high surface area oxides. The products obtained with such matrices are very pure due to the purity of the carbon, and they are obtained as microspheres, resembling the shape of the carbon parent spheres. Using a rotary furnace, the synthetic method has been scaled up, and it is now routinely possible to synthesize several ten grams per day of such high surface area mixed metal oxides. By inclusion of magnetic compounds during the formation of these oxides, magnetic oxides have been produced which are stable against leaching and can form the basis for magnetically separable catalysts and supports.

Publications resulting from this research area: 6, 85, 94, 95, 96, 97, 105, 106, 107, 108, 112, 116, 131, 148, 161, 165, 175, 181, 187, 189, 191, 198, 199, 222, 291, 306, 307, 330, 331, 334, 335, 358, 360, 374, 390, 501, 519, 520

External Funding: DFG Schm936/3-1, IMPRS SURMAT, BAT

Cooperations: E. Bill (MPI bioanorganische Chemie, Mülheim, DE); J.Kärger (Leipzig, DE); S. Kaskel (Dresden, DE); B. Tesche (Mülheim, DE); H. Zabel (Bochum, DE).

2.3.4 Research area "Nanoengineered Catalysts" (F. Schüth)

Involved: P. Arnal, C. Baltes, P. Bazula, M. Comotti, L. Huang, C.J. Jia, W.C. Li, A.H. Lu, N. Muratova, M. Paul, W. Schmidt, U. Specht, H. Tüysüz, S. Vukojevic, C. Weidenthaler, C.M.Yang

Objective: Over the last years, progress in the synthesis of high surface area materials with controlled structure and porosity on the one side, and in the synthesis of metal nanoparticles with controllable size and surface properties on the other side have made it possible to synthesize catalysts which could rightfully be called "nanoengineered". The objective in this group of projects is the targeted synthesis of catalysts with predetermined properties by the combination of predefined components. This research was already started in the previous reporting period with the synthesis of the magnetically separable ordered mesoporous carbons and ordered mesoporous silica. This field has now grown to such an extent that it justifies a separate discussion in the present report.

Results: Nanoengineering was used both for the synthesis of catalysts with novel properties, such as enhanced thermal stability, and for fundamental studies concerning metal-support interactions. Gold was used in many cases as the active material. This is due to two reasons: firstly, gold is an extremely interesting catalytic material, secondly, gold nanoparticles can be produced by many different methods in monodisperse form over a wide range of particle sizes.

Gold catalysts are intensively investigated as very high activity catalysts for CO oxidation. However, in spite of intensive research efforts over approximately two decades, it is so far not clear, what the influence of the support on the catalytic activity is. This is due to the fact that during the conventional synthetic pathway, deposition-precipitation, the support influences both the development of the gold particles during synthesis and possibly the activity during reaction. It was therefore decided to decouple the gold particle synthesis and the deposition on the support. If differences in activity are

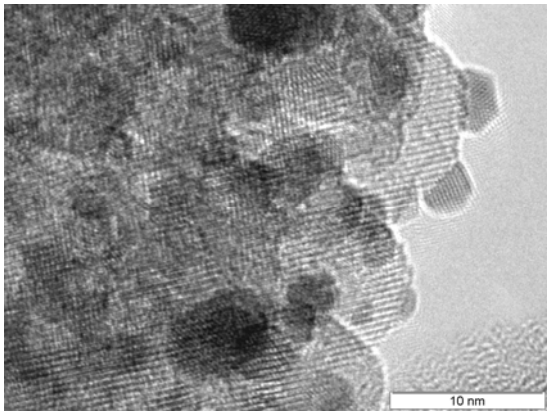


Fig. 1: TEM of Au/ZrO_2 synthesized by colloidal deposition. The gold particles, which are spherical after synthesis, develop a pronounced faceting upon deposition on different supports.

observed for different support materials, this must be due to the influence of the support, since the gold particles are identical for different supports. Four different supports (TiO_2, ZrO_2, Al_2O_3 and ZnO) have been impregnated with polyvinylalcohol-stabilized gold colloids with a particle size of approximately 3 nm and evaluated in CO oxidation. The temperatures for 50 % CO conversion (T_{50}) were very different for these four supports, i.e. around -10 °C for TiO_2 and Al_2O_3, about 50 °C for ZnO, and 90 °C for ZrO_2. Obviously, other than previously thought, the redox-activity of the support material is not directly correlated with the catalytic activity. However, upon colloidal deposition, the particles develop a pronounced faceting (Fig.1), and currently we are investigating whether different support materials induce different faceting. Because differently facetted particles have a different surface concentration of step and kink sites, this could be responsible for the different catalytic activity. The colloidal deposition method was also used to study the influence of different titania polymorphs on the catalytic activity in CO oxidation, but the influence was found to be negligible. Using a nanocast CeO_2 support, colloidal deposition was useful for the synthesis of methanol partial oxidation catalysts which were so active that the reaction ignited at room temperature and operated autothermally at space velocities of several 100.000 $cm^3 g_{cat}^{-1} h^{-1}$.

For many catalyst materials, sintering at high temperatures is a severe problem. Recent developments have allowed the suggestion of a solution for this problem. It relies on the idea that for sintering processes proceeding via particle-particle aggregation, isolation of metal particles in a void with pores smaller than the particle size would prevent contact of the particles and thus the sintering. Based on this idea, the pathway described schematically in Fig. 2, together with TEMs of the corresponding samples, was developed. First, gold colloids are synthesized, on these, silica is grown via a modified Stöber process, and finally, the silica surface is covered by a porous layer of zirconia by a process which had been previously developed in the department for the synthesis of zirconia hollow spheres. After leaching of the silica, the gold particles can move freely in the zirconia spheres, but due to the small pore size in the shell can not leave the shells. Sintering is thus effectively prevented, the materials show unchanged catalytic activity in CO oxidation after heating the catalysts at 800 °C. Since the principle is general, the concept could be extended to other compositions. Shells have been produced from TiO_2 and – by a second process step – from carbon. In addition to gold catalysts, also platinum and palladium metal particles have been placed in the interior of the shell, and it seems possible to extend the concept even further. Moreover, the hollow shells themselves are highly interesting, since they are investigated as building blocks for photonic crystals in cooperation with the group of F. Marlow.

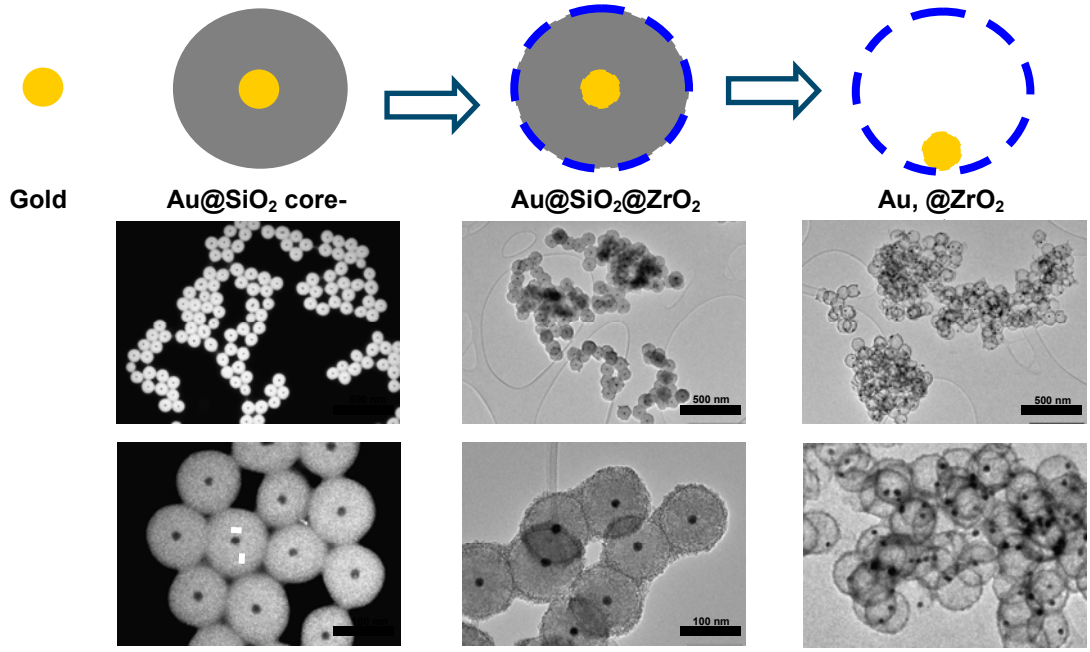


Fig. 2: Schematic representation of the synthetic pathway for the production of sinter stable catalysts (top) and TEMs after each step (bottom).

In the last reporting period, the group of H. Boennemann had described the synthesis of colloidal metal particles by reduction of metal salts with metal alkyls. This method has been used to produce copper nanoparticles, as reducing agents both aluminum alkyls or zinc alkyls have been employed. This allows the combination of the components of the commercial methanol synthesis catalyst in quasi-homogeneous phase to create highly dispersed copper. These particles were found to be very active in methanol synthesis under quasi-homogeneous conditions. Productivities at 170 °C over aluminum-stabilized particles were as high as those of the commercial catalyst at 240 °C, the presence of Zn was found to be unnecessary. Zn-stabilized systems also showed activity at approximately the same level, but higher concentrations of methylformate as product were observed. Depositing such particles on CMK-5 type carbon supports allowed the synthesis of catalysts for the heterogeneous reaction, where also high activity was observed.

CMK-5 was also used for direct impregnation with copper to produce catalysts active in steam reforming of methanol. By adjusting the carbon support hydrophilicity and selection of a suitable copper precursor, well dispersed copper particles on CMK-5 could be synthesized (Fig.3). Such catalysts had surprisingly high activity in methanol steam reforming, considering the relatively low copper

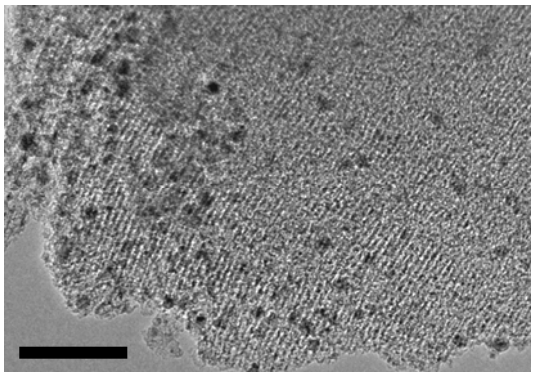


Fig. 3: TEM of Cu/CMK-5. The CMK-5 was preoxidized to make it more hydrophilic, copper was introduced as nitrate. Scale bar 100 nm.

loadings, and the fact that no oxidic support was present, as is normally thought to be required for good steam reforming catalysts. In other reactions, in which high dispersion copper is active, however, such as hydrogenations, the catalysts performed comparatively poorly, for which presently the reason is still unclear.

Finally, the methods for sequentially removing template from the mesopores and then the micropores of SBA-15 were used to deposit metal nanoparticles exclusively in the micropores. For this, the template was first removed from the mesopores, which were subsequently passivated with trimethylchlorosilane. After removal of the template from the micropores, vinyl groups were grafted to the micropore surface, and subsequently brought to reaction with Pd-ions. After reduction, palladium nanoparticles were exclusively present in the micropores. Each step was closely monitored and by HAADF-STEM it could be proved that the Pd-particles were indeed located in the micropores in the walls (Fig. 4).

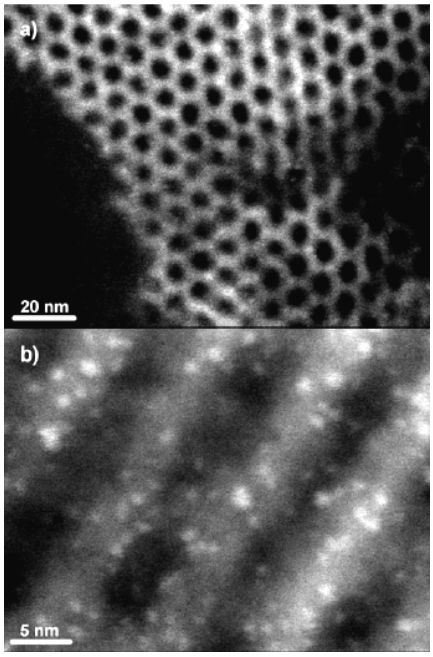


Fig. 4: HAADF STEM image of Pd-particles in the micropores of SBA-15.

Publications resulting from this research area: 10, 91, 157, 158, 185, 213, 214, 215, 220, 249, 310, 311, 319, 430, 476, 477

External Funding: DFG SFB 558

Cooperations: V. Caps (Paris, FR); R. Fischer (Bochum, DE); H. Gies (Bochum, DE); J.D. Grunwaldt (Zürich, CH); M. Muhler (Bochum, DE); B. Tesche (Mülheim, DE), C.M.Yang (Taipeh, TW).

2.3.5 Research area "Light metal hydrides for hydrogen and energy storage" (F. Schüth / B. Bogdanović)

Involved: J. Döring, M. Felderhoff, K. Hauschild M. Mamatha, R. Pawelke, A. Pommerin, W. Schmidt, N. Spielkamp, G. Streukens, J. von Colbe de Bellosta, C. Weidenthaler, B. Zibrowius

Objective: Complex light metal hydrides with $NaAlH_4$ as one of the most popular reversible hydrogen storage materials are still in the focus of the research activities. With the principle description of the processes during the hydrogenation and dehydrogenation and the status of the catalyst, this and similar materials become interesting in demonstration projects. The objective is to show the practicability in systems together with HT-PEM fuel cells. Further research activities are the understanding of the thermodynamics of the systems and the research in new light complex metal hydrides with higher hydrogen content compared to $NaAlH_4$.

Results: $NaAlH_4$ remained in the center of attention, since this system is not only closest to reach technical benchmark criteria for practical applications, it is the model system for the fundamental understanding of the processes in complex aluminum hydrides during the doping reaction and the hydrogenation and dehydrogenation reaction. For commercial applications a fast and cheap preparation method of $NaAlH_4$ is necessary. Therefore we have developed a new synthesis method for doped $NaAlH_4$, starting from cheap industrial chemicals. A highly reactive doped $NaAlH_4$ was synthesized from Al-metal, NaH and $TiCl_3$ under a hydrogen pressure of approx. 80 bars with the ball-milling method. Telemetric data transfer of the process parameters pressure and temperature allows the *in situ* observation of the reaction progress (Fig. 1). Further advantages over the normal synthesis route are shorter reaction times, lower reaction temperatures and excellent kinetics of the prepared material. With this reactive ball-milling method different other metal hydrides (e.g. CaH_2, TiH_2, ZrH_2) were prepared. This reactive synthesis method can also used for different other gas-solid reactions.

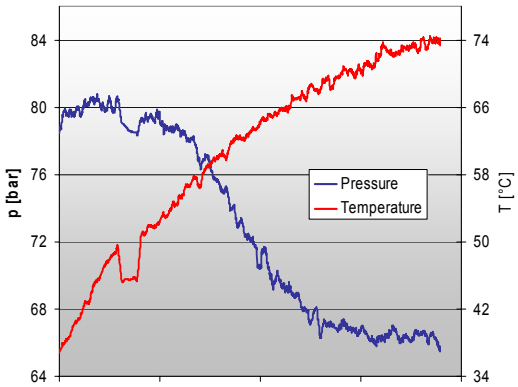


Fig. 1: Pressure and temperature progression during the direct synthesis of doped $NaAlH_4$.

After the description of the state of the titanium catalyst from the doping process and during the hydrogenation and dehydrogenation reactions in the last reporting period, the change of thermodynamics of $NaAlH_4$ upon different doping levels and dopants was now investigated. From pressure-composition isotherms (PCIs) the equilibrium pressure of a given material can be determined. This equilibrium pressure is a function of the thermodynamics at a given temperature. Indeed, an increase of the dissociation pressure with increasing doping levels was observed for the first time in the field of complex aluminum hydrides. A model based on the thermodynamics of the Ti-Al phase, which is formed during the doping reaction, was developed. This model describes the changes in thermodynamics with the stepwise dilution of a $TiAl_3$ phase through Al-metal produced during the decomposition of $NaAlH_4$ (and vice versa for the hydrogenation). The fact, that the thermodynamics of $NaAlH_4$ can be influenced by the type and the amount of a dopant is of great importance for new applications of doped complex metal hydrides.

Doped $NaAlH_4$ was further discovered as a reduction catalyst in organic reactions of CC and CO-multiple bonds, different to the stoichiometric reductions with other complex hydrides. First the catalytic hydrogenation of tolane was discovered as a model system in a batch reactor, then the hydrogenation process was even transferred to the gas phase reduction of ethylene. In both cases complete hydrogenation with sub-stoichiometric amounts of doped $NaAlH_4$ and Na_3AlH_6 is possible in the presence of hydrogen. For selective reduction of different multiple bonds or the reduction of multiple bonds with heteroatoms, the optimization of the conditions of the process is necessary and still under investigation.

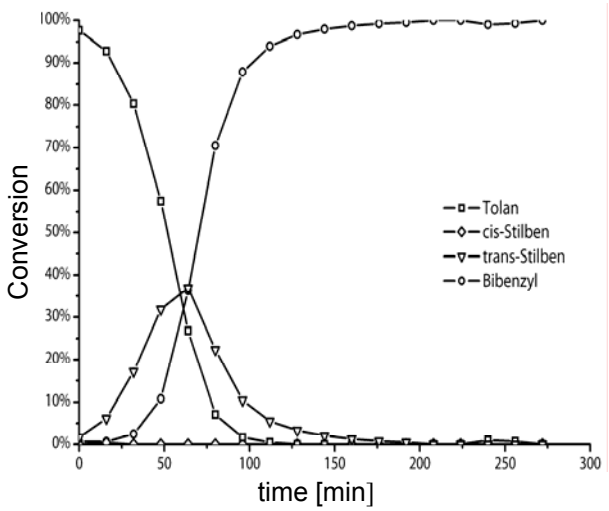


Fig. 2: Reaction progress during the catalytic hydrogenation of tolane with doped $NaAlH_4$.

Other complex metal hydrides, e.g. $Mg(AlH_4)_2$, $Ca(AlH_4)_2$, $LiMg(AlH_4)_3$ with high hydrogen content were synthesized from a metathesis reaction via ball-milling (as shown for $Mg(AlH_4)_2$) and characterized.

$$MgCl_2 + 2\,NaAlH_4 \xrightarrow{\text{ball-milling}} Mg(AlH_4)_2 + 2\,NaCl$$

Unfortunately none of them show reversibility under acceptable technical conditions and thus they can't be used as reversible hydrogen storage materials. Other research

activities focus on the development of unstable complex hydrides with high hydrogen content. These materials are only stable at higher hydrogen pressure (up to 300 bars) at room temperature. The combination of an unstable metal hydride and a high pressure tank can increase the possible storage capacity of a hydrogen storage system necessary for automotive application.

After ten years of research in the field of complex metal hydrides the synthesis and the doping processes of the material are optimized. The next step must be the demonstration of the usability of these materials as hydrogen storage materials in combination with fuel cells. In a demonstration project, together with the ZBT and IUTA in Duisburg, we develop and prepare doped complex metal hydrides as hydrogen storage materials for HT-PEM fuel cells. With the waste heat (150°C) of a HT-PEM fuel cell both decomposition steps of the alanate can be used without additional external heating. Preparation of different material batches in the kg-range is in progress.

Publications resulting from this research area: 13, 156, 190, 229, 233, 321, 322, 364, 367, 376, 392, 417, 434, 435

External Funding: GM/Opel, AIF, Powerfluid

Cooperations: A. Heinzel (Duisburg, DE); J. Wartmann (Duisburg, DE).

2.3.6 Research area "Nanostructured Carbon Materials" (F. Schüth / A. H. Lu)

Involved: P.A. Bazula, J.J. Nitz, M. Feyen, C. Weidenthaler, W. Schmidt

Objective: In this project, we focus on developing methods for the synthesis of nanostructured carbon-based porous materials, and magnetically separable catalysts or adsorbents. These materials are synthesized to have tunable properties, including surface area, pore size, pore volume, surface functionality and morphologies. Such materials with well-defined structures and properties are very important for the understanding of fundamental issues in the application of carbon materials in adsorption and catalysis. This will provide the underpinning for real design of carbon-based functional materials.

Results: Using mesoporous silica SBA-15 as template, ordered mesoporous carbon with hexagonal symmetry can be synthesized. For tuning the pore size and pore wall thickness of that kind of carbon, we have developed a new method for removing the surfactant in SBA-15, low-T $KMnO_4$ chemical oxidation, thus preventing structural shrinkage of the silica template. Using this silica as template, mesoporous carbon with thick pore walls and relatively small mesopores can be cast (Fig. 1). Interestingly, the analysis of the micropore volume based on the DFT method shows that these carbon replicas have a large fraction of micropores with respect to the total pore volume. These micropore rich carbon materials could be candidates as molecular sieve type adsorbents and catalyst supports.

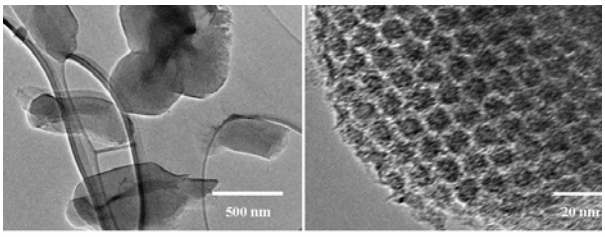


Fig. 1: TEM images of ordered mesoporous carbon with thick pore wall.

Nanocast carbon monoliths exhibiting a multi-modal porosity have been prepared by one-step impregnation, using silica monoliths, also containing a multi-modal porosity, as the scaffold (Fig. 2). It is shown that the carbon monolith represents a positive replica of the starting silica monolith on the micrometer length scale, while the volume templated

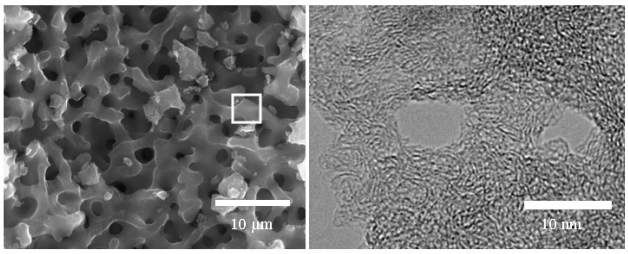


Fig. 2: SEM and TEM images of nanocast carbon monolith with multi-modal pore size distributions

mesopores are a negative replica of the silica scaffold. In addition to the meso- and macropores, the carbon monoliths also exhibit microporosity. The different modes of porosity are arranged in a hierarchical structure-within-structure fashion, which is thought to be optimal for applications requiring a high surface area in combination with a low pressure drop over the material.

We have also developed a new synthetic method for the preparation of hierarchically structured carbon monoliths by self-binding and salt templating (Fig. 3), which involves the mixing and shaping of SBA-15/poly(furfuryl alcohol) composites with small particle NaCl. After carbonization and leaching out the salt with water and the silica with NaOH solution, hierarchically structured carbon monoliths are obtained, which show the presence of macropores and mesopores derived from the removal of salt and silica, respectively. The advantages of the current synthesis are the use of furfuryl alcohol both as the carbon source and the binder, as well as the inexpensive, thermally stable and water soluble NaCl as macropore generator. This approach can be extended to prepare other carbon monoliths containing differently ordered mesopores and macropores, by judicious choice of the silica templates such as M41S materials or those of the SBA-n series.

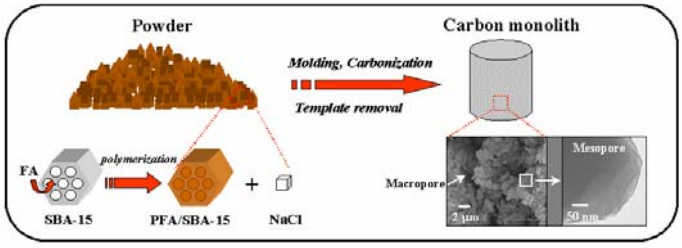


Fig. 3: Synthetic pathway for the fabrication of hierarchically structured carbon monoliths.

To obtain mesoporous carbon with highly dispersed nanoparticles or catalytically active sites in the carbon walls, the foreign metallic species need to be confined in a confining space, to prevent their growth during processing. We have successfully synthesized ordered mesoporous carbon containing molecular-level dispersed Pd clusters in the carbon walls via a nanocasting pathway. Typically, polyacrylonitrile was first introduced into mesoporous silica, followed by low temperature oxidation, adsorption of Pd cations, and pyrolysis (up to 750 ^{o}C). Due to the confinement from both the silica template and the carbon source itself, high dispersion of Pd on ordered mesoporous carbon is achieved. The catalysts exhibit strikingly high selectivity (>99%) for alcohol (benzyl alcohol, 1-phenylethanol and cinnamyl alcohol) oxidation to the corresponding aldehydes while at the same time having relatively high activity.

Another research direction is the preparation of graphitic porous carbon with high surface area and narrow pore size distribution. High surface area graphitic carbons are of great interest in emergent applications including catalysis and energy storage, because of the well-developed crystalline structure, high electronic conductivity and

thermal stability, and satisfactory oxidation resistance at low temperature. We have developed the synthesis of porous graphitic carbon with a large and accessible surface area via synthesis of carboxyl containing polymer particles, followed by ion-exchange and pyrolysis at low temperature (850°C) (Fig. 4). Especially, the development of mesoporosity resulting from continuously catalyzed carbonization by the in situ formed cobalt nanoparticles can be clearly recognized. Further nitric acid oxidation leads to an increase of the pore volume due to the removal of cobalt nanoparticles and opening of closed pore entrances. Moreover, the use of silica as isolating shell facilitates the formation of high surface area graphitic carbon (Fig. 5).

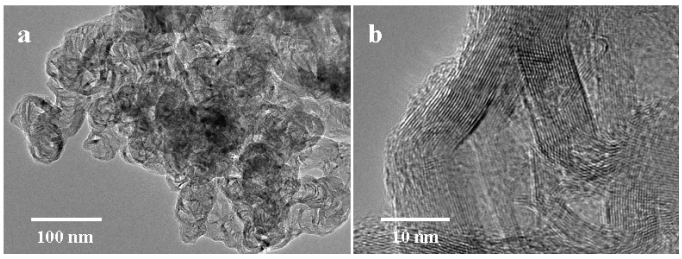


Fig. 4: TEM images of porous graphitic carbons

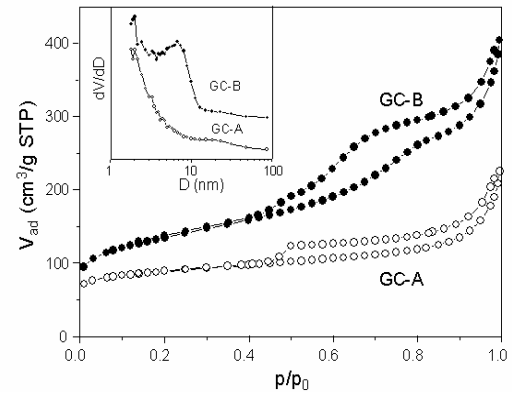


Fig. 5: Nitrogen sorption isotherms and pore size distributions (insert) of graphitic carbons: GC-B obtained from GC-A after leaching SiO_2 and cobalt.

Magnetization measurements show that the graphitic carbon/cobalt composites exhibit ferromagnetic properties, and the cobalt nanoparticles are stable under air for more than 10 months without degradation of their magnetic properties.

For many catalytic processes in the liquid phase, nanosized catalyst particles lead to the blocking of filters and valves. Nanosized particles are almost impossible to separate by conventional means. Thus, structurally stable magnetic nanoparticles can play an important role in the separation of such small particles from a liquid phase. To protect magnetic nanoparticles from oxidation or erosion, carbon materials are among the most suitable candidates as the protective shell because of their thermal stability, chemical resistance and biocompatibility.

We have succeeded in the design of magnetically separable catalysts based on magnetic cobalt nanoparticles attached to a catalyst support. A protection strategy was

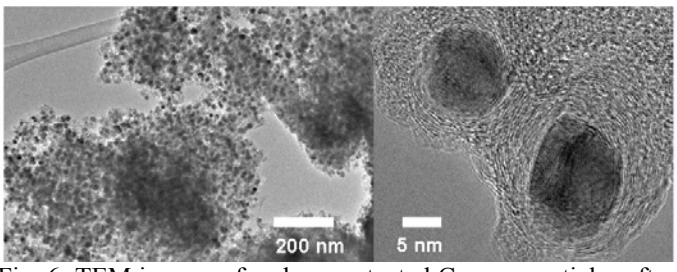


Fig. 6: TEM images of carbon protected Co nanoparticles after 1 month treatment in 53% HNO_3.

employed to cover the magnetic core with a carbon shell that shows resistance to corrosive media and high temperature sintering (Fig. 6).

Using mesoporous silica as the support loaded with a thin layer of Fe^{3+} on the pore walls, we have observed the formation of amorphous carbon nanotubes on a mesoporous silica matrix during a catalytic CVD process (Fig. 7). This may supply a versatile approach to fabrication of carbon nanotubes with various morphologies.

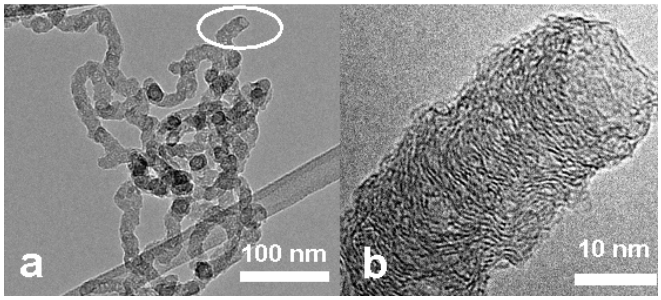


Fig. 7: TEM images of amorphous carbon nanotubes.

Publications resulting from this research area: 111, 112, 113, 114, 115, 116, 117, 316, 317 318, 319, 476, 477, 501

External Funding: none

Cooperations: H. Bönnemann (Mülheim, DE); W. Li (Dalian, CH); W. Kiefer (Würzburg, DE); M. Lindén (Heidelberg/Abo, FI)

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

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

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 are developing a novel technique combining information technology and chemical analysis.

Results: A novel strategy to increase the sample throughput in a chromatographic system has been elaborated by using rapid structured sample modulations based on pseudo-random binary sequences. These sequences represent a bar-code encoding the overall chemical composition of the samples injected in a GC system. However this increases only the duty cycle of the separation system. To increase the throughput this barcode was divided in bar-codelets encoding individual samples and conserving the sample concentrations. To put this strategy into practice a six-port multiplexing injector was designed and placed onto a GC injector (cf. Figure 1).

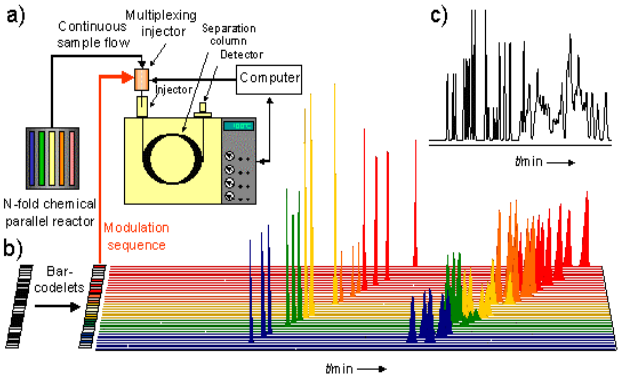


Figure 1. htMPGC. a) Schematic experimental setup for analyzing the sample composition of an N-fold chemical parallel reactor. b) 2D plot of the temporally shifted chromatograms obtained by repetitive sample injections. c) Convoluted chromatogram, which represents the sum of the chromatograms depicted in b).

Samples are rapidly injected by the multiplexing injector onto the separation column according to the bar-codelets of a *n*-bit binary pseudo-random sequence (black: bar-code, colored: bar-codelets). These bar-codelets are used to control the time shifted repetitive injections of each sample by a computer. Long *n*-bit binary pseudo-random sequences with N elements ($N = 2^n$-1), which are

derived from Hadamard matrices, consist of 50% of the elements 0 (no sample injection) and of 50% of the elements 1 (sample injection) and therefore the overall duty cycle of the separation system is increased to 50%. These sequences are unique and therefore encoded information can be later unambiguously identified by application of the HT. Furthermore, with increasing sequence length N the SNR is improved (maximum gain $=\sqrt{N}/2$). Structured repetitive injections are necessary to unambiguously identify the individual samples. The analytes of each injection are separated in the separation column yielding time shifted chromatograms. The measured chromatogram is a convolution of these overlapping time shifted chromatograms.

In the current design short and precise injection intervals (time bin intervals Δt) in the range of 500 to 2000 ms and short and highly reproducible injection pulses could be achieved. Compared to a conventional injection system, e.g. liquid autosampler, these short injection pulses lead to very narrow sample volumes. In average the peak width w_h decreases by a factor of 3 ± 20%, which in turn improves the separation efficiency (~ $(1/w_h)^2$) and the multiplexed chromatogram.

Whereas typically the time bin interval Δt also defines the injection pulse duration, and leads to rectangular (box-car) shaped concentration profiles on the separation column, here the injection pulses were chosen considerably shorter (in the range of ms) than the time interval Δt to improve the resolution of the obtained chromatogram and therefore allow to further increase the information density. With the multiplexing injector up to 3,000 injections/ h (Δt = 0.6 s, 50% duty cycle) from different sample ports were achieved (cf. Figure 2) corresponding to 453 samples/ h and an increase by a factor of 38 compared to the respective conventional separation.

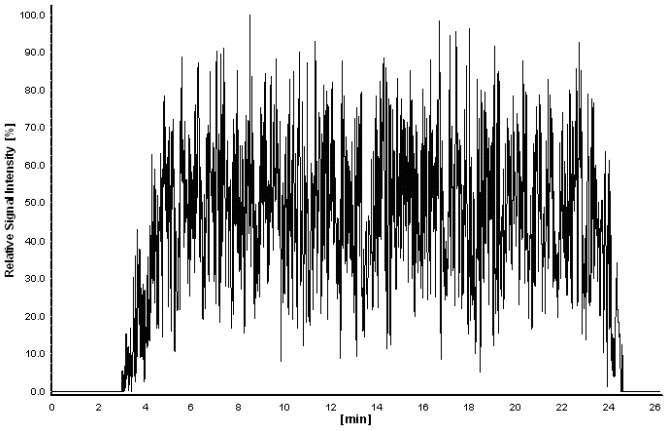


Figure 2. Experimental chromatographic data obtained by htMPGC. 200 samples with 5 analytes of varying concentrations were injected by the prototype multiplexing injector according to a 11-bit (2,047 time bins) binary pseudo-random sequence with injection pulses of 1 ms. Time bin interval Δt = 600 ms (3,000 injections/ h), 5 injections/ sample (453 samples/ h).

To obtain the relative concentrations of the analytes in each sample a deconvolution algorithm for the raw data was developed and applied to these data sets. This algorithm is based on the Hadamard transformation to obtain an overview chromatogram containing the information about the number of analytes and then a matrix system is

derived which is solved by a Gauss-Jordan algorithm to obtain the individual concentration of the samples.
Future research directions are the coupling with other analytical techniques, *i.e.* mass spectrometry or a second chromatographic dimension, to further increase the information density and allow identification of products at the same time and coupling with parallel reactors to perform high-throughput kinetic studies of catalysts. The application of this approach to other chromatographic and electrophoretic techniques and in particular to ultra-fast separation techniques is envisaged to maximize the sample throughput in future applications.

Publications resulting from this research area: 89, 180, 385, 386, 536

External funding: DFG (Emmy Noether Program); FCI; Merck Research Laboratories

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

2.3.8 Research Area "High-Throughput On-column Reaction Chromatography" (O. Trapp)

Involved: T. Bäcker, B. Barth, S. Bauch, H.-W. Hofstadt, M. Spallek, B. Spliethoff, S.K. Weber

Objective: Microfluidic systems are currently revolutionizing chemical synthesis, because physical processes can be more easily controlled, low operation volumes save reagents and detection is integrated. However, there are still many challenges which need to be solved, among these are the control of mixing, because diffusion rates contribute to apparent reaction rates, incompatibility with standard analytical instruments and interfacing with MS, only to mention a few. In this group of projects a strategy is developed, which truly unites synthesis and analysis by combining catalytic activity and separation selectivity in the polymeric stationary phase of a chromatographic separation capillary. 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 bond catalysts on polysiloxane matrices. Furthermore equations are derived to efficiently evaluate such experiments.

Results: Over the last decades one of the major challenges in dynamic chromatography, which allows the dynamic study of interconverting stereoisomers – which is of great importance to investigate the stereostability of drugs - in a chromatographic system, was the evaluation of the experimental chromatograms to obtain reaction rate constants. Evaluation procedures based on iterative computer simulations are very slow and require considerable computing power. Despite the advances over the last couple of years a direct access to reaction rate constants was desirable. We overcame this problem by deriving the unified equation to evaluate elution profiles of reversible as well as irreversible (pseudo-) first order reactions in dynamic chromatography and on-column reaction chromatography. Rate constants k_1 and k_{-1} and Gibbs activation energies are directly obtained from the chromatographic parameters (retention times t_R^A and t_R^A of the interconverting or reacting species A and B, the peak widths at half height w_A and w_B, and the relative plateau height h_p), the initial amounts A_0 and B_0 of the reacting species, and the equilibrium constant $K_{A/B}$. The calculation of rate constants requires only a few iterative steps without the need of performing a computationally extensive simulation of elution profiles. Currently up to 120,000 experiments can be evaluated within 10 s. The unified equation was validated by comparison with a dataset of

125,000 simulated elution profiles to confirm the quality of this equation by statistical means, and to predict the minimal experimental requirements. Surprisingly, the recovery rate from a defined dataset is in average 35% higher using the unified equation compared to the evaluation by iterative computer simulation. The here derived unified equation opened the possibility to investigate catalysts in an on-column reaction chromatographic setup in a high-throughput fashion.

We focused on hydrogenations over Pd nanoparticles embedded in an inert polydimethylsiloxane matrix without any interfering protecting shell, i.e. tetraalkylammonium salts as surfactants. Therefore we prepared methylvinyl-siloxanedimethylsiloxane copolymer (4.5% $Si(O)(CH_3)$ ($CH=CH_2$) groups) to coordinate Pd ions to the vinyl groups in diethylether. To this mixture hydridomethyldimethylpolysiloxane copolymer (25.7% $Si(O)(CH_3)H$ groups) was added for the reduction of Pd^{2+} to Pd^0 and to crosslink with the methylvinylsiloxanedimethylsiloxane copolymer in a hydrosilylation reaction, catalyzed by Pd, to form a stabilizing matrix. The Pd nanoparticles are spherical and crystalline with a narrow size distribution, determined by TEM, of 3.2 nm ± 0.7 nm.

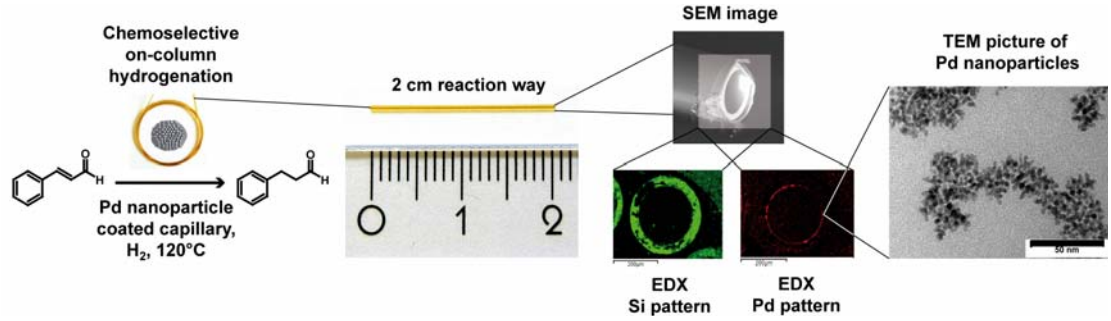


Figure 1. On-column hydrogenation over highly active Pd nanoparticles. Capillaries of only 2 cm coated with Pd nanoparticles stabilized in a polysiloxane matrix are used as reactor. SEM and Si/ Pd EDX measurements show the coating of the fused silica micro capillaries (i.d. 250 µm, 0.25 µm film thickness).

The obtained viscous brownish-grey polymers are coated as a thin film of 0.25 µm onto the inner surface of fused-silica capillaries (i.d. 250 µm) resulting in a permanently bonded polymer. The Pd loading is extremely low, only 0.73×10-12 mol/ cm capillary (corresponding to ~27 billion Pd nanoparticles/ cm with 1600 to 1700 Pd atoms/ particle).

On-column catalysis was performed by coupling this Pd nanoparticle micro capillary between a pre-separation capillary (1 m) and a separation column (25 m). The purpose of the pre-separation column is to thermally equilibrate the reactants and to spatially separate the educts of the injected compound library, which enables ht kinetic investigations because of the absence of competing reactions. Reaction educts and products were identified and quantified by GC-MS. Educt libraries consisting of 22

unsaturated compounds (alkenes, alkines, aromatic hydrocarbons) and functionalized compounds (nitro compounds, aldehydes, ketones) to investigate the chemoselectivity were simultaneously injected onto this column configuration at different temperatures and gas flows to vary the reaction time and to obtain temperature de-pendent kinetic data. We observed extraordinary fast hydrogenations leading to complete conversion of the reaction educts even for Pd nanoparticle capillaries of only 5 cm length and low temperatures of 60°C. Therefore, to achieve incomplete conversions for the kinetic measurements all experiments were performed with a 2 cm capillary and reaction times in the range of 20 ms to 1 s. From temperature and flow (contact time) dependent conversion measurements for each compound we obtained data sets which were put into kinetic models based on a Langmuir-Hinshelwood mechanism to determine reaction rate constants k and activation parameters (Gibbs activation energy $\Delta G^{\ddagger}$, activation enthalpy $\Delta H^{\ddagger}$ and activation entropy $\Delta S^{\ddagger}$).

The high activity of the Pd nanoparticles was corroborated by the activation parameters, showing low activation enthalpies $\Delta H^{\ddagger}$ and negative activation entropies $\Delta S^{\ddagger}$, which corresponds to a restraint transition state. It is important to note that our experimental setup has the advantage of precise temperature control and that diffusion processes can be quantified and furthermore experimentally controlled by the used polysiloxane. Because we inject simultaneously large educt libraries we achieved experimentally a throughput of 5880 reactions in 40 hours. This corresponds to the determination of a complete set of activation parameters in less than 2 hours. Such a throughput allowed us to screen 40 systematically varied Pd nanoparticle samples and to correlated the activation energy $\Delta G^{\ddagger}$ with the structure of the particles.

Furthermore we focused on ring closure metathesis (RCM) catalyzed by Grubbs 2nd generation catalyst. Catalytically active micro columns were obtained by dissolving Grubbs 2nd generation catalyst in dimethylpolysiloxane (GE SE 30) and coating micro capillaries (10 m) with a film thickness of 1 µm under strict exclusion of oxygen. The catalyst loading is only 1.6 µg/ m (1.9×10-9 mol/ m) capillary. The on-column catalysis was performed by coupling such columns with a pre-separation column of 1 m.

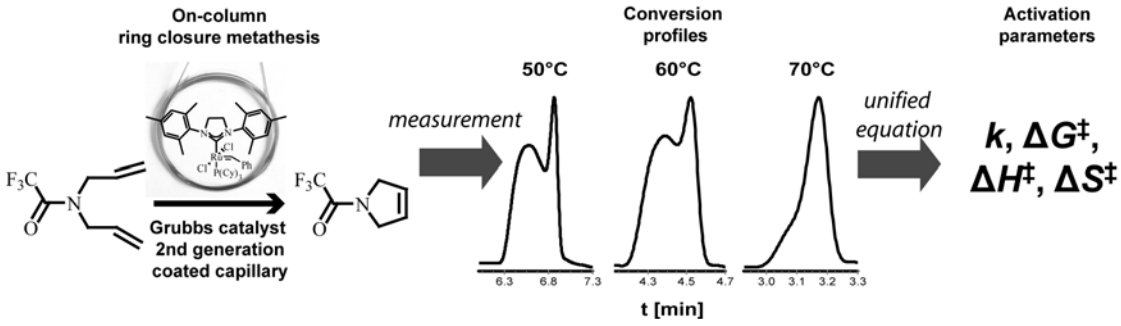


Figure 2. On-column metathesis over Grubbs 2nd generation catalyst.

We simultaneously injected an educt library of 12 different compounds for ring closure metathesis onto the catalytically active separation column. In these experiments we obtained elution profiles characterized by a plateau formation between the reaction educt and product (cf. Figure 2), which were analyzed by the unified equation to obtain reaction rate constants. Activation parameters obtained, corroborated recently reported theoretical calculations performed in an effort to explain the high activity of Grubbs 2nd generation catalyst. Also in these experiments by the simultaneous injection of an educt library we achieved an extraordinary high throughput in the determination of reaction rate constants (36 rate constants/h).

Because these catalytically active separation capillaries are easy to handle and to prepare we used them in a modular design for a two-step cascade reactions. Therefore we coupled a 80 cm column, coated with the dissolved Grubbs 2nd generation catalyst, and a 10 cm Pd nanoparticle column, followed by a separation column for product analysis. We used hydrogen as a carrier gas, but the experiment could also be performed with helium in the first column section and adding hydrogen in the second section. We demonstrate that metathesis of N,N-diallyltrifluoroacetamide followed by on-column hydrogenation is possible in less than 6 min with an overall yield of 49% The here outlined strategies can be generally applied to other catalytic processes, and we found that they can be utilized in the comprehensive kinetic characterization of catalysts and materials. Furthermore it can be envisioned that catalytic capillaries are also useful for selective transformations in analytical applications for structure elucidation. Moreover, for a preparative scale-up only a stack of reactor capillaries is necessary to increase the productivity. In this approach the advantage of heterogeneous catalysis to easily separate catalyst and reaction product is also conserved, which is normally a problem for nanoparticular and homogeneous catalysts.

Publications resulting from this research area: 179, 185, 285, 381, 382, 383, 384, 397, 535, 537

External funding: DFG (Emmy Noether Program); FCI, Merck Research Laboratories

Cooperations: F. Schüth (Mülheim/Ruhr, DE); N.H.H. Heegaard (Copenhagen, DK); V. Schurig (Tübingen, DE); C. Welch (Rahway, USA); S. Allenmark (Göteborg, SE); F. Dondi (Ferrara, I); B. Tesche (Mülheim/Ruhr, DE)

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

Involved: H. Bretinger, R. Brinkmann, D. Konjhodzic, H. Li, I. Popa

Objective: Ordered porous materials are highly interesting hosts for optically functional materials. Micro, meso, and macro pores have specific effects on molecular guests and electromagnetic fields and both of these effects can be exploited for the construction of materials. Synthesis, modification, and characterization of such materials are investigated in this research area in order to develop novel functional materials.

Results: Three different directions have been pursued within this field of research: photonic crystals, low-n materials, and PZT films.
The field of macroporous materials is directly relevant for photonic crystals which have attracted much attention since they are key materials for future optical technologies. We succeeded to fabricate well-shaped opals and inverse opals which are expected to show photonic band gaps. We have developed a new efficient method 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 opals which cannot be avoided in layer systems.
The detailed understanding of the opal self-assembly process is another topic of basic and application interest. The opal formation can be divided into two temporal phases: the wet assembly and the drying. Both are of relevance for the quality of the opals. We can follow these phases in-situ by optical spectroscopy and found out that during drying interesting slow rearrangement processes take place. On a time scale of hours the final nanosphere arrangement is formed.
An attempt for application of opal-type photonic crystals will be the demonstration of slow photon effects. Because of the interaction of these materials with electromagnetic waves it is possible to realize waves with very low group velocity (“slow photons”). These can drastically enhance the efficiency of photochemistry and other light-matter interactions.

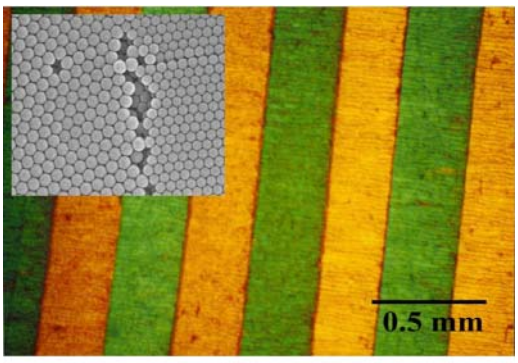


Fig. 1: Optical and SEM picture of an opal hetero structure. This stripe arrangement of different opals shows that the opal deposition can be accurately controlled. This is of importance for any application of this type of photonic crystals.

The field of mesopores is also explored for the construction of optical materials. Here low-n materials are the most successful example because of their use in optical waveguide devices. Waveguiding is a key requirement in most future photonic elements. However to keep the waves confined in a functional layer one has to surround this layer by materials with low refractive index. There is a big lack of such materials and, therefore, the mesoporous substances which can have a refractive index down to 1.14 are a highly interesting solution. We have improved one mesopore synthesis resulting now in reproducible, perfect films with a thickness up to 1 µm. These films proved to be suited for further microstructure processing such as organic and inorganic layer deposition, lithographic structuring and reactive ion etching. This has been demonstrated in the fabrication of several 2-dimensional photonic crystals (Figure 2).

A further important step is the combination of such layer systems with more effective functional materials. Therefore we investigate the deposition and structuring of ferroelectric PZT layers on mesoporous films.

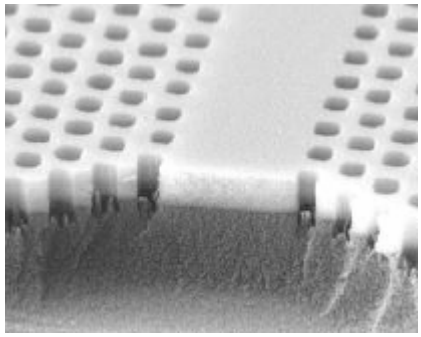


Fig. 2: An example of a 2-dimensional waveguide structure consisting of two finite photonic crystals separated by a photonic "defect". Here the defect can serve as a nanoscopic waveguide. The structured waveguide core consists of tantalpentoxide and the support is mesoporous SBA-15-like (Cooperation with the IPHT Jena).

Publications resulting from this research area: 93, 103, 104, 120, 305, 309, 433, 468, 524, 544

External funding: DFG SPP 1113 "Photonic Crystals"

Cooperations: M. Eich (TU Hamburg-Harburg, DE); S. Schröter (IPHT Jena, DE); F. Schüth (Mülheim/Ruhr, DE); E. Mazur (Harvard, USA); G. Ozin (Toronto, CA)

2.3.10 Research Area "Novel Mesostructures" (F. Marlow)

Involved: H. Bretinger, R. Brinkmann, A. Khalil, M. Stempniewicz, U. Wilczok

Objective: In the investigation of mesoporous fiber lasers and low-n films novel types of solid state organization (circular structures and sustained layer structures) have been found. These findings require detailed structural investigations as well as investigations concerning the formation mechanism and the physical consequences of these structures.

Results: The normal synthesis of circularly structured mesoporous fibers delivers a mixture of products. This mixture is not a result of condition fluctuations but of a thermodynamic coexistence of different structures. A way to control this mixture was found by the use of surfaces. A surface can select a special kind of products and a structured surface can order these products as shown in Fig. 1. Such arrays offer new perspectives for investigations and applications. The arrays allowed analyzing the hierarchical structure of the circular objects exactly. It turned out that the pores in every individual particle are arranged in densely packed spirals as for fibers. The difference to the fibers is only the combination of the packing with the way of coiling. This results in very similar energetic properties, but different shapes.

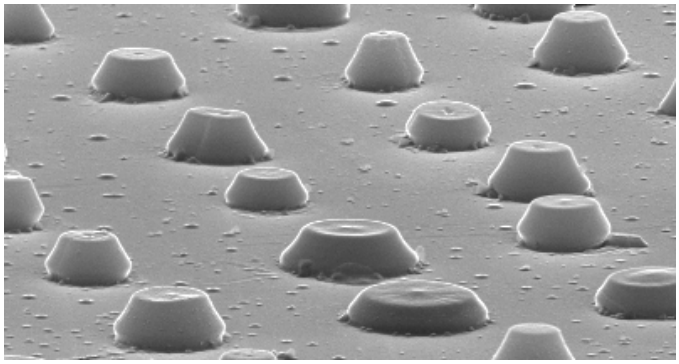


Fig. 1: Controlled deposition of circular mesostructures. A glass support was modified by micro contact printing and then exposed to a SBA-3-like synthesis solution. The ordered growth of one kind of circular mesostructure was observed reproducibly.

The circular fibers and particles represent a new type of solid state organization with modified physical properties. Diffusion is one of the interesting modified phenomena in these solids. The coiling of the mesochannels (Fig. 2) makes the diffusion along the channels ineffective in

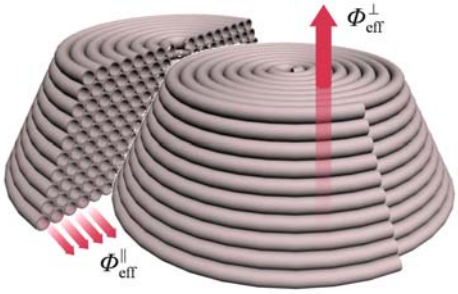


Fig. 2: Schemes of the particle structure and the possible flux directions of guests in the mesopores. Particles with open channels were produced by cutting particles.

phenomena like release and uptake. This fact allows the study of competing processes such as cross-wall transport. Such kind of transport was indeed detected and quantified. In addition, a significant surface barrier was found. The studied mesoporous system proved to be interesting for release applications for example in corrosion protection systems (Cooperation with the MPI for Iron research).

Publications resulting from this research area: 119, 178, 298, 323, 324, 380, 478, 528, 529, 530

External funding: DFG SPP 1113 “Photonic Crystals”, IMPRS “SurMat”

Cooperations: M. Rohwerder (MPI für Eisenforschung, Düsseldorf, DE); F. Schüth (Mülheim/Ruhr, DE); C.W. Lehmann (Mülheim/Ruhr, DE); B. Tesche (Mülheim/Ruhr, DE)

2.4 Department of Organometallic Chemistry

Director:

Alois Fürstner (born 1962)
Publications: 1, 15, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 60, 98, 118, 121, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 407, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 489

Further group leaders:

Stefan Hecht (born 1974)
left the Institute in September 2006
Publications: 8, 9, 34, 71, 72, 86, 87, 122, 209, 218, 299, 300, 301, 302, 339, 340, 375, 481, 500, 532, 541

Lisbet Kvaerno (born 1974)
joined the Institute in September 2007

Other publications: 38, 208

Curriculum Vitae: Alois Fürstner

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

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

Special Activities

1997-	Member, Editorial Board of "Topics in Organometallic Chemistry"
2000-	Member, Advisory Board of "Advanced Synthesis & Catalysis"
2001-2007	Scientific Editor, "Chemical Communications"
2001-2006	Member, Board of Editors of "Organic Syntheses"
2002-2004	Member, Editorial Advisory Board of "Journal of Organic Chemistry"
2002-	Member, Advisory Board (Wissenschaftlicher Beirat) of the Institut für Organische Katalyseforschung, Rostock
2002-	Member, Selection Committee of the Alexander-von-Humboldt Foundation (Feodor-Lynen-Program)
2004-	Member, Board of Governors, German Chemical Society
2005-	Member, Editorial Advisory Board of "Progress in Heterocyclic Chemistry"
2006-	Chairman, Selection Committee of the Alexander-von-Humboldt Foundation (Feodor-Lynen-Program)
2007-	Member, Advisory Board of "Nachrichten aus der Chemie"

Research in the Department of Organometallic Chemistry

The Department of Organometallic Chemistry in its present form was created in 1998 when Prof. Fürstner was appointed as Director at the Institute. Its mission is the development of organometallic reagents and catalysts and their use as tools for advanced organic chemistry, notably the total synthesis of structurally complex and biologically relevant compounds. So far, the Department has hosted three junior groups in addition to Prof. Fürstner's own research team:

- Prof. Frank Glorius (2001-2004) started his independent career in Mülheim before he became Professor of Organic Chemistry at the University of Marburg (now Full Professor, University of Münster). His research focused on the development of new ligands (NHC's with flexible steric demands), the asymmetric hydrogenation of pyridines, and organocatalysis.
- Prof. Stefan Hecht (2005-2006) established a group working on organic materials chemistry. After completing his Habilitation (06/2006), he became Full Professor of Organic Chemistry at the Humboldt-University of Berlin.
- Dr. Lisbet Kvaerno joined the Institute only recently (09/2007). After finishing postdoctoral work under the guidance of Prof. D. A. Evans, Harvard University, Dr. Kvaerno managed to win an "Independent Junior Research Group" advertised by the Max-Planck-Society. Her projects deal with the development of new catalysts for asymmetric synthesis.

Prof. Fürstner's own research is dedicated to the development and understanding of organometallic reagents as enabling tools for advanced organic synthesis. By far the largest part of his agenda relates to homogeneous catalysis as one of the most important areas of contemporary chemistry research. Long term goals pursued in the Department comprise, inter alia:

- The development of catalysts based on cheap, non-toxic, benign and readily available transition metals, most notably iron, as substitutes for traditional noble metal complexes ("cheap metals for noble tasks")
- Attempts to unravel and exploit the complementary logic of olefin metathesis, and the extension of metathesis beyond its traditional scope (e. g. ring closing metathesis of alkynes, formal metathesis reactions catalyzed by noble metal salts etc.)

- The outline of novel concepts which eventually allow one to replace notoriously stoichiometric processes of proven versatility by catalytic regimens (eg. Nozaki-Kishi reactions catalytic in chromium, carbonyl coupling catalytic in titanium, Friedel-Crafts acylations catalytic in Lewis acid etc.)
- Benign catalysis by activation of π-systems with the aid of carbophilic Lewis acids
- Isolation and characterization of (short-lived) intermediates relevant for the catalytic cycles of interest.

A very significant part of our work is dedicated to the application of organometallic catalysts to the total synthesis of biologically active compounds, most notably complex natural products. This allows us to scrutinize – in a most stringent manner – the methodologies pursued in the Department, and, at the same time, provides meaningful amounts of highly valuable materials for testing. The targets are usually chosen according to the posed structural challenges, their biological significance, and non-availability from natural sources. Where appropriate, we are also committed to prepare collections of carefully designed structural variants for further evaluation by diverted total synthesis ("non-natural natural products").

As a consequence, we entertain and foster collaborations with many experts outside the Institute to allow for proper testing of the natural products and analogues prepared by the group. One such collaboration enjoys even institutional support by central funds of the Max Planck Society: thus, Prof. Fürstner is a founding member of the Chemical Genomics Center (CGC) Initiative of the MPG (2005-).

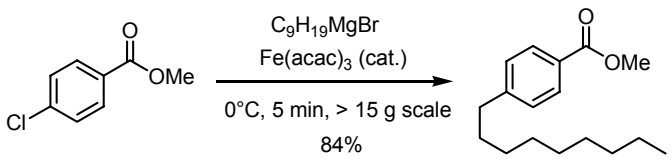
In addition, Prof. Fürstner's team works closely together with several other groups at the Institute. Examples from the report period are: (i) an extended collaboration with Prof. Thiel concerning the understanding of the binding properties of macrolide antibiotics endowed with high affinity to the actin cytoskeleton, (ii) an ongoing collaboration with the Thiel group aiming at a better understanding of "through space" electronic communication within a newly designed planar chiral ligand scaffold, (iii) a fruitful exchange of information with Prof. Jonas in the field of organoiron chemistry. Last but certainly not least, the excellent contacts to the analytical groups of the Institute must be pointed out. Their support and expertise is an essential ingredient for much of the research carried out in this Department.

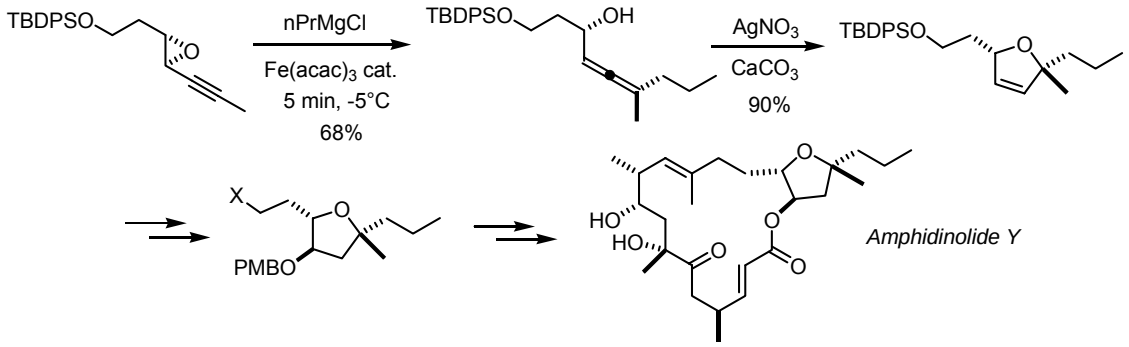
2.4.1. Research Area: "Cheap Metals for Noble Tasks" (A. Fürstner)

Involved: E. Kattnig, H. Krause, K. Majima, R. Martin, G. Seidel, C. Stimson

Objective: Late transition metals, and in particular the noble metals, dominate a significant part of contemporary catalysis research. Their use, however, is handicapped by the high price, the need for expensive ligands, toxicity issues and environmental concerns (nickel, cobalt). Therefore it is a worthwhile yet difficult endeavor to search for alternatives in a quest for more affordable and sustainable methodology.

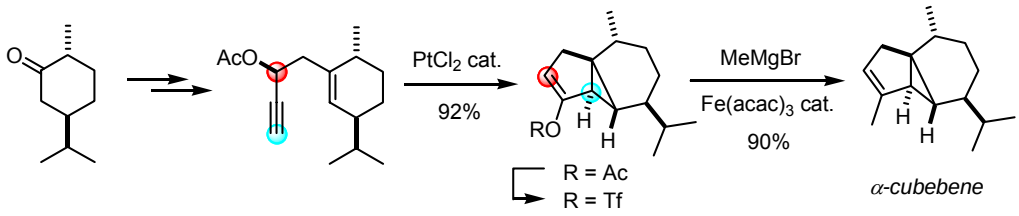
Results: Pioneering studies published by Kochi et al. as early as 1971 had shown that simple iron salts qualify as precatalysts for certain cross coupling reactions of vinyl halides with Grignard reagents. Because of the overwhelming success of palladium- and nickel catalyzed cross coupling discovered shortly thereafter, Kochi's result largely fell into oblivion for decades. Since 2001, our group has recapitalized on these lead findings (see previous report). Most notably, we were able to show that iron catalyzed cross coupling is much broader in scope than Kochi's results may have suggested. It allows some of the most difficult types of substrates to be activated with ease (aryl chlorides, aryl tosylates, *alkyl* bromides, alkynyl epoxides, enol triflates and –phosphates, acid chlorides, thiolesters etc.), yet is compatible with many functional groups due to the mild conditions and unprecedentedly fast reaction rates. In most cases, cheap, non-toxic, air-stable, non-hygroscopic and environmentally benign $Fe(acac)_3$ qualifies as precatalyst. A representative example is the large scale preparation of 4-nonyl-benzoic acid (successfully checked by *Organic Synthesis*), a valuable component of high performance liquid crystalline materials.



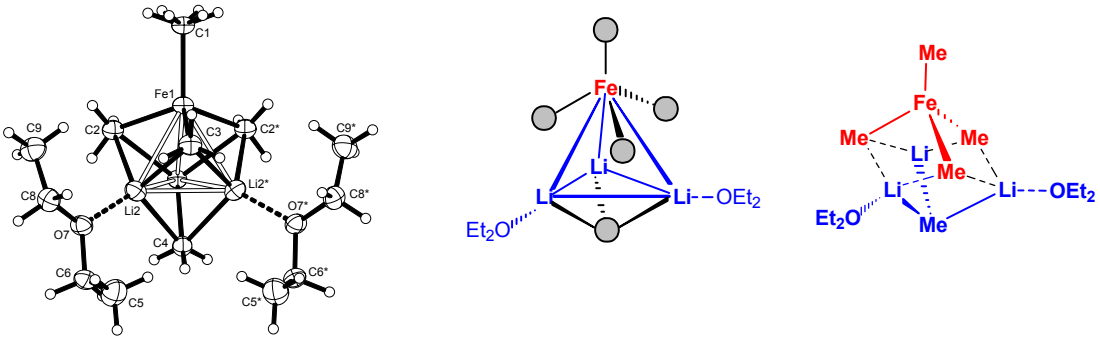


This methodology has also served as a key transformation in various natural product syntheses. A notable example from the 2005-2007 report period is the conquest of the

extremely scarce and highly cytotoxic marine macrolide **amphidinolide Y**, in which a *syn*-selective iron-catalyzed propargyl epoxide opening allowed us to conveniently install a quarternary center via a "relay" (central → axial → central) chirality transfer. The completion of the total synthesis of the sesquiterpene **(–)-α-cubebene** provides another illustration for the power of this methodology (this synthesis also features a $PtCl_2$-catalyzed cycloisomerization developed in our group, cf. Chapter 2.4.2).

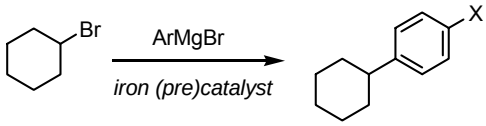


The biggest handicap of such Fe-catalyzed reactions, however, is the poor understanding of the mechanistic basis. The active species, generated in situ, is highly sensitive, short-lived, paramagnetic, non-stabilized and hence difficult to characterize. There is not even a consensus in the literature on its oxidation state. Therefore we launched a program aiming at the investigation of the underlying organoiron chemistry. In this context, we were able to show that iron-catalyzed C-C-bond formations may proceed along, at least, two distinctly different mechanistic pathways:



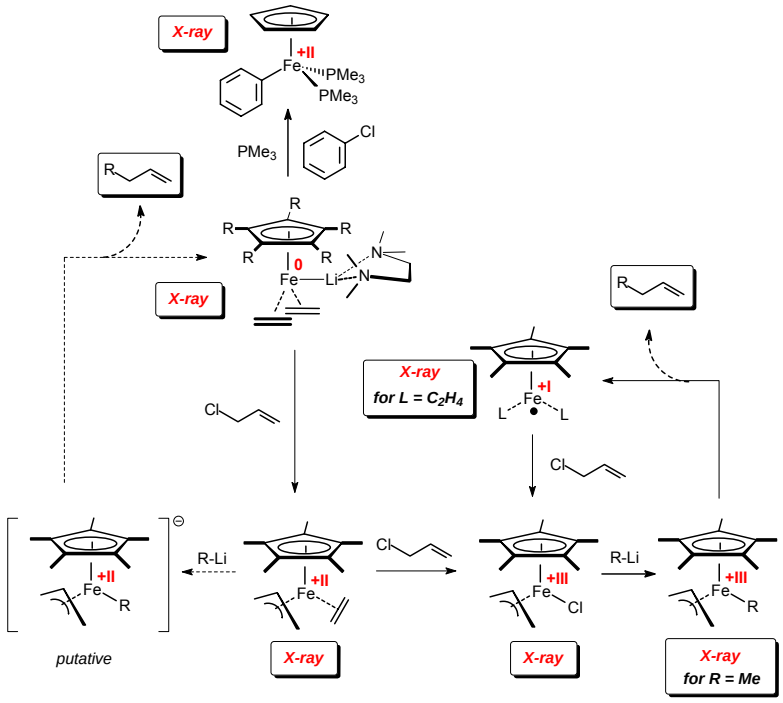
Specifically, iron catalyzed reactions of nucleophiles that cannot undergo β-hydride elimination (MeMgBr, MeLi, PhMgBr etc.) most likely involve organoferrate complexes as reactive intermediates. We were able to fully characterize such a compound – despite its *exceptional* sensitivity – which has truly remarkable structural attributes. Thus, reaction of $FeCl_3$ and MeLi affords the "super-ate" complex $[(Me_4Fe)(MeLi)][Li(OEt_2)]_2$, which not only comprises a homoleptic ferrate moiety, but also incorporates an extra equivalent of MeLi to complete a tetrahedral metallic frame end-capped by a methyl ligand devoid of any direct contact to the iron center. Unstabilized compounds of this type were previously unknown but show the exact reaction behavior characteristic for iron-catalyzed processes involving methyl donors.

In contrast, organomagnesium compounds with two or more C-atoms reduce the FeX_3 precatalyst to low valent clusters of the formal composition $[XFe(MgX)]_n$ and $[Fe(MgX)_2]_n$. The behavior of such intermetallic species can be mimicked with the aid of the structurally well defined lithium ferrate complexes $Li[CpFe(C_2H_4)_2]$ and $Li_2[Fe(C_2H_4)_4]$ pioneered by Jonas et al., which carry kinetically labile olefin ligands and hence exhibit a "bare" metal center of the formal oxidation states 0 and –II, respectively. Such complexes are exceedingly useful catalysts even for the most difficult cross coupling of *alkyl* halides.



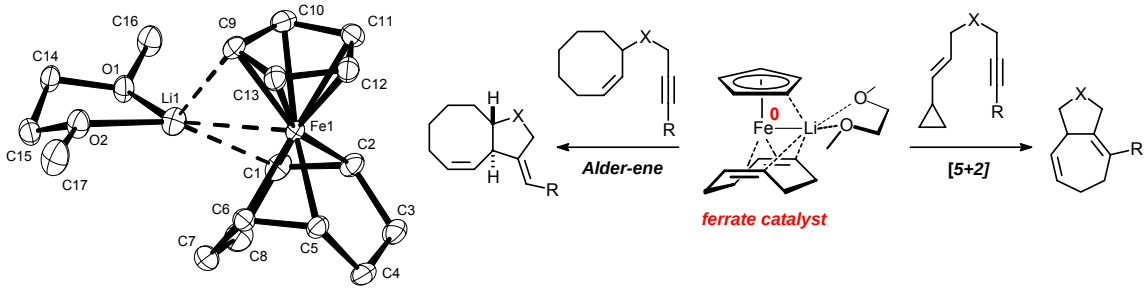
$Fe(acac)_3$	69% (X = Me)
$Li_2[Fe(C_2H_4)_4]$	94% (X = H)
$Li[CpFe(C_2H_4)_2]$	81% (X = H)

Once the functional relationship between the "in situ" catalysts and the Jonas-type ferrate complexes had been established, the latter were used to investigate the structure of putative reactive intermediates. We were able to show that they undergo not only regular oxidative insertion reactions but also single electron transfer processes on reaction with aryl-, alkyl- or allyl halides. Most of the resulting intermediates could be characterized by X-ray crystallography, despite their high sensitivity. On this basis, it was possible for the very first time to provide experimental evidence for the elementary steps of the catalytic cycle(s) responsible for iron-catalyzed cross coupling.

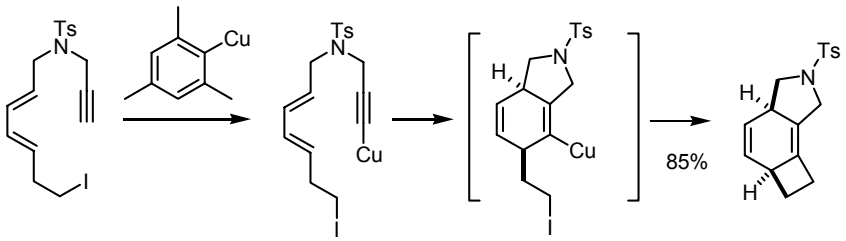


The kinetic lability of the olefins in such low-valent ferrate complexes provides additional opportunities. Specifically, they effect a variety of cycloaddition and cycloisomerization reactions of the Alder-ene, [4+2], [5+2] and [2+2+2] type. These reactions are thought to proceed via initial ligand exchange followed by oxidative cyclization of e. g. an enyne substrate. During the report period, such skeletal rearrangements have been extensively studied and compelling evidence for the proposed

metallacyclic intermediates has been obtained. Although Alder-ene and higher order cycloadditions have previously been the domain of palladium-, rhodium- and ruthenium catalysts, this investigation emphasizes that very cheap and benign iron complexes also hold considerable promise.



In addition to the iron catalyzed skeletal reorganizations, we developed a new copper-based method that allows [4+2] cycloadditions to be combined with a subsequent alkylation (acylation) step into a reaction tandem. This unprecedented cascade proceeds via copper acetylide/vinyl copper intermediates, delivers tricyclic products in high yield and excellent diastereoselectivity, and therefore opens new vistas for the venerable Diels-Alder reaction.



Publications resulting from this research area: 53, 54, 55, 270, 272, 452

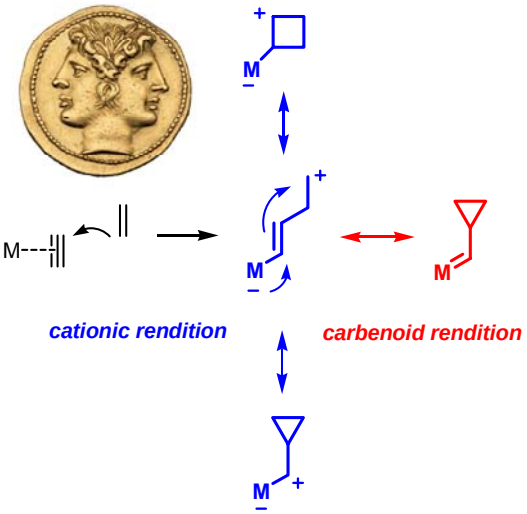
External funding: Alexander-von-Humboldt Foundation (stipend to R. M.), Pfizer Inc. (stipend to K. M.), Deutsch-Israelische Projektkooperation (DIP)

Cooperations: K. Jonas (Mülheim/Ruhr, DE)

2.4.2. Research Area "Novel Concepts for Catalysis" (A. Fürstner)

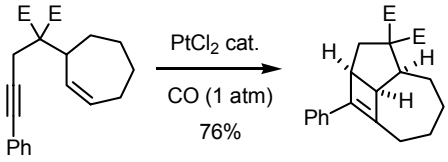
Involved: C. Aïssa, M. Alcarazo, V. César, T. Gress, P. Hannen, E. Heilmann, J. Kennedy, D. Kremzow, P. Davies, G. Seidel, A. Schlecker

Objective: We aim at developing conceptually novel catalytic cycles and try to explore complementary access routes to catalysts of proven utility. The activities in this field during the report period mainly concerned the use of noble metal salts (e. g. $PtCl_2$, LAuCl, $CpRu^+$) as user-friendly yet highly efficient π-acids, and the preparation and use of unconventional N-heterocyclic carbene ligands.



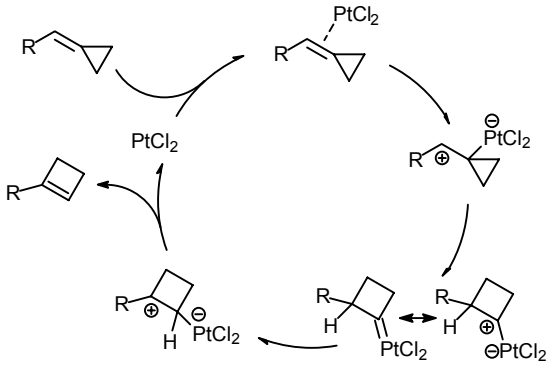
Results: In 1998, our group was the first to interpret skeletal rearrangements catalyzed by $PtCl_2$ and related noble metal templates (e. g. LAu^+) in terms of electrophilic metal cyclopropyl "carbenoids" endowed with considerable "non classical" carbocation character. Since then, this field of research has gained considerable momentum and is presently one of the most rapidly growing areas of homogeneous catalysis research. It is rewarding to see that our original mechanistic hypothesis has been able to account for a host of diverse transformation by extension of the underlying principles. Therefore we have compiled a comprehensive review, which summarizes the many preparative advances in the field and provides the first in depth discussion of the structural basis responsible for the capacity of platinum- and gold catalysts to activate π-bonds.

This mechanistic insight also powers a hypothesis-driven program directed toward the exploration of new reaction modes. Specifically, we were able to show that enynes bearing an arene group on their alkyne terminus readily convert into highly strained

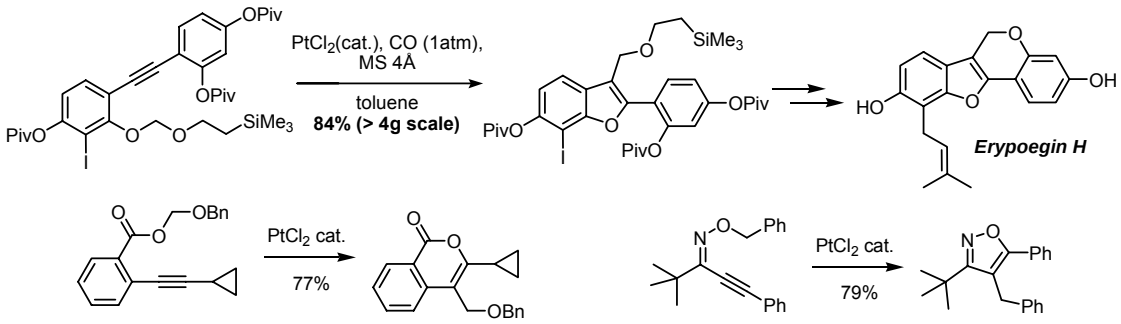


cyclobutene derivatives that are very difficult to prepare otherwise. Such previously unknown reactions are substantially accelerated when performed under an atmosphere of CO; this simple trick has already found widespread use in the community. Cyclobutenes are also accessible via $PtCl_2$-catalyzed rearrangements of alkylidene cyclopropanes through a

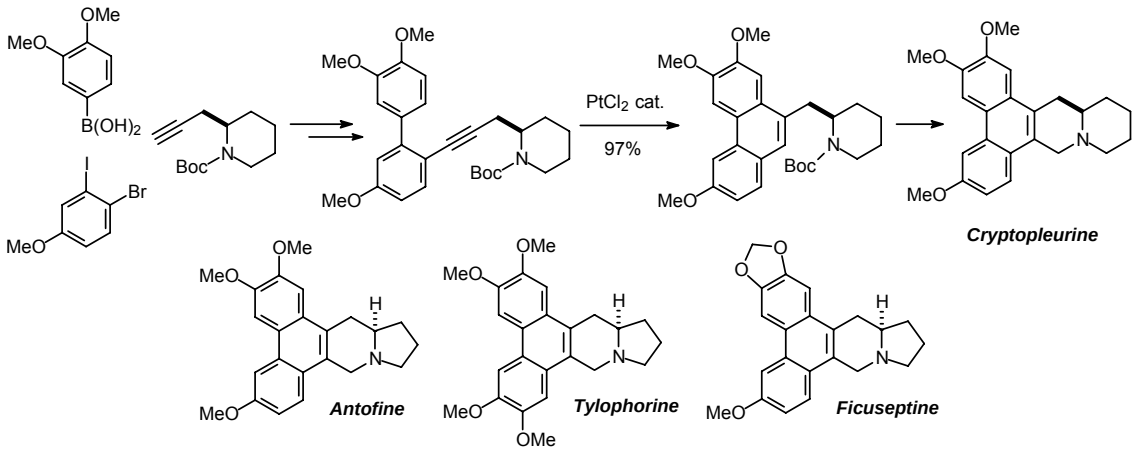
catalytic cycle that nicely illustrates the dual character of the putative intermediates. Because of the strain inherent to such products, this rearrangement can be combined with further transformations such as ring-opening/ring closing metathesis into productive catalysis cascades, if suitable olefinic tethers are placed in vicinity to the incipient cyclobutene ring.



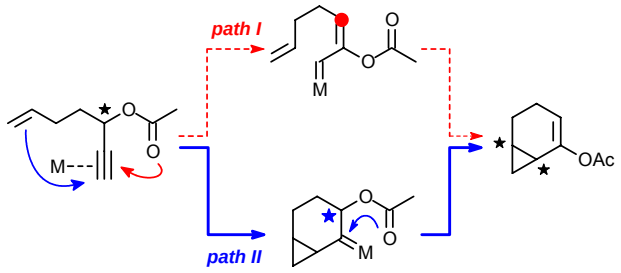
Noble metal catalyzed cycloisomerizations have been extensively used for the preparation of heterocycles. Particular mention deserves an efficient, scalable and low-tech transformation of O-allylated, –benzylated or alkoxy-methylated 2-alkynyl phenol derivatives into the corresponding benzofurans. Thereby, the substituent readily migrates from oxygen to the C-3 position of the heterarene scaffold in a formal carbo-alkoxylation process. This methodology paved the way for a concise total synthesis of the antibiotic erypoegin H and cognates, which exhibit promising activity against a panel of methicillin- and vancomycin-resistant bacterial strains. The compatibility of the C-I bond shows that the behavior of Pt(2+) is orthogonal to that of conventional late transitions metal catalysts in that it does not open the usual redox manifolds. Furthermore, the underlying concept is by no means limited to benzofurans but can also be used for the synthesis to other important types of heterocycles (indoles, benzothiophenes, isoxazoles, isocoumarins etc.)

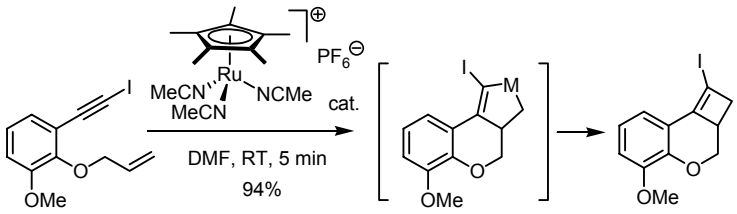


A Pt-catalyzed rearrangement also opened a straightforward entry into the phenanthro-indolizidine alkaloid series. Because of the modularity of this approach, we were able to prepare a collection of such anti-tumor compounds that enabled our partners at the Yale University School of Medicine to conduct detailed SAR studies concerning cytotoxicity and NF-κB signaling. This study led to the remarkable finding that structurally very closely related compounds may nevertheless not be functional analogs.



An important chemical insight was gained during the total synthesis of cubebene based on a $PtCl_2$-catalyzed cycloisomerization (see also Chapter 2.4.1). Thus, it was shown for the first time that the configuration of the center carrying the propargyl acetate translates into the product stereostructure. It is hence impossible that this center is planarized before the new cyclopropane has formed; this finding, in turn, advocates the notion that the reaction path involves cyclopropyl metal carbenes rather than vinyl carbenes as key intermediates.



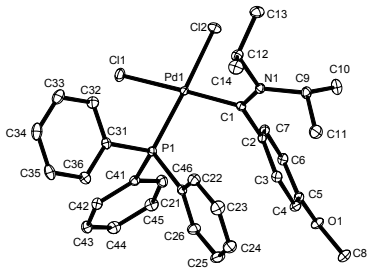


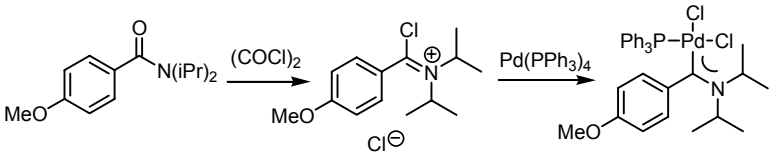
Further studies in the cycloisomerization arena concerned the surprisingly facile ruthenium catalyzed transformation of enynes bearing halide substituents at their alkyne terminus into strained halo-cyclobutene derivatives, although a redox cycle is believed to be operative in this case.

Another important topic are N-heterocyclic carbenes (NHC's) and metal complexes thereof. The following contributions have been made during the report period:

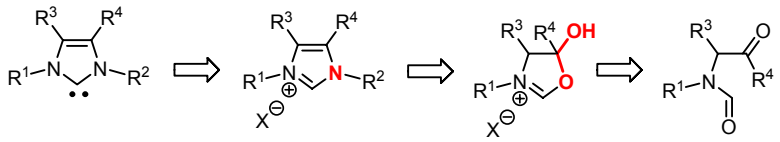
(1) We had previously shown that metal-NHC complexes can be obtained by oxidative insertion of a low-valent metal into 2-chloro-1,3-disubstituted imidazolinium salts. This method is complementary to the commonly used route

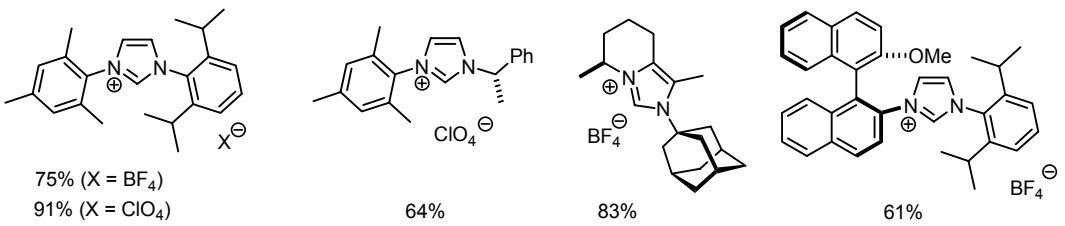
based on ligand exchange and allows to prepare complexes that are difficult to form otherwise, including Fischer-type carbene complexes of palladium and nickel. The scope of this new method has been extensively studied and the resulting complexes were used as catalysts for various C-C- and C-N-bond forming reactions.





(2) Depite the huge number of NHC's known in the literature, several obvious and seemingly trivial substitution patterns remain largely unexplored. This includes NHC's with two different aryl groups on the N-atoms; likewise non-symmetrical imidazolium salts (as NHC precursors) with one N-aryl and one N-alkyl group are rare and essentially limited to those having primary N-alkyl substituents. These gaps in the structural landscape reflect the limitations of the established syntheses routes. We were able to devise a user-friendly, scaleable and highly flexible new entry based on a heterocycle interconversion strategy which allows one to obtain such elusive substitution patterns with ease. We are now exploring the potential of such imidazolium salts and NHC's derived thereof in catalysis.





75% (X = BF_4)
91% (X = ClO_4)

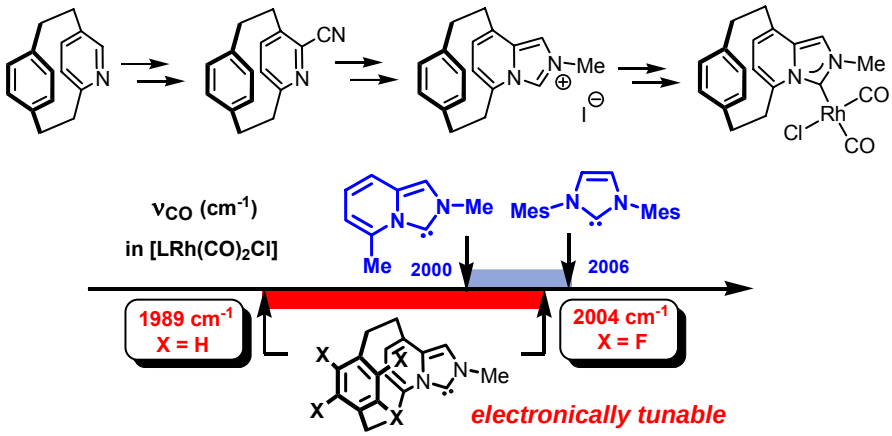
64%

83%

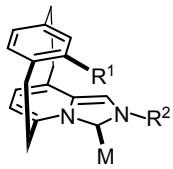
61%

(3) An unprecedented type of *planar chiral* NHC has been designed which holds considerable promise for the following reasons: The parent compound of this series is the strongest donor amongst all diamino-stabilized five-membered NHC's known to date. Importantly, however, substitution of the lid of the cyclophane with four fluorine atoms allows to down-regulate the donor capacity

to a previously unknown degree by "through space communication" with the carbene center underneath, while maintaining the steric demand of the ligand virtually unchanged.



Moreover, the novel ligand set is not only planar chiral, but also allows one to precisely position a suitable substituent R^1 on top of the bound metal center, such that the chiral binding pocket is clearly defined. Ongoing work in this laboratory is trying to exploit these favorable structural attributes.



Publications resulting from this research area: 48, 49, 98, 263, 265, 269, 271, 273, 407, 442, 445, 452

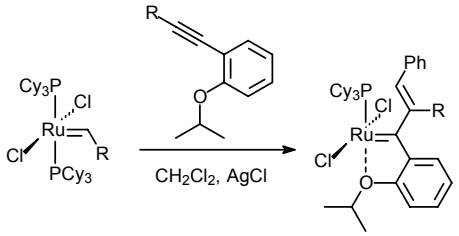
External funding: Alexander-von-Humboldt-Foundation (stipend to V. César), Spanish Ministerio de Educación y Ciencia (stipend to M. Alcarazo), Canadian NSERC (fellowship for J. Kennedy), Fonds der Chemischen Industrie, Deutsch-Israelische Projektkooperation (DIP).

Cooperations: W. Gao, Y.-C. Cheng (Yale University School of Medicine, USA).

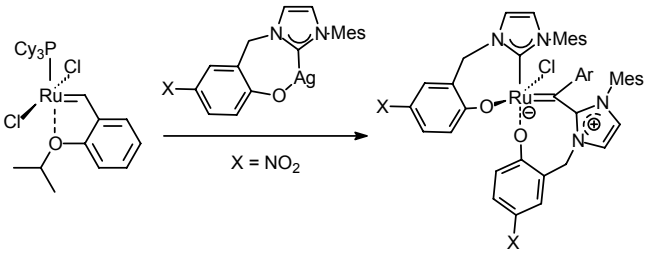
2.4.3. Research Area "Metathesis" (A. Fürstner)

Involved: M. Bindl, J. Blank, M. Bonnekessel, P. Davies, B. Fasching, S. Flügge, L. Jean, A. Korte, O. Larionov, C. Müller, C. Nevado, T. Nagano, G. O'Neil, L. Turet

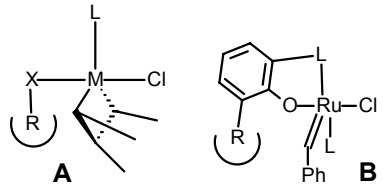
Objectives: Olefin metathesis has revolutionized organic synthesis during the last decade. While we continue to apply this transformation, our major focus has shifted toward alkyne metathesis, which, we believe, qualifies as a similarly enabling tool.



Results: Exposure of terminal alkynes to suitable metal carbene complexes usually results in "living" polymerization with formation of polyacetylene derivatives by stepwise insertion of the monomer into the catalytically active $M=CR_2$ bond terminating the growing chain. We showed that this process can be interrupted after the first insertion step with an alkyne that carries a chelating substituent. Phenylacetylene derivatives bearing an *ortho*-isopropoxy group are particularly effective, which cleanly deliver vinylcarbene complexes of the Hoveyda-type by a versatile and general new route.

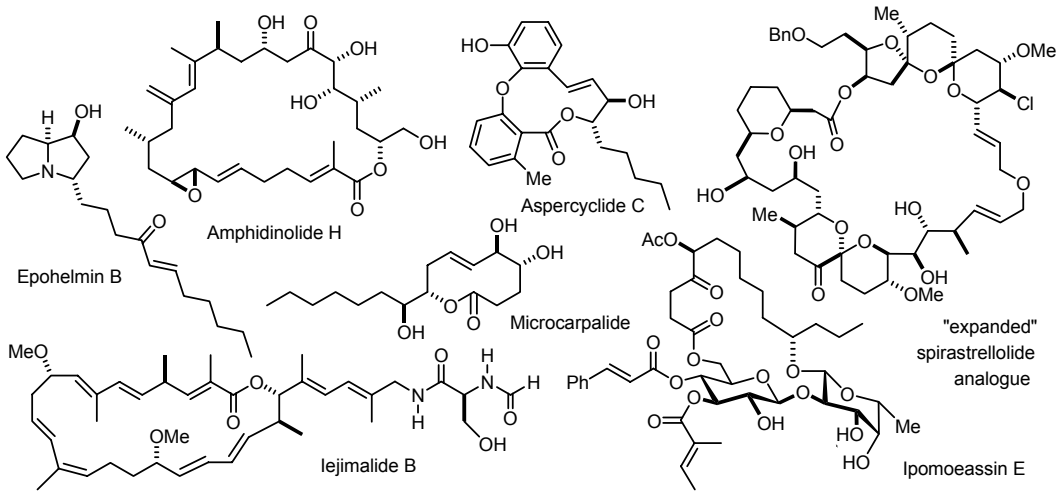


We have also found evidence that N-heterocyclic carbenes, which serve as ancillary ligands in some of the most powerful alkene metathesis catalysts known to date, may not be as innocent as usually assumed. Upon trans-metallation of a Ag-NHC complex with a standard metathesis catalyst, a respectable amount of a new ruthenium species (with some zwitterionic character) has been isolated and characterized by X-ray crystallography, in which an NHC unit has attacked the alkylidene moiety. This observation has implications for the stability and degradation pathways of the commonly used olefin metathesis catalysts.



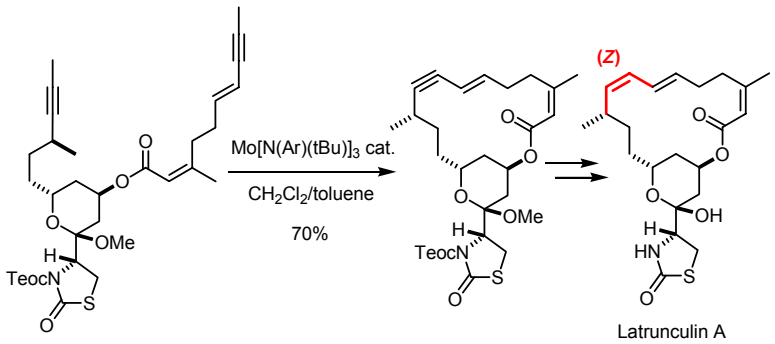
Arguably the biggest challenge for alkene metathesis is the development of stereoselective catalysts. Despite the fact that computational studies (including those from the Thiel group) provide a fairly detailed picture of the elementary steps on the reaction coordinate, no such system is presently available and our own efforts in this area also met with only limited success. It is assumed that a *Z*-

selective catalyst must be able to block one side of the incipient metallacyclobutane intermediate **A**, which we intend to accomplish with the aid of complexes of the general type **B**. After several attempts, we have very recently learned how to graft prototype alkylidenes of this type, which now undergo testing in the laboratory.

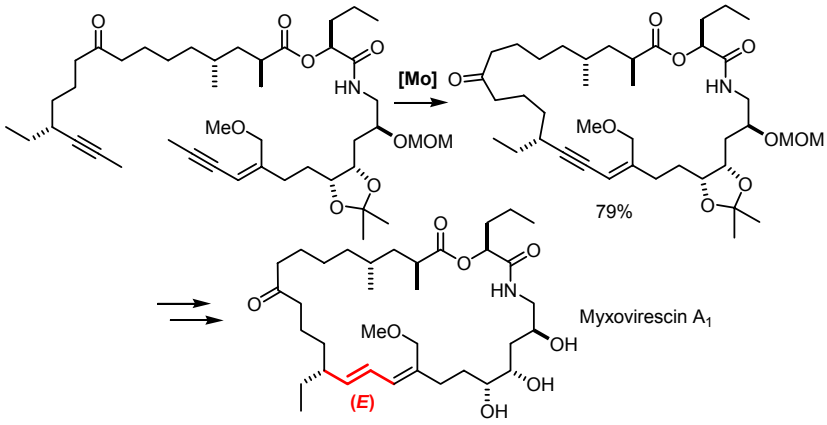


Apart form these daunting issues, alkene metathesis keeps serving our synthetic purposes exceedingly well. Several complex natural products were obtained during the report period using RCM and CM as key transformations. Since most of the targets had been chosen for their biological significance, some projects will be discussed in more detail in Chapter 2.4.4 ("Catalysis Based Syntheses and Evaluation of Bioactive Natural Products"). All of them, however, explore the very limits of contemporary metathesis chemistry. Specifically, the cyclization of ***aspercyclide C*** posed considerable challenges due to the very high strain inherent to its polyunsaturated frame (seven sp^2 hydridized C-atoms in an 11-membered ring!). The first total synthesis of the highly cytotoxicity macrolide ***amphidinolide H*** features an exceptionally rare example of productive metathesis of a vinyl epoxide, whereas the synthesis of ***ipomoeassin*** 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 unsaturated esters in the periphery. Our first attempt to prepare the phosphatase inhibitor ***spirastrellolide*** revealed a present limitation of RCM, as the densely functionalized macrocycle would not form, even though a "relay metathesis" was envisaged to assist ring closure; only a ring expanded product could be obtained, forcing us to revise our original synthesis plan. The arguably most impressive example, however, is the successful preparation of ***iejimalide B*** by selective activation of two out of no less then 10 (!) double bonds in the cyclization precursor. This result must also be seen in the light of an attempted formation of this potent anticancer agent by a lactonization strategy, which – in sharp contrast to RCM – had failed miserably.

Whereas RCM is now widely embraced by the synthetic community, the ring closing metathesis of alkynes (RCAM) still lags behind. This transformation was first described by our group in 1998 using a Schrock tungsten alkylidyne catalyst; shortly thereafter, we introduced an alternative system based on molybdenum trisamido complexes activated in situ. Although both types of catalysts are air- and moisture sensitive, their remarkable application profile makes us believe that RCAM qualifies as a truly enabling tool for organic synthesis. We are committed to demonstrate its outstanding performance and very wide scope by applications to increasingly complex cases.

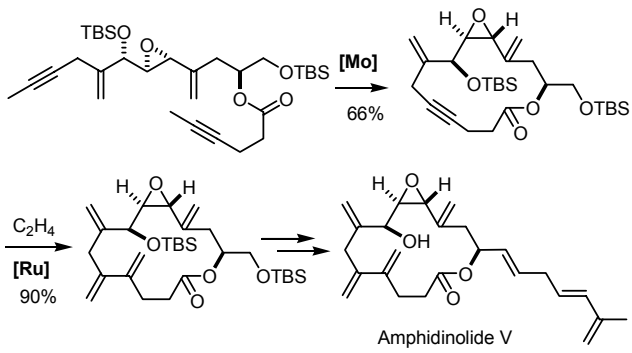


A representative example is the total synthesis of the actin-binding marine natural product ***latrunculin A***. The catalyst generated in situ from $Mo[N(Ar)(tBu)]_3$ and CH_2Cl_2 allows to forge a highly strained 16-membered ring, and rigorously distinguishes between the triple- and the double bonds of the polyfunctionalized substrate. Lindlar reduction of the RCAM-product to the *Z-alkene* resulted in a stereoselective synthesis of latrunculin A, which is presently inconceivable with the aid of regular alkene metathesis.



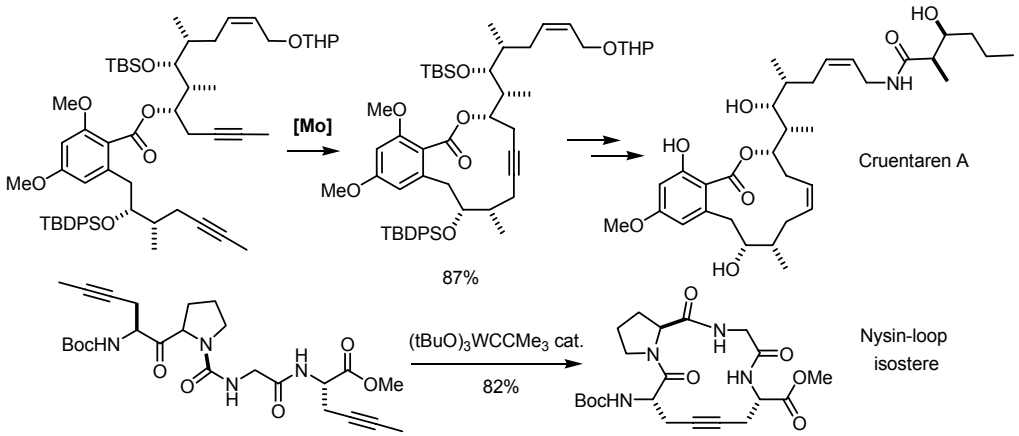
The orthogonal character of alkyne- and alkene metathesis was equally instrumental for a largely catalysis-based approach to the antibiotic ***myxovirescin A***. In this particular case, the cycloalkyne was transformed via *trans*-hydrosilylation/desilylation into the corresponding *E-alkene*, thus showing that RCAM opens stereoselective entry into either olefinic series.

An entirely different use of RCAM is illustrated by our approach to ***amphidinolide V***. Gratifyingly, the molybdenum catalyst turned out to be compatible with the very fragile vinylepoxide as well as the allylic alcohol group of the substrate. The resulting cycloalkyne was then subjected to an enyne cross metathesis with ethylene gas to build the characteristic vicinal *exo*-methylene branches of the target. Due to the flexibility of



the chosen approach, it was possible to prepare all conceivable stereomers without undue efforts, which allowed us to establish the previously unsecured stereostructure of this natural product.

Similarly instructive examples are the successful use of RCAM for the stereoselective synthesis of ***cruentaren A***, a potent anticancer agent and selective F-ATPase inhibitor, as well as the preparation of an alkynylogous isostere of the peptidic lantibiotic ***nysin Z***. Overall, we believe that these examples provide compelling evidence that alkyne metathesis applies to highly functionalized targets at the forefront of organic synthesis, just as RCM does. We take this as an encouragement to further expand its scope and improve the arsenal of catalyst, e. g. in terms of stability.



Publications resulting from this research area: 46, 47, 50, 56, 58, 60, 121, 274, 437, 443, 444, 446, 447, 448, 449, 450, 489

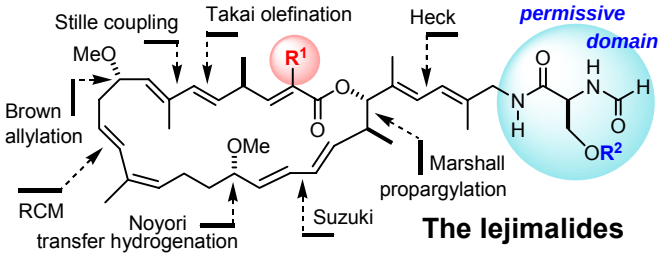
External funding: Alexander-von-Humboldt Foundation (stipend to J. Blank, G. O'Neil, C. Nevado), Fonds der Chemischen Industrie (stipends to A. Korte, M. Bonnekessel, S. Flügge, C. Müller)

Cooperations: V. Jensen (University of Bergen, NO); R. M. J. Liskamp (University of Utrecht, NL); M. R. Buchmeiser (University of Innsbruck, AT, now Leipzig)

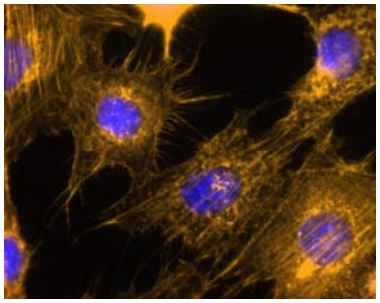
2.4.4 Research Area "Catalysis Based Syntheses and Evaluation of Bioactive Natural Products" (A. Fürstner)

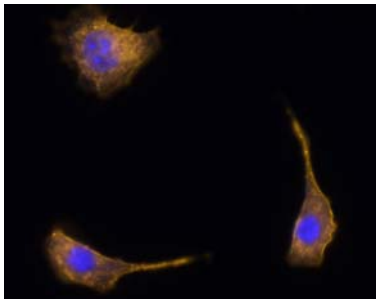
Involved: C. Aïssa, P. Buchgraber, J. Ceccon, C. Chevrier, M. Domostoj, B. Fasching, M. Fenster, J. Gagnepain, C. Godbout, E. Kattnig, E. Moulin, C. Müller, T. Nagano, G. O'Neil, C. Nevado, K. Radkowski, F. Téply, M. Tremblay, L. Turet, M. Waser, M. Wuchrer

Objectives: We pursue the synthesis of complex natural products by largely catalysis-based routes, evaluate their biochemical and biological properties, and investigate possible structure/activity relationships by systematic editing.

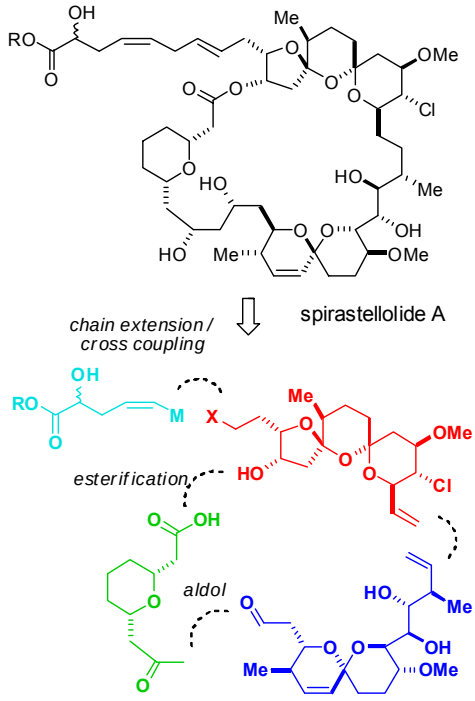


Results: A concise total synthesis of the highly cytotoxic marine natural products **iejimalide A-D** was developed based on an effective ring closing metathesis (RCM) reaction of a cyclization precursor containing no less than 10 double bonds. Because of the exceptional sensitivity of this polyunsaturated intermediate and its immediate precursors toward acid, base and even gentle warming, the assembly process hinged upon the judicious choice of protecting groups and the careful optimization of all individual transformations. As a consequence, particularly mild protocols for Stille as well as Suzuki reactions of elaborate coupling partners have been developed that hold considerable promise for applications in other complex settings. Moreover, a series of non-natural "iejimalide-like" compounds was prepared, in which the entire framework of the natural lead has been systematically edited. With the aid of these compounds it was possible to uncover the previously unknown effect of iejimalide and analogues on the actin cytoskeleton, and their equally unknown capacity to up-regulate caspase-3, a key enzyme of the signal transduction cascade leading to apoptosis. Moreover, our sample collection allowed us to demonstrate the exceptional cytotoxicity of such macrolides against a panel of 36 human cancer cell lines, with the lowest IC_{70} values reaching the picomolar / low nanomolar range. Since these data suggest that the iejimalides might qualify as lead structures for the development of novel anticancer agents, we actively pursue our investigations of this very demanding class of polyene macrolides.



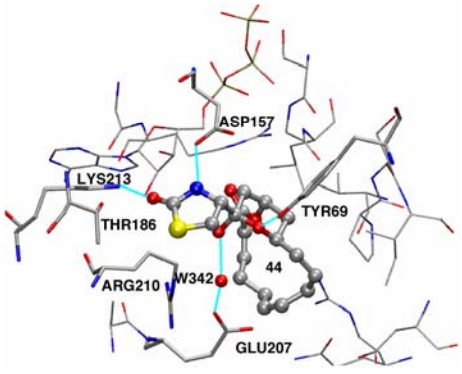


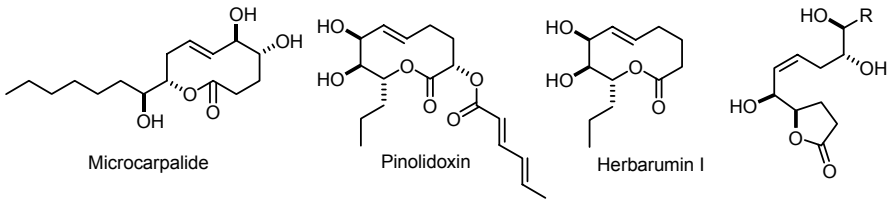
Fluorescence micrographs (250×) of NIH3T3 fibroblasts before (left) and after incubation with iejimalide B (right), showing the actin depolymerization capacity of the macrolide.



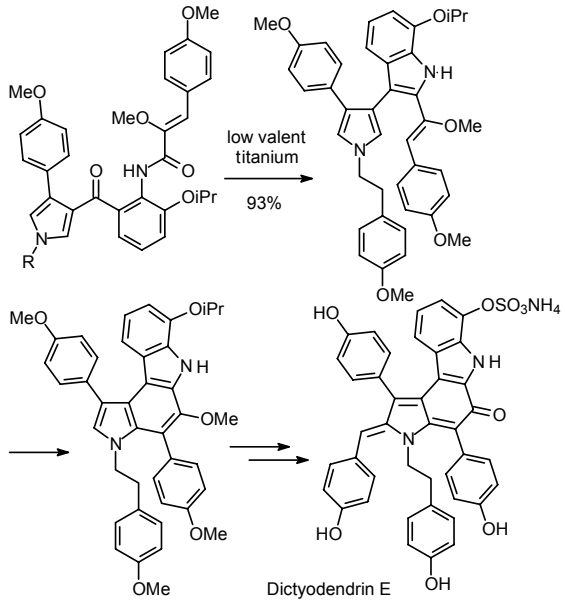
Our studies directed toward **spirastrellolide A** are also quite advanced, although the total synthesis of this protein phosphatase 2A inhibitor of unheard selectivity remains to be completed. This project had to cope with the fact that the stereostructure of the target – containing no less than 21 chiral centers in a 38-membered ring – was yet unknown at the outset of our studies. We managed to develop scaleable and reliable routes to all necessary subunits and have commenced to investigate their assembly. As mentioned in Chapter 2.4.3, however, the envisaged macrocyclization via RCM failed even if the "relay concept" was applied. Therefore we are presently revising the end game based on the intelligence gathered in the exploratory studies.

A particularly fruitful project, that came to an end during the report period, was the targeted pursuit and biochemical evaluation of the **latrunculins** (see also previous report). Alkyne metathesis opened a very satisfactory entry into this product class, which allowed us to prepare a sizeable number of latrunculin-like macrolides with deep-seated structural modifications. Importantly, some of these synthetic analogues turned out to be significantly more active than the natural products themselves in their capacity to depolymerize actin protein filaments in fibroblast cells. With the help of extensive QM/MM calculations performed by the Thiel group have we now been able to provide a rationale for this highly rewarding result.

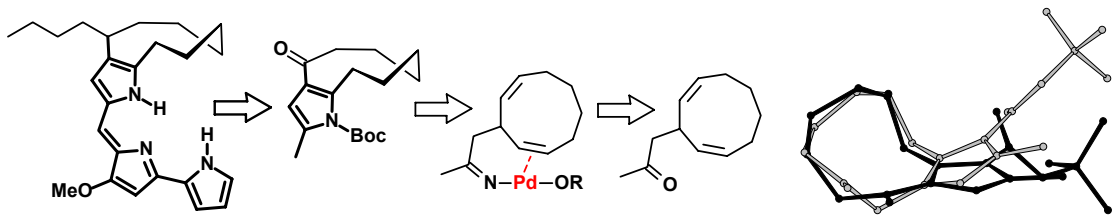




Microcarpalide also constitutes a valuable lead in the quest for selective actin binders. Therefore we have developed the most productive synthesis of this nonenolide known to date, and have also demonstrated that related 10-membered lactones and even much simpler butanolides exhibit similar levels of microfilament disrupting activity. Even though somewhat less potent than the best latrunculins, such compounds have the distinct advantage of being much less toxic and may hence be useful entry points for more focused programs in the realm of medicinal chemistry or crop protection.

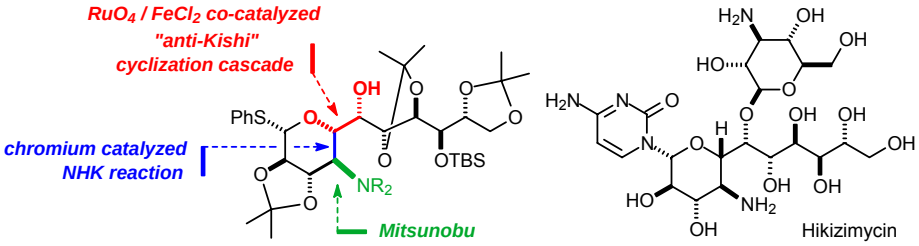


Entirely different challenges were posed by the **dictyodendrins**. These intriguing pyrrolo-carbazole alkaloids are the first telomerase inhibitors isolated from a marine source. Since telomerase is overexpressed in ca. 90% of all malignant tumors, small molecule inhibitors of this key regulatory enzyme are on high demand. With the aid of a titanium-induced reductive indole synthesis, previously developed by our group, followed by an efficient 6π-electro-cyclization event as the key steps has it been possible to prepare substantial amounts of three naturally occurring dictyodendrins and a host of synthetic analogues. While the evaluation of their telomerase inhibitory activity is still pending, the pronounced but previously unrecognized capacity of such alkaloids to cleave double stranded DNA was firmly established.



"**Butylcycloheptylprodigiosin**" constitutes another demanding heterocyclic target that came into reach during the report period. Its highly strained *ortho*-pyrrolophane scaffold was accessed by a palladium catalyzed reaction of an oxime ester with a suitably located

olefin in vicinity (Narasaka-Heck reaction) followed by a site-selective isomerization. Many conformational peculiarities of nine-membered cycloalkenes surfaced during this project, an area surprisingly void of secured information prior to this investigation. A small collection of analogues has also been prepared which allowed us to demonstrate that the nuclease-like activity of such alkaloids is innately linked to the presence of an intact tripyrrolic backbone. Furthermore, it was shown that prodigiosins exhibit promising inhibitory activity against various phosphatases, including *Mycobacterium tuberculosis* protein tyrosine phosphatase A, an enzyme believed to be responsible for a complex biochemical mechanism enabling survival of this pathogen in host organisms.



Finally, an unprecedentedly short approach to the 'higher-sugar' core of the complex anthelmintic nucleoside antibiotic **hikizimycin** was developed. Key to success were a chromium-catalyzed Nozaki-Hiyama-Kishi reaction following a protocol previously developed in this laboratory, as well as a dihydroxylation/cyclization cascade co-catalyzed by RuO_4 and $FeCl_2$, which seemingly violates established stereochemical rules and outperforms conventional dihydroxylation protocols.

Publications resulting from this research area: 1, 15, 51, 52, 57, 58, 118, 264, 266, 267, 268, 270, 271, 274, 275, 443, 444, 445, 446, 447, 448, 449, 450, 451

External funding: Chemical Genomics Center (MPG), AvH (stipends to M. Domostoj, M. Fenster, G. O'Neil, C. Nevado), Association pour la Recherche sur le Cancer, France (stipend to E. Moulin), Fonds der Chemischen Industrie (stipend to C. Müller), Fonds de Recherche sur la Nature et les Technologies, Quebec (stipend to C. Godbout), NSERC Canada (stipend to M. Tremblay), FWF Austria (stipend to M. Waser), Deutsch-Israelische Projektkooperation (DIP), Merck Research Council

Cooperations: H. Waldmann, O. Müller (MPI Dortmund, DE), Oncotest GmbH (Freiburg, DE), W. Gao, Y.-C. Cheng (Yale University School of Medicine, USA)

2.4.5 Research Area "Functional (Macro)molecular Architectures" (S. Hecht)

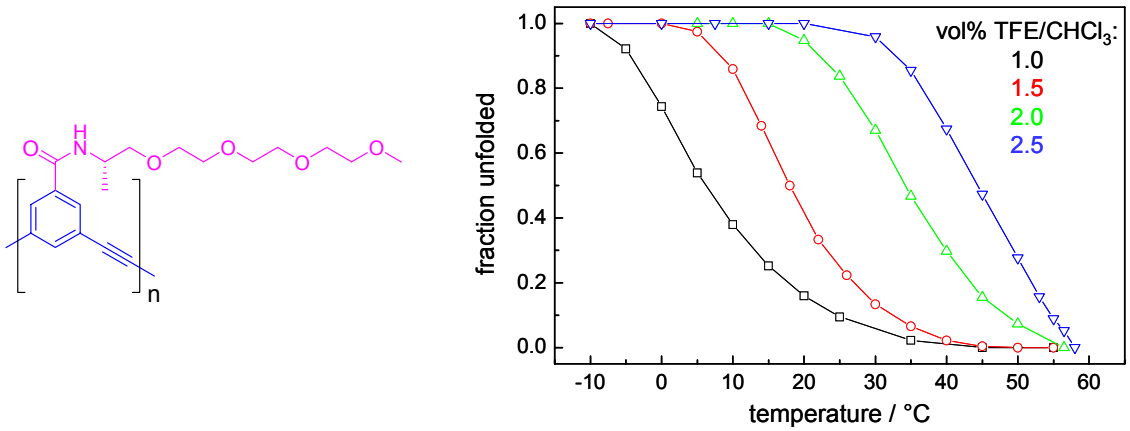
Involved: M. A. Balbo-Block, A. Khan, R. M. Meudtner, M. V. Peters, R. S. Stoll, R. Goddard

Objective: Our research program aims at developing new chemical approaches to the emerging nanosciences by designing (macro)molecular entities of defined size and shape with desired implemented functionality and external adressability.

1. Tubular and Responsive Foldamers

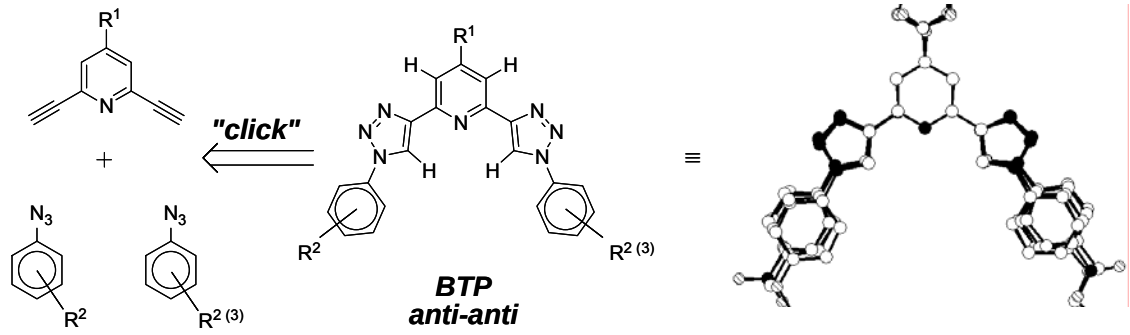
The design of artificial oligomeric and polymeric strands capable of adopting well-defined secondary – and to a certain degree – higher order structures has gained considerable attention in recent years due to the many potential applications of such compounds in both the bio and materials sciences. Our major focus has been on various phenylene ethynylene oligomers and polymers as well as extended heteroaromatic backbones aiming at the design of adressable and regioselectively functionalized organic nanotubes and responsive dynamic systems.

Among the many backbones – so called "foldamers" – amphiphilic oligo(*meta*-phenylene ethynylene)s offer the important advantage of a void interior, which can be exploited for the design of tubular structures. The advantage over self-assembled structures relies in control over the tube dimensions (inner/outer width as well as length) and their adressability. We have recently developed a novel synthetic route to access lengthy and defect-free poly(*meta*-phenylene ethynylene)s (P*m*PEs) via an *in-situ* deprotection and Pd-catalyzed Sonogashira-Hagihara polycondensation protocol. After folding the polymeric strand into the corresponding hollow helix, covalent bonds were used to lock the fragile folded equilibrium structure by means of dimeric crosslinks introduced by photodimerization of cinnamates. To overcome the structural perturbation associated with covalent linkage, we have more recently developed non-covalently stabilized nanotubes based on P*m*PEs with hydrogen-bonding amide based side chains. The polymers form extremely stable helices in various media and show a remarkable thermal renaturation behavior, i.e. "inverse melting behavior" (Scheme 1), contrasting typical biopolymers such as polypeptides and DNA. The polymers could be prepared with a high degree of polymerization, especially considering the employed step-growth polycondensation methodology, and display a significant persistence length. Furthermore, π-conjugated *ortho*-linked as well as alternating *ortho-para*-linked phenylene ethynylene oligomers and polymers were successfully synthesized.



Scheme 1. PmPE with alanine-derived side chains and unusual thermal renaturation behavior.

To improve the photochemical stability of the foldamer backbone, important for photoswitchable systems (see below), and to introduce responsiveness to chemical stimuli such changes in pH or metal ion concentration we have engaged in the design of a new family of foldamers based on alternating triazole-pyridine scaffolds. The so called "clickamers" were readily obtained using modern Cu-catalyzed 1,3-dipolar cycloaddition reactions. Initially, a variety of symmetrical 2,6-bis(1-phenyltriazol-4-yl)pyridines (BTPs) carrying electron-withdrawing and –donating groups at both the terminal phenyl as well as the central pyridine moieties were synthesized. Non-symmetrical derivatives could also be prepared via a repetitive synthesis, which most recently enabled preparation of discrete oligomers up to the pentaeicosamer (25mer). Both in solution and in the solid state, the backbone adopts a kinked horseshoe-like *anti-anti* conformation (Scheme 2).



Scheme 2. Retrosynthesis of various BTP derivatives and overlay of single crystal X-ray structural analyses (side chains partially omitted for clarity).

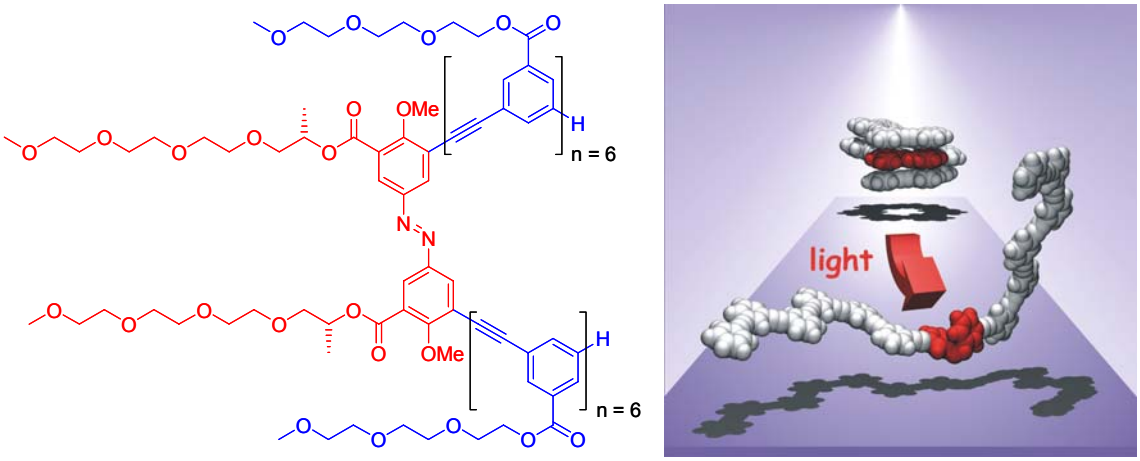
The conformational preference is based on the destabilization of the *syn-syn* conformation due to electrostatic repulsion of the adjacent heterocyclic nitrogen atoms' lone pairs and steric repulsion of the neighboring *ortho*-hydrogen atoms. The longer oligomers adopt a helical secondary structure in solution and show an unexpected

response, i.e. helix reversal, to pH changes and/or metal ions. The BTP scaffold represents furthermore a new and promising ligand platform as shown by the interesting spin and luminescence behavior of the corresponding iron and europium complexes, respectively.

2. Photoswitchable Transporters and Catalysts

The realization of molecular-scale devices is inevitably tied to the design of molecular entities capable of carrying out a desired function ideally under external control. As light represents perhaps the most attractive external stimulus since it is non-invasive and allows for both spatial and temporal resolution, we have engaged in the design of photoresponsive and more precisely photoswitchable systems, offering the advantage of truly reversible behavior. Major focus has been on the design of photoswitchable foldamer hosts and nucleophiles/bases as "smart" transporters and organocatalysts, respectively. In addition various photoswitches have been investigated on the single molecular and ensemble level on surfaces.

Photoisomerizable azobenzene units were incorporated into the central backbone of a *meta*-phenylene ethynylene oligomer. Due to the attachment of both oligomeric foldamer substrands to the *meta*-positions of the central photochromic azobenzene unit the resulting oligomer adopts a folded conformation in the *trans* form, i.e. "dark state". Irradiation lead to helix denaturation due to the large structural changes associated with the photochemical *trans*→*cis* isomerization (Scheme 3). This transition is readily reversed by using light of the appropriate wavelength or simply heat.

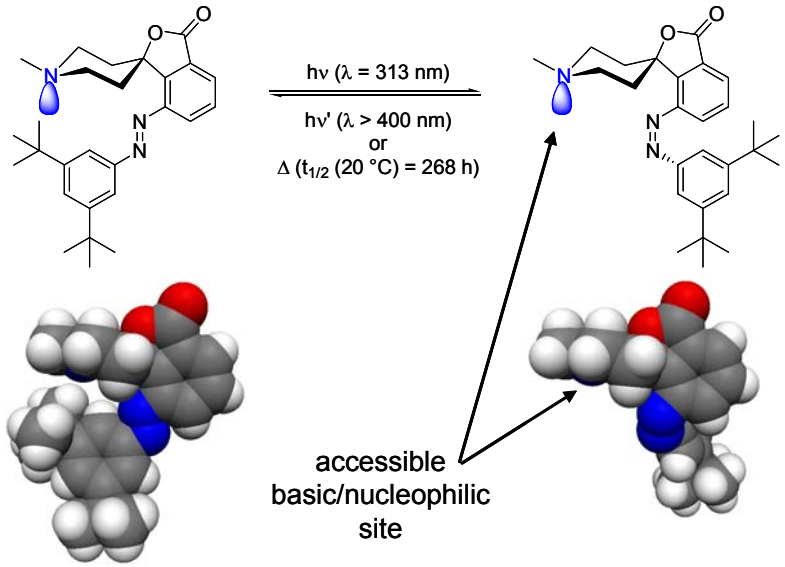


Scheme 3. Structure and illustration of a prototypical photoswitchable foldamer (transporter).

More importantly, we could show that hydrophobic guest molecules can efficiently be encapsulated into the interior of the foldamers host, allowing for the controlled transport of chemical species. Currently, the efficiency and loading capacity of the transporter is

being improved by increasing the azobenzene content – in fact a foldamer family composed entirely of azobenzene units is being synthesized – and extending to a polymeric system.

Photoisomerizable azobenzene units have also been utilized to reversibly shield a reactive site, therefore enabling the design of photoswitchable catalysts. While initial attempts to design photoswitchable metalloporphyrins failed due to detrimental energy transfer from the azobenzene to the metalloporphyrin inhibiting photoisomerization, a first successful example is based on a spiro-fused N-alkylated piperidine (Scheme 4). In the *trans*-isomer the sterically bulky azobenzene efficiently shields the axial lone-pair of the piperidine nitrogen atom. Irradiation leads to a large structural reorganization and enables access to the basic/nucleophilic site in the *cis*-isomer. Indeed, in the nitroaldol reaction (Henry reaction) of 2-nitroethane and 4-nitrobenzaldehyde the irradiated catalyst showed an approximately 10-fold increased activity. While this catalyst potentially allows for temporal and spatial control over catalysis – in particular interesting in the context of polymerization catalysis – the system is currently being improved by varying the substitution pattern on the azobenzene fragment, the piperidine nitrogen atom, and the lactone moiety.



Scheme 4. Photoswitchable organocatalyst (single crystal X-ray structural analysis for the *trans*-isomer and DFT model for the *cis*-isomer) employed in a nitroaldol, i.e. Henry reaction.

Publications resulting from this research area: 8, 9, 71, 72, 86, 87, 209, 218, 299, 300, 301, 302, 339, 340, 481, 532, 541

External funding: DFG

Cooperations: M. Bühl (Mülheim/Ruhr, DE), L. Grill (FU Berlin, DE), J. P. Rabe (HU Berlin, DE)

2.5 Department of Theory

Director:

Walter Thiel (born 1949)
Publications: 5, 32, 33, 40, 59, 62, 63, 66, 73, 78, 81, 82, 84, 88, 101, 132, 145, 153, 167, 168, 170, 174, 177, 186, 188, 202, 203, 204, 205, 206, 207, 211, 212, 235, 245, 246, 261, 262, 278, 279, 287, 290, 293, 294, 341, 387, 388, 399, 400, 401, 402, 406, 408, 425, 426, 446, 454, 456, 462, 463, 464, 465, 482, 483, 490, 512, 526, 527, 534, 538, 539, 540, 547, 551, 553

Further group leaders:

Klaus Angermund (born 1958)
Publications: 40, 145, 195, 279, 464

Michael Bühl (born 1962)
Publications: 24, 25, 26, 27, 28, 68, 134, 135, 236, 237, 238, 239, 240, 241, 242, 243, 286, 289, 308, 359, 389, 419, 420, 421, 422, 423, 424, 431, 457, 515, 543, 545, 546, 547

Other publications: 83, 169, 244, 361

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

Special Activities

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 of "Theoretical Chemistry Accounts" and "Journal of Computational Chemistry"
1999-	Editor of "Encyclopedia of Computational Chemistry"
2000-2008	Reviewer (Fachkollegiat) of the Deutsche Forschungsgemeinschaft
2000-2006	Member of the Board (Lenkungsausschuss) of the Bavarian Supercomputer Center (Höchstleistungsrechenzentrum Bayern)
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-	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 of "Angewandte Chemie"

Research in the Department of Theory

The Department of Theory comprises the research groups of Prof. W. Thiel and PD Dr. M. Bühl, and integrates the modeling activities that are pursued at the Institute (PD Dr. K. Angermund). Dr. Bühl has accepted the position of Full Professor (Chair of Computational Chemistry) at the University of St. Andrews (UK) and will move to Scotland in January 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 Prof. Thiel, the main field of research is quantum chemistry. Methodological developments and chemical applications are considered to be of equal importance. The research interests range from accurate and almost quantitative calculations on small molecules to the approximate modeling of very large molecules.

The activities of the group cover

(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),
(e) classical force fields.

Recent applications in these five areas focus on

(a) vibration-rotation spectroscopy of small molecules,
(b) catalytic reactions of transition metal compounds,
(c) electronically excited states in large molecules,
(d) reaction mechanisms in enzymes,
(e) directed evolution in lipases.

The group of Dr. Bühl carries out independent research in computational chemistry, using ab initio and density functional methods including DFT-based molecular dynamics to study structural, spectroscopic, and energetic properties. The recent work has concentrated on NMR chemical shifts of transition metal compounds including metallproteins, on the reactivity of transition metal complexes, and on the properties of uranyl complexes in solution.

Dr. Angermund continues to develop and apply molecular modeling methods, mostly for transition metal chemistry. His recent activities include modeling studies on Ziegler-

Natta polymerization of norbornene and DFT investigations on enantioselective hydrogenation.

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 concerning the enantioselectivity in lipase-catalyzed ester hydrolysis and in Rh-catalyzed asymmetric hydrogenation (Reetz), the stereochemistry of zirconocene-catalyzed olefin polymerization (Fink), and the mechanism of Pd-catalyzed cross coupling reactions (Gooßen) which have involved six coworkers engaged in DFT and QM/MM studies. Moreover, there are several smaller joint projects that employ quantum-chemical calculations as well as molecular modeling (Fürstner, List, Schüth, Pörschke).

More detailed information on the research areas of the Department is available in the following six individual reports and in the 110 scientific papers published in 2005-2007. 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 modeling of large systems. A major new activity is theoretical research on electronically excited states (SFB 663). Other projects that have started or intensified over the past three years, include the accurate variational treatment of nuclear motion in ab initio vibration-rotation spectroscopy, the development of QM/MM techniques with improved accuracy and sampling, multi-scale modeling, and the study of dynamic events. 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 become even more prominent in the research of the Department, both with regard to methodological developments and chemical applications.

Concerning infrastructure, the Institute has made a major investment and built a new computing center in the basement of the main laboratory building that had become available after other reconstruction measures. The new computing center has ample space (more than 200 m^2) and sufficient modular capacity for uninterrupted electric power supply and for cooling. The area previously occupied by the computing center in the physics building has been converted to much needed office space for the Department.

2.5.1 Research area "Ab initio methods" (W. Thiel)

Involved: J. Breidung, H. Lin, M. Schreiber, A. Yachmenev, S. N. Yurchenko, J. Zheng

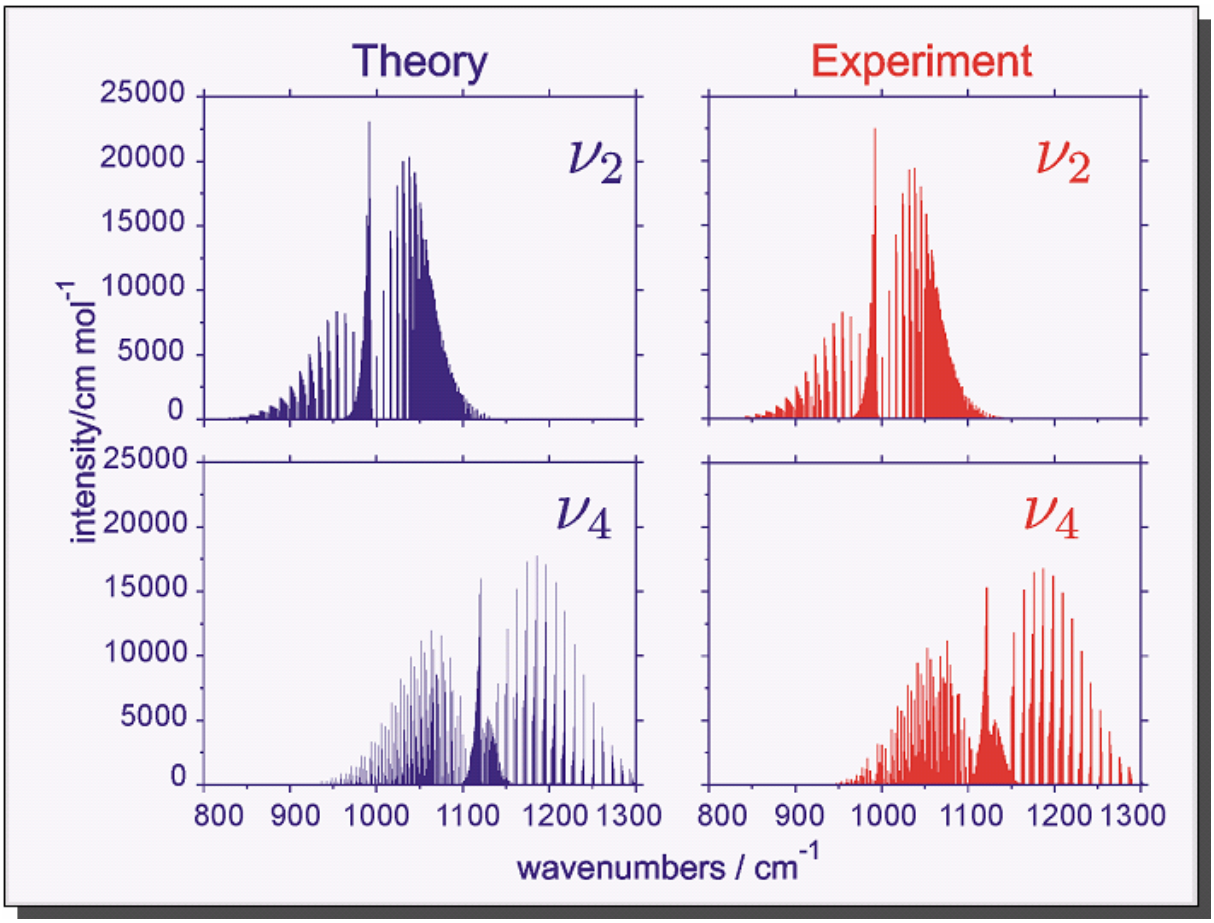
Objective: Vibration-rotation and electronic spectra of small molecules are computed with high accuracy using high-level ab initio calculations with large basis sets. This includes the development of a general variational treatment of nuclear motion that allows the prediction of rovibrational energies 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 relativististic 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. The corresponding theory for the energies [204] and intensities [205] was first formulated for pyramidal XY_3 molecules and later generalized [551]. A distinctive feature of our approach is that the kinetic energy operator is not derived explicitly, but generated numerically via recursion relations to any desired accuracy. As a result of this development, we now have a general and robust variational code for nuclear motion which has been shown to yield converged results [551].

This program has been applied to study NH_3 [203, 207], PH_3 [206, 399], SbH_3 [400], and BiH_3 [202, 400]. In the protypical case of ammonia, the challenge is to compute the complete vibration-rotation-inversion spectrum as accurately as possible. This involves the calculation of the six-dimensional (6D) potential energy surface at the CCSD(T)/CBS level with corrections for core-valence correlation and relativististic effects (using up to 51816 grid points), the computation of the 6D dipole moment surface at the CCSD(T)/aug-cc-pVTZ level, the fitting of these surfaces to a suitable analytical form, and the 6D variational treatment of nuclear motion, with definition of appropriate basis functions and construction and diagonalization of the corresponding

Hamiltonian matrices. This purely ab initio approach leads to errors of 1.9 cm^{-1} for 24 inversion splittings and 4.3 cm^{-1} for 34 vibrational term values which are mostly due the neglect of higher excitations in the coupled cluster calculations. Since these errors are rather systematic, they can be reduced significantly (to 0.8 and 0.4 cm^{-1}, respectively) by a slight empirical adjustment of the ab initio potential. The computed rovibrational intensities agree very well with the available experimental data, and they are accurate enough to assist in line-by-line assignments of high-resolution spectra.

To illustrate the results obtained in a similar manner for phosphine, the computed and observed spectra for the ν_2 and ν_4 fundamental bands are shown in the Figure. It is obvious that the ab initio calculations reproduce the experimental spectra remarkably well.



Intensities of the ν_2 and ν_4 bands in phosphine: Ab initio theory vs. experiment

In the case of PH_3 [206] and its higher homologues SbH_3 and BiH_3 [400], our variational calculations predict rotational energy clusters with sixfold degeneracy at high rotational excitation. The corresponding energy-level scheme is qualitatively

different from the standard pattern for symmetric tops, due to centrifugal-force-induced dynamic symmetry breaking beyond a certain J threshold value, which in a semiclassical picture is associated with predominant rotation around any of the three X-H bonds. This phenomenon has been predicted theoretically and later confirmed experimentally in the case of XH_2 molecules. Our present calculations indicate that it should also be observable for XH_3 molecules that are close to the local mode limit.

Concerning further ab initio studies of vibration-rotation spectra, we have investigated the two lowest electronic states of the PH_2 radical to guide the assignment of the disperse fluorescence spectra measured by our experimental partners [290], and identified rotational energy clustering in its electronic ground state through variational calculations [401]. For the two lowest electronic states of the CH_2^+ cation, we have computed improved potential energy surfaces and a spin-orbit coupling surface, as input to variational calculations that yield excellent agreement with recently observed high-resolution spectra [425]. Using second-order rovibrational perturbation theory in combination with an ab initio (CCSD(T)/aug-cc-pVQZ) anharmonic potential, we have determined the relevant spectroscopic parameters of SbD_3 which are fully consistent with the analysis of the experimental high-resolution spectra [32, 245].

Our focus in the ab initio area is on vibration-rotation spectroscopy, but we also use ab initio methods in other projects (see below) for validation purposes. One noteworthy example is a benchmark study on electronically excited states that covers typical organic chromophores (28 molecules, 213 singlet and triplet excited states). Extensive ab initio calculations using multi-configuration perturbation theory (CASPT2) and coupled cluster theory (CC2, CCSD, CC3) have been performed to generate a reference data base (similar to the established ground-state thermochemistry data bases) that can be used for the assessment and development of lower-level theoretical methods.

Publications resulting from this research area: 32, 202, 203, 204, 205, 206, 207, 235, 245, 290, 341, 399, 400, 401, 402, 425, 551

External funding: European Research Training Network QUASAAR (MRTN-CT-2004-512202), German Research Council (DFG, SFB 663, project C4)

Cooperations: V. Boudon (Dijon, FR), P. R. Bunker (Ottawa, CA), H. Bürger (Wuppertal, DE), L. Fusina (Bologna, IT), P. Jensen (Wuppertal, DE), S. P. A. Sauer (Copenhagen, DK); other QUASAAR partners include A. Campargue (Grenoble, FR), J.-M. Flaud (Paris, FR), L. Halonen (Helsinki, FI), M. Herman (Brussels, BE), T. Rizzo (Lausanne, CH) and J. Tennyson (London, UK).

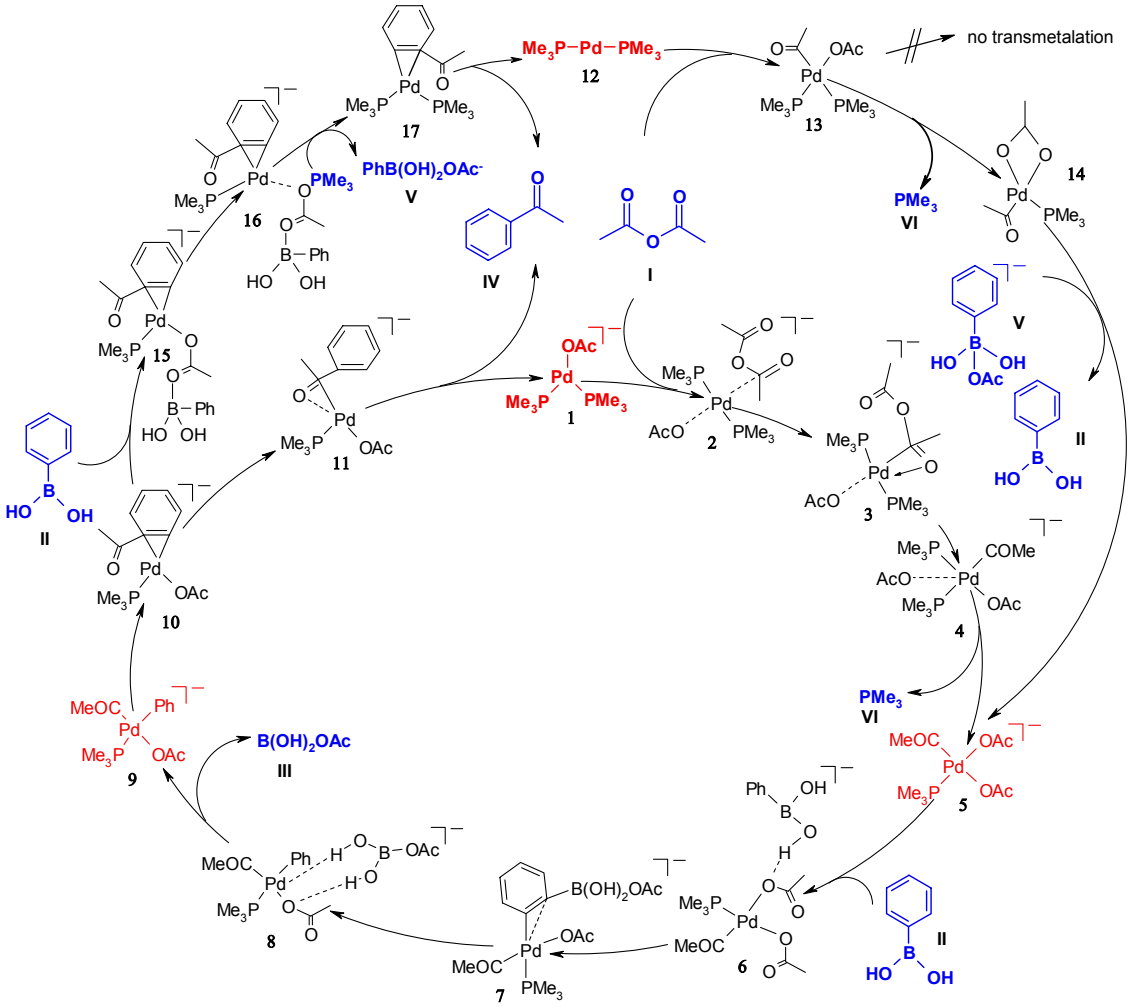
2.5.2 Research Area "Density Functional Methods" (W. Thiel)

Involved: A. Anoop, Z. Chen, A. Fu, M. Graf, H. Hermann, M. N. Jagadeesh, D. Koley, T. Tuttle, S. F. Vyboishchikov , 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.

Palladium-catalyzed cross coupling reactions have been investigated in cooperation with the Gooßen group [62, 63, 278]. The DFT calculations provide a plausible mechanism for the initial step, i.e., the oxidative addition of aryl halides to anionic three-coordinate Pd(0) complexes: the halide coordinates linearly to the palladium to form a hypervalent four-coordinate complex, that subsequently rearranges to the desired addition product without ever forming a five-coordinate Pd(II) intermediate as previously assumed [62]. More extensive DFT computations have been performed for the cross coupling reaction between phenylboronic acid and acetic anhydride, considering altogether five interconnected catalytic cycles that start from neutral PdL_2, anionic PdL_2X^-, and anionic $PdLX^-$ complexes (L=phosphine, X=acetate); two of these are sketched in the Figure. According to the calculations, the anionic pathways are overall more favorable. The initial oxidative addition of acetic anhydride to the anionic complexes leads to anionic Pd(II)monophosphine species with two acetate ligands (cis or trans, slight preference for cis variant) which then undergo transmetalation and reductive elimination [63, 278]. The computed catalytic cycles offer detailed mechanistic insight.



Main intermediates in two of the calculated catalytic cycles for
Pd-catalyzed cross coupling of phenylboronic acid to acetic anhydride

The joint studies with the Fink group on propene polymerization have been completed. Previous work had established the connection between the microstructure of zirconocene-based catalysts and the tacticity of the formed polymer, with excellent agreement between computed and observed pentad distributions at low temperatures. The DFT calculations indicate that the larger deviations at higher temperatures are due to the onset of (originally neglected) epimerization (back-skip) processes that become more favored at high temperatures for entropic reasons [279]. Car-Parrinello molecular dynamics (CPMD) simulations show that the activation of other internal motions does not play a significant role in this regard, but support the fundamental assumption of statistical propagation models that each insertion is independent of the preceding ones [81]. Concerning the zirconocene-catalyzed oligomerization of norbornene, the proposed σ-bond metathesis mechanism has been corroborated, and the helical microstructure of polynorbornene has been simulated [464]. Finally, the single-center

two-state model for the observed broken rate order in zirconocene-catalyzed ethylene polymerization has been investigated through DFT calculations of the relevant agostic conformers and the corresponding transition states [82].

Experimental work in the Reetz group has shown 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 of the two diastereomeric prochiral catalyst-substrate complexes [145]. We have performed a detailed DFT study of the enantioselective hydrogenation of itaconic acid using a chiral Rh(phosponite)$_2$ catalyst, combined with kinetic Monte Carlo simulations, to explain the differences between the two types of catalysts (see also section 2.5.5).

There are several other collaborative DFT projects within the Institute. The ring-closing metathesis reaction of large sterically hindered α,ω-olefins has been studied to understand the stereochemistry (Z/E preferences) observed in the Fürstner group during the synthesis of salicylihalamid and related model compounds [186]. The mechanism of the proline- and 2-methylproline-catalyzed alpha-alkylation of aldehydes has been investigated in cooperation with the List group, focusing on the crucial intramolecular nucleophilic substitution in the enamine intermediate: the added base accelerates the reaction through the electrostatic activation of the leaving group and affects the stereoselectivity by stabilizing the anti and syn transition states to a different extent, which offers an explanation for the differences found experimentally between proline and 2-methylproline [261]. An ongoing project with the List group concerns asymmetric organocatalytic reactions mediated by ion pairs. Motivated by experimental work in the Schüth group, we have studied the properties of the proton sponge 4,9-dichloroquino[7,8-h]quinoline and the role of its catalytically active palladium complexes in the Heck reaction.

Several DFT studies have been carried out without involvement of experimental groups from the Institute, for example on the noncovalent catalysis of the the Diels-Alder reaction by the neutral hydrogen bond donors thiourea and urea [262] and on ruthenium-based colorimetric sensors for fluoride [462]. In an external cooperation with an industrial partner, we have computed the mechanism of olefin hydrosilylation catalyzed by $RuCl_2(CO)_2(PPh_3)_2$ and $[RuCl(NCCH_3)_5]^+$ complexes [388, 540]: in both

cases, a σ-bond metathesis mechanism (with formation of a hydride intermediate) is favored over the conventional Chalk-Harrod mechanism that operates in the case of Pt-based catalysts. The computational results for these and other Ru-based catalysts are consistent with the available experimental evidence, and the mechanistic insight gained may be helpful for further optimization of these catalysts in an industrial setting.

Publications resulting from this research area: 40, 62, 63, 78, 81, 82, 145, 186, 261, 262, 278, 279, 388, 454, 462, 464, 540

External funding: Consortium für elektrochemische Industrie GmbH (München); European COST program (working group D17/010/02).

Cooperations: K. Angermund (Mülheim/Ruhr, DE), G. Fink (Mülheim/Ruhr, DE), A. Fürstner (Mülheim/Ruhr, DE), B. Ganguly (Gujarat, IN), L. Gooßen (Mülheim/Ruhr, DE), V. R. Jensen (Bergen, NO), B. List (Mülheim/Ruhr, DE), M. T. Reetz (Mülheim/Ruhr, DE), P. v. R. Schleyer (Athens, USA), F. Schüth (Mülheim/Ruhr, DE)

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

Involved: E. Fabiano, T. Keal, A. Koslowski, Y. Lu, M. Ramos da Silva, M. Scholten, R. Steiger

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 labelled 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.

Motivated by our participation in SFB 663 (Molecular Response after Electronic Excitation) we have concentrated on semiempirical methods for electronically excited states during the reporting period. Our code provides an implementation of the GUGACI method in a semiempirical context such that general CI expansions can be handled efficiently in a relatively small active space. It allows for CI calculations with about 100000 configurations, for all excitation classes up to full CI. We have now included a semi-analytic GUGACI gradient code for the OMx methods which executes all the expensive steps analytically and evaluates only the integral derivatives numerically, resulting in the same scaling behaviour as in the case of a fully analytic implementation [132].

Our program allows an exploration of excited-state potential energy surfaces at the OMx-GUGACI level, e.g., the location of minima and transition states. Since conical intersections play a central role in photochemistry, we have implemented three methods for finding them: for a test set of 12 well-characterized conical intersections, the Lagrange-Newton method (Yarkony) turns out to be most efficient, closely followed by the projected gradient method (Bearpark-Schlegel), while the penalty function method performs less well [465]. Given the short time scale of photophysical and photochemical events, it will often be of interest to study the dynamics after electronic excitation, and we have therefore also implemented the surface hopping method with

the fewest switches algorithm (Tully). The code offers different schemes for the computation of the required nonadiabatic couplings (analytic vs numerical vs approximate) and ensures proper orbital and state tracking. In three case studies (ethylene, methaniminium ion, and methanimine) the OM2-CI approach yields decay times and dynamics paths similar to high-level ab initio results.

In the context of our general validation project for electronically excited states (see section 2.5.1) we have continued the evaluation of the OMx-CI methods for vertical excitation energies, oscillator strengths, excited-state dipole moments, and excited-state geometries. The results are very satisfactory especially for the OM2-CI approach, in spite of the fact that the OM2 parameterization was performed with regard to ground-state properties only. We shall therefore check in the near future whether further improvements are possible by an OM2 parameterization that employs both ground-state and excited-state reference data.

In collaboration with the Elstner group, the OM2-CI method has been applied to the calculation of absorption shifts in retinal proteins. An initial validation study concludes that the response to external fields generated by the protein environment is not captured properly by a number of commonly used theoretical methods (including CASSCF and TDDFT), but is well represented by ab initio CI approaches (such as SORCI) and by OM2-CI [188]. These methods have therefore been used to study the mechanism of color tuning in the rhodopsin family of proteins, by comparing the optical properties of bacteriorhodopsin (bR) and sensory rhodopsin II (sRII) [287]. The results indicate that several sources contribute to the spectral shift between bR and sRII, the main factors being the counterion region at the extracellular side of retinal and the amino acid composition of the binding pocket. A number of other OM2-CI applications are currently in progress in the SFB project, especially QM/MM (quantum mechanical/molecular mechanical) calculations where OM2-CI serves as QM components. Examples include carotenoids, molecules with intramolecular charge transfer excitations, and proteins with LOV1 domain.

Turning to methodological advances for semiempirical ground-state treatments, a smooth solvation model SCOSMO has been developed in cooperation with the York group. SCOSMO has been implemented for semiempirical methods with an spd-basis [88]. It provides smooth energies and gradients by overcoming discretization errors and thus allows numerically more stable geometry optimizations and reaction path

calculations in solution. The MNDO/d-SCOSMO approach has been applied successfully to study transphosphorylation thio effects in solution [66].

The self-consistent-charge density functional tight binding method (SCC-DFTB) has been evaluated in comparison with MNDO-type and OMx methods using standard test sets [490]. SCC-DFTB is found to be a viable semiempirical method with specific strengths and weaknesses. The overall accuracy of SCC-DFTB and the other semiempirical methods is in the same range, with an overall tendency AM1 < SCC-DFTB < OM2, which may however vary depending on the properties and compounds considered.

Recent advances and applications of semiempirical methods have been reviewed [177].

Publications resulting from this research area: 66, 88, 132, 174, 177, 188, 287, 465, 490, 534

External funding: Fonds der Chemischen Industrie, German Research Council (DFG, SFB 663, project C4), DAAD (stipend to M. Ramos da Silva)

Cooperations: M. Elstner (Paderborn, DE), S. Patchkovskii (Ottawa, CA), K. Schulten (Urbana, USA), D. M. York (Minneapolis, USA)

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, G. Gillies, Y. Hsiao, J. Kästner, T. Keal, D. Kumar, T. Leyssens, H. Lin, S. Metz, N. Otte, M. Parac, J. C. Schöneboom, H. M. Senn, S. Thiel, T. Tuttle, D. Wang, 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. Geometry optimization techniques are commonly employed to determine reaction paths and the relevant minima and transition states. For further improvements beyond this standard QM/MM level, one needs to consider the issues of accuracy and sampling.

Concerning accuracy, we have explored the use of correlated ab initio methods in QM/MM calculations and carried out a case study on the hydroxylation reaction catalyzed by p-hydroxybenzoate hydroxylase (PHBH), in collaboration with the Werner group [246]. This involved B3LYP/GROMOS optimizations of reaction paths and stationary points, single-point ab initio QM/MM energy evaluations using local correlation methods up to the LCCSD(T0) coupled cluster level, and AM1-based determinations of the small zero-point vibrational, thermal, and entropic corrections. Careful validation of the applied local correlation methods with regard to all computational parameters has established that the QM contribution to the barrier should be converged to within 1 kcal/mol, which is supported by the excellent agreement with the available experimental data [246].

The accuracy of the computed QM/MM barriers is mostly determined by the quality of the QM treatment (for sufficiently large QM regions), but the influence of the MM

contributions and the QM/MM interactions may be non-negligible. It is therefore desirable to move from the standard force fields with fixed MM charges to polarizable force fields. In a cooperation with the van Gunsteren group, we have implemented a particular variant of polarizable force fields, the charge-on-spring (COS) model, into our ChemShell QM/MM software [456]. The COS model has the advantage that it is entirely formulated in terms of point charges and is thus consistent with any QM code that can handle external point charges. In the initial QM/MM(COS) test, we studied the identity S_N2 reaction between NH_2Cl and the chloride anion in liquid dimethyl ether (MM solvent described by a polarizable force field). Including solvent polarization raised the barrier by 3 kcal/mol due to a better solvation of the separate reactants [456]. In subsequent work we have shown that semiempirical OM3/MM molecular dynamics (MD) simulations of a QM water solute in liquid MM water also benefit from the use of a polarized MM model for water.

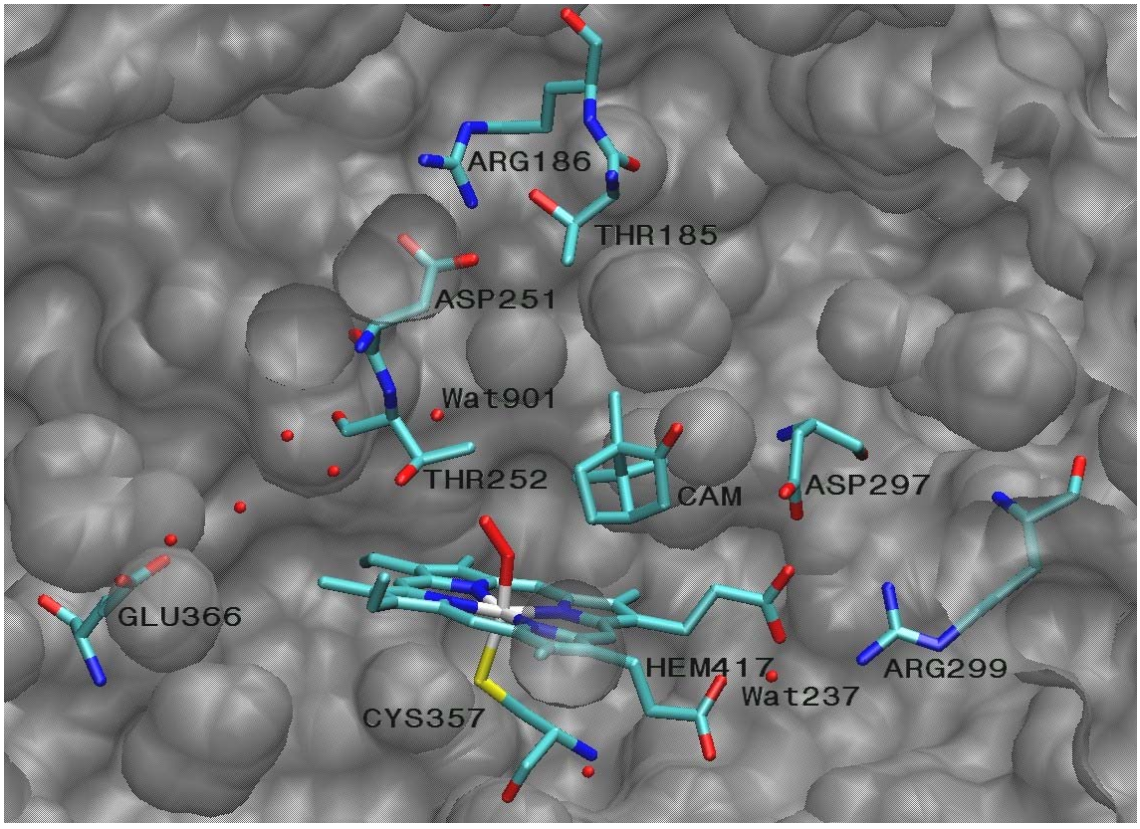
Concerning sampling, the conformational complexity of enzymes calls for extensive explorations of the underlying potential energy surfaces that go beyond performing geometry optimizations for some selected snapshots. When aiming for barriers, this may be achieved by MD simulations for points along a suitable reaction path, with the reaction coordinate being constrained to a fixed value (as in thermodynamic integration) or restrained by a harmonic bias potential (as in umbrella sampling). We have implemented both these techniques into the ChemShell QM/MM package (with proper attention to convergence and error control) and have shown for the test case of PHBH that both yield the same converged free energy barrier [84, 168]. In the course of this work, we noted some drawbacks in the weighted histogram analysis method (WHAM) that is commonly used in umbrella sampling, and we therefore introduced an alternative analysis method called umbrella integration which employs only quantities with easily controllable equilibration and greatly reduces the statistical error compared to WHAM [84]. As an additional advantage, it is possible to derive approximate expressions for the statistical errors which leads to rules for the choice of the bias potential and the sampling parameters [294]. The straightforward application of these MD-based free energy techniques to enzymatic reactions is computationally very demanding and currently only practical at the semiempirical QM/MM level. We have therefore implemented an approximate QM/MM free energy perturbation (FEP) method into ChemShell (originally proposed by Yang) and tested a number of options in the treatment of the link atoms and the QM/MM electrostatic interaction [293]. We find that it is adequate to approximate the QM density by electrostatic-potential-fitted point charges during the FEP-MD runs which makes QM/MM-FEP affordable for any QM

method. Concerning geometry optimization, we have further improved the microiterative approach in the case of electrostatic and polarized embedding [463].

In ongoing methodological work, we develop the tools that are needed for QM/MM investigations of electronically excited states. This includes the adaptation of conical intersection search routines and of surface hopping algorithms (see section 2.5.3) in a QM/MM framework and the definition of protocols for QM/MM calculations of condensed-phase electronic spectra.

Turning to QM/MM applications, cytochrome P450cam remains the enzyme that is studied most extensively in our group, usually at the B3LYP/CHARMM level (often in collaboration with the Shaik group). The earlier work has been summarized in a review [170]. In the reporting period, we have continued to characterize the intermediates in the catalytic cycle including the pentacoordinated ferric and ferrous complexes [5], the ferrous dioxygen and ferric peroxo complexes, the last experimentally accessible intermediate Cpd 0 [406], and the yet unobserved reactive species Cpd I [153]. In addition, we have investigated several key reactions, in particular the proton transfers that generate Cpd 0 and Cpd I [101, 406], and camphor hydroxylation by Cpd I [73, 211, 212, 408, 553]. In all these cases, the comparison between B3LYP/CHARMM calculations for the complete solvated enzyme (around 25000 atoms) and B3LYP calculations for the isolated QM region (typically 40-200 atoms) allows us to assess the role of the protein environment in P450cam. In the following, we outline a few selected results. For Cpd I, the earlier B3LYP/CHARMM prediction of an almost degenerate electronic ground state, with the doublet slightly below the quartet, has been confirmed by ab initio MRCI/CHARMM calculations, and the EPR and Mössbauer parameters have been predicted to facilitate the experimental search for this yet unknown species [153]. Excited states of penta-radical character are found to lie only 12-14 kcal/mol above the tri-radical ground state of Cpd I [153], and subsequent B3LYP calculations have shown that this gap diminishes along the reaction pathway of hydroxylation, due to the cumulative exchange stabilization of the more open-shell species, which might give rise to multi-state reactivity [73]. Contrary to recent suggestions by others, excited states of Cpd I with an Fe(V)-oxo moiety are too high in energy to be mechanistically relevant, and one-electron reduced species (Cpd II) show only sluggish reactivity compared with Cpd I [408]. The hydrogen abstraction from camphor by Cpd I has been investigated systematically to identify the factors that may affect this reaction [211,212]: the claim of remote transition state stabilization (via larger electrostatic interactions between the A-propionate side chain of the heme and the Arg299 residue) has been refuted, the crystallographic water903 has been found to act as a catalyst

(through differential hydrogen bonding), and the role of other environmental residues has been clarified (Asp297, His355). Different mechanisms have been considered for the proton transfer that transforms Cpd 0 into Cpd I [101, 406]. In the enzyme, where the proton can come from Glu366 and Asp251 (see Figure), the best computed mechanism starts with an initial O-O cleavage followed by a concomitant proton and electron transfer in the Asp251 channel to yield Cpd I and water. According to the QM/MM calculations, this is more favorable than the alternative textbook mechanism (protonation followed by O-O cleavage). Hydrogen bond networks play a crucial role in these proton transfer processes, and it is thus not surprising that the latter are affected by mutations of active-site residues which influence these networks. Ongoing QM/MM studies on proton transfer in five such mutants of P450cam reproduce the experimentally observed effects of the mutations and rationalize how they control activity and product distribution (uncoupling vs hydroxylation). As a final remark on P450cam, we mention a methodological study showing that it is feasible to treat the entire catalytic cycle with a common QM/MM setup [553].



Active-site environment in cytochrome P450cam. Red dots indicate crystal water molecules.

In continuation of the collaboration with the Reetz group on directed evolution in lipases, we have used classical MD and QM/MM calculations in order to understand the enantioselectivity in the lipase-catalyzed ester hydrolysis and its optimization through successive mutagenesis. In previous work, we proposed a relay mechanism involving only two out of six mutations in the "best" mutant, to account for the source of the enhanced enantioselectivity. The corresponding double mutant S53P/L162G has meanwhile been prepared and has indeed been found to be even more enantioselective [512]. In control experiments, we have also replaced His83 which is assumed to provide a crucial additional hydrogen bond in the proposed relay mechanism (only in the favored enantiomer). Enantioselectivity is suppressed (as expected) upon substitution by phenylalanine which is of similar size, but largely retained upon substitution by the smaller alanine. MD simulations indicate that a water molecule can assume the role of His83 in the latter case and provide the stabilizing hydrogen bond [512]. Related work on a lipase from *Bacillis subtilis* has demonstrated that the combination of computational prescreening and experimental library construction can accelerate enzyme optimization by directed evolution: both QM/MM-based calculations and molecular biology experiments find His76 as a residue that strongly affects catalytic activity [59]. Further unpublished work on this lipase has identified a number of possible binding modes for the substrate 1-(2-naphthyl)-ethyl-acetate, which provide starting points for QM/MM calculations (DFT/CHARMM geometry optimizations and SCC-DFTB/CHARMM umbrella sampling MD runs) that give qualitative insight into the origin of the observed enantioselectivity.

A number of other biomolecular systems have been studied at the QM/MM level during the reporting period, often motivated by cooperations with other groups. We list ten such applications.

(a) Enzymatic C-F bond formation by a fluorination enzyme has been found to follow an S_N2 reaction mechanism, while the alternative elimination-addition mechanism can be excluded as well as the route via sulfur ylides [167].
(b) The enzymatic activity of 4-oxalocrotonate tautomerase and seven synthetic mutant analogues has been analyzed by classical MD simulations and QM/MM calculations. Replacing arginine (Arg) by citrulline (Cit) has only minor effects in the case of the Arg61Cit mutation (because of the flexibility of this residue), while the Arg11Cit and Arg39Cit mutations disrupt the binding site and strongly impair the catalytic activity [387].
(c) An in-depth QM/MM study of the wild-type 4-oxalocrotonate tautomerase has led us to propose a new model for the reactive substrate orientation which combines

favorable substrate binding geometries with reasonable barriers and is consistent with the experimental evidence from mutation studies concerning the catalytic ability of specific residues in the binding site [539].

(d) In cooperation with the Fürstner group, we have studied the binding of latrunculin and its synthetic analogues to actin and rationalized the differences between these compounds in terms of the possible hydrogen bond networks [446].

(e) In collaboration with the Engels group, we have examined the importance of the active site histidine residue for the activity of epoxide- and aziridine-based inhibitors of cystein proteases and the particular role of a water molecule that is required to establish an efficient relay system for proton transfer [482].

(f) To characterize the active site of vanadium chloroperoxidase, ten models with different protonation patterns have been optimized at the DFT/CHARMM level and then subjected to ^{51}V NMR computations (see section 2.5.6), which allowed us to identify the two most likely candidate structures on the basis of the computed anisotropic NMR chemical shifts [547].

(g) In cooperation with the Cremer group, we have studied the Bergman cyclization of dynemicin A in a DNA environment. According to the DFT/CHARMM calculations, acyclic enediynes can undergo this reaction in the minor groove with a much smaller barrier than in the gas phase, while the DNA environment has less effect in the case of cyclic enediynes [538].

(h) In collaboration with the Cao group, the deprotonation mechanism in the *Escherichia coli* ammonium transporter AmtB has been investigated using QM, QM/MM, and QM/MM MD techniques. We find a stepwise rather than a concerted mechanism, with the carboxylate group of Asp160 acting as the proton acceptor, which clarifies why mutations of the preserved residue Asp160 reduce or disable the activity of AmtB [426].

(i) In cooperation with the Hildebrandt group, the Raman spectra of the phycocyanobilin chromophore in α-C-phycocyanin have been computed at the B3LYP/CHARMM level. This provides a substantially improved description of the experimental resonance Raman spectra of the protein-bound cofactor (compared with gas-phase QM model calculations) and allows an assessment of the protein-cofactor interactions [483].

(j) Ongoing unpublished QM/MM work addresses the mechanism of oxidation reactions catalyzed by molybdenum-containing enzymes such as aldehyde oxidoreductase and xanthine oxidase.

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 [526, 527].

Publications resulting from this research area: 5, 33, 59, 73, 84, 101, 153, 167, 168, 170, 211, 212, 246, 293, 294, 387, 406, 408, 426, 446, 456, 463, 482, 483, 512, 526, 527, 538, 539, 547, 553

External funding: Deutsch-Israelische Projektkooperation (project DIP-F.6.2), VolkswagenStiftung (project I/80454), German Research Council (DFG, SFB 663, project C4), Triple-M Research Initiative of the Max Planck Society, Fonds der chemischen Industrie (stipend to S. Metz), Alexander-von-Humboldt Foundation (fellowship to T. Leyssens)

Cooperations: M. Bühl (Mülheim/Ruhr, DE), Z. Cao (Xiamen, CN), D. Cremer (Göteborg, SE), B. Engels (Würzburg, DE), R. A. Friesner (New York, USA), J. N. Harvey (Bristol, UK), P. Hildebrandt (Berlin, DE), K.-E. Jaeger (Jülich, DE), E. Keinan (Haifa, IL), C. Marian (Düsseldorf, DE), A. J. Mulholland (Bristol, UK), F. Neese (Bonn, DE), D. O'Hagan (St. Andrews, UK), M. T. Reetz (Mülheim/Ruhr, DE), S. Shaik (Jerusalem, IL), P. Sherwood (Daresbury Laboratory, UK), W. F. van Gunsteren (Zürich, CH), H.-J. Werner (Stuttgart, DE), Y. D. Wu (Hong Kong, HK)

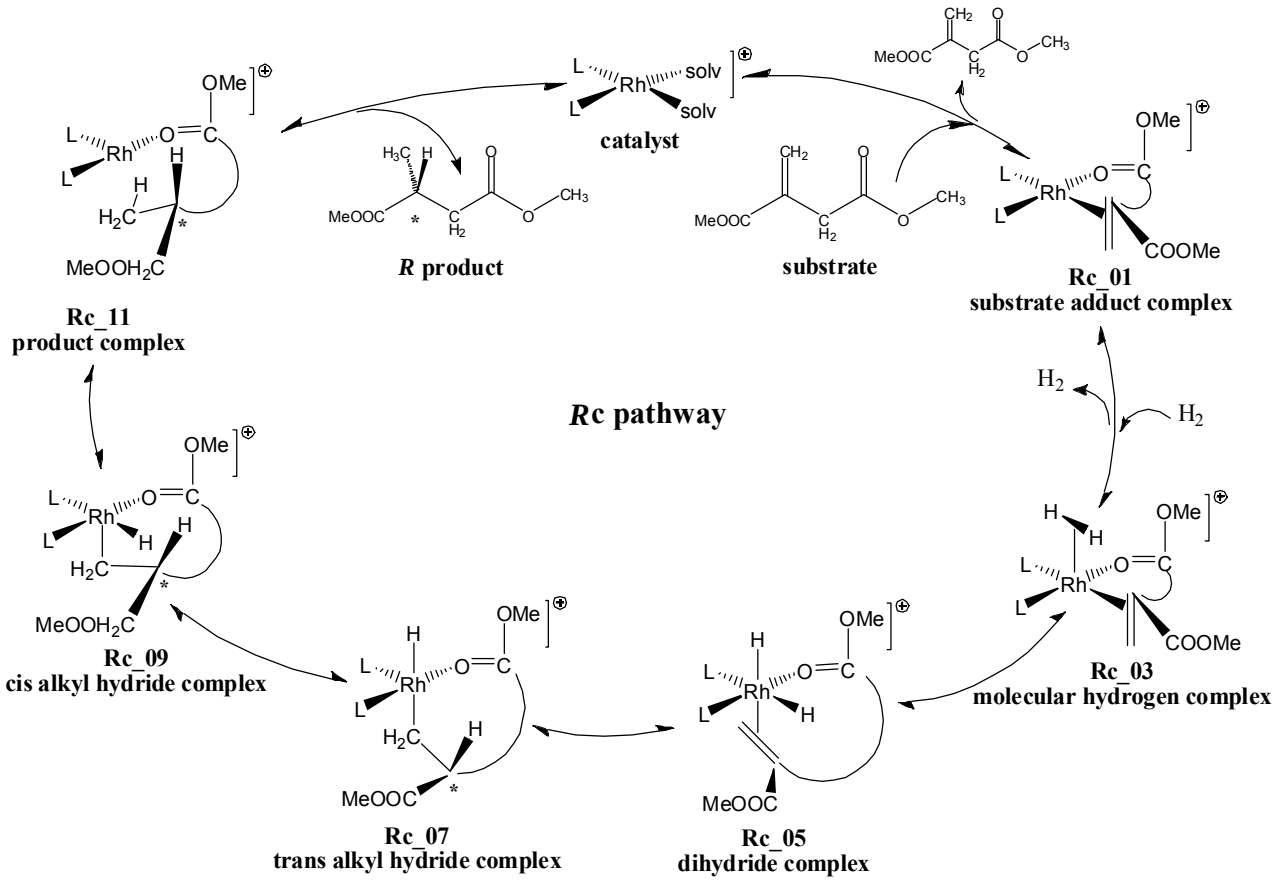
2.5.5 Research Area "Molecular Modeling" (K. Angermund)

Involved: A. Anoop, M. Graf

Objective: Molecular modeling and DFT procedures are applied in close cooperation with local experimental groups to provide computational evidence on structure, reactivity and enantioselectivity, mostly in transition metal chemistry.

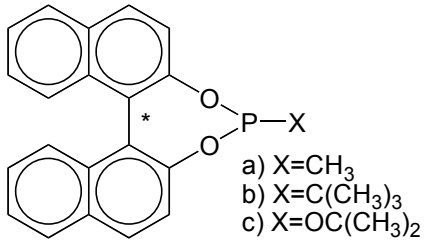
Results:

Enantioselective Rh-catalyzed hydrogenation of functionalized olefins: Experiments with monodentate phosphorous compounds as ligands in the Rh-catalyzed hydrogenation of functionalized olefins show high enantioselectivity. DFT calculations of seven pro-*R* and pro-*S* substrate adduct complexes with $\Delta G_{298} < 3$ kcal/mol result in an calculated enantiomeric excess (ee) of 91 % *R* compared to an experimental value of



98 % *R* (L = *R*-c). The good agreement strongly suggests that in contrast to the widely accepted mechanism for the reaction with chelating P-ligands at the metal center (formation of the less stable, "minor" adduct determines the preferred enantiomer of the product) the more stable, "major" adduct determines the enantiomeric outcome of the

reaction for these non-chelating phosphorous ligands. To further explore the differences four reaction pathways of each type of reaction have been calculated using DFT. While the overall energy profiles are similar stochastic kinetic simulations reveal that for a "minor – major" system as proposed for chelating ligands the barriers for the back reaction of the substrate adduct complexes to catalyst and substrate have to be smaller than the highest barriers of the subsequent reaction pathways, while in the case of a Rh-catalyst with monodentate P-ligands the barriers for the back reactions are higher than the highest barriers of the subsequent reaction pathways leading to a "major – major" system. The calculated dissociation energies of the substrate adduct complexes support these findings.



(*R*/*S*) Ligand

Polymerization using zirconocene catalysts: The force field calculations on the microstructure of polynorbornene were completed. In combination with high-resolution NMR results of norbornene oligomers a consistent picture of the bonding in polynorbornene could be developed.

Publications resulting from this research area: 40, 145, 195, 279, 464

External funding: None

Cooperation: H. Bönnemann (Mülheim/Ruhr, DE), G. Fink (Mülheim/Ruhr, DE), H. Gies (Ruhr-Universität Bochum, DE), M. T. Reetz (Mülheim/Ruhr, DE), W. Thiel (Mülheim/Ruhr, DE).

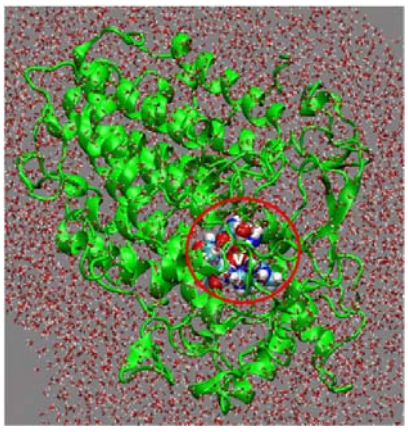
2.5.6 Research Area "Computational Chemistry of Transition-Metal Compounds" (M. Bühl)

Involved: R. Diss, K. R. Geethalakshmi, V. Golubnychiy, S. Grigoleit, H. Kabrede, J. Macháček, T. C. Ramalho, R. Schurhammer, I. Vinkovic Vrček, V. Vrček, M. P. Waller

Objective: Our research focuses on the application of modern quantum-mechanical methods to obtain information on structural, energetic, and spectroscopic properties of transition-metal compounds. Special attention is called to the simulation of dynamical and solvent effects on the properties of interest, mainly NMR chemical shifts.

Results:

1. NMR chemical shifts of transition-metal compounds: Computational NMR spectroscopy of transition metal complexes is now a mature area within the field of density-functional theory (DFT). Systematic performance tests have been conducted in order to identify the functionals that are best suited for computation of geometrical parameters of 3d-metal complexes in general (prerequisite for accurate property calculations), and for ^{53}Cr and ^{59}Co chemical shifts in particular. For highly charged Co complexes in aqueous solution, DFT-based molecular dynamics (MD) simulations have revealed large but opposite effects of dynamical averaging and hydration on the $\delta(^{59}\text{Co})$ values. Qualitatively similar effects are found upon perturbational inclusion of quantum-mechanical zero-point corrections, which are not accounted for in the MD simulations, and which were evaluated for the first time in a polarizable continuum modeling the solvent. Such zero-point corrections can also be used to reproduce and rationalize subtle isotope effects on $\delta(^{59}\text{Co})$.

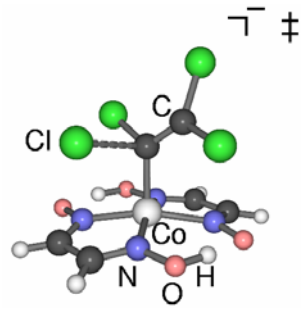


QM/MM-computation of the ^{51}V chemical-shift tensor of vanadium chloroperoxidase. Circle: QM part.

For protonated ferrocene, a highly fluxional molecule, the averaged ^{57}Fe and ^{1}H chemical shifts turned out to be very sensitive to the DFT level and can thus be used to probe the accuracy of the whole reactive path of the potential energy surface that is being sampled. MD simulations have also been applied to study the speciation of vanadate-dipeptide and peroxovanadate complexes in water, using the computed $\delta(^{51}\text{V})$ values for structural assignments.

A mixed quantum-mechanical/molecular-mechanical (QM/MM) approach has been used for the first time to compute the ^{51}V chemical-shift tensor of a whole enzyme, vanadium-containing chloroperoxidase. Several structural models have been considered that differ in the protonation state of the central vanadate moiety and details of the H-bond network around it. Based on best accord between the theoretical NMR tensor elements and those obtained from recent solid-state NMR data, only a limited number of these models are compatible with experiment. Such NMR computations can thus be used to obtain detailed structural information of active sites in enzymes, information that is not readily available via standard protein X-ray crystallography.

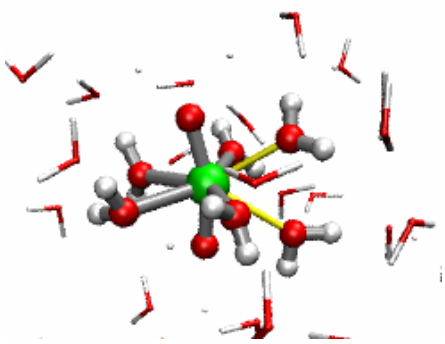
2. Reactivities of Transition-Metal Complexes: Theoretical computations of key intermediates and transition states have been used to rationalize fluxional behaviour of metal complexes and possible reaction mechanisms with substrates in a catalytic cycle. In collaborations with M. Biruš, R. A. Layfield, and K. Pörschke, intramolecular rearrangement pathways of, respectively, vanadium-hydroxyurea, manganese-allyl, and nickel-allyl complexes have been computed. A viable pathway for formation of cobalt-vinyl complexes from chloroalkenes and reduced cobaloxim model complexes has been identified. These findings have implications for the reductive dehalogenation of chlorinated olefins, a process of substantial environmental interest, which can be catalyzed by vitamin B_{12}.



A possible transition state for reductive dehalogenation of perchlorethylene at a cobalt center.

3. Uranyl Complexes: Initiated by a collaboration with G. Wipff, the first Car-Parrinello-MD simulations have been performed for uranyl(VI) hydrate in aqueous solution, including evaluation of free energies by thermodynamic integration along predefined reaction pathways. With this approach it has been shown that in water, five solvent molecules are coordinated to the uranyl moiety, UO_2^{2+}. Experimental observables for this hydrate, namely its acidity constant and the activation barrier for water exchange with the bulk, can be reproduced computationally within ca. ±10 kJ/mol, a respectable accuracy for a DFT method. The simulations also furnish evidence that water exchange follows an associative interchange, rather than a dissociative mechanism.
Subsequently, these simulations have been extended to complexes of uranyl with nitrate ligands and a chelating diamide, prototypical models for the species present during reprocessing of nuclear waste. Solvation is indicated to promote the transition of bi-

dentate to monodentate coordination mode of the nitrate ligands, to the extent that uranyl mononitrate is predicted to exist as $[UO_2(H_2O)_4(\eta^1\text{-}NO_3)]^+$, in apparent defiance of the usual chelate effect.



Transient hexaquo uranyl complex involved in exchange of a coordinated water ligand against a solvent molecule from the bulk.

It has also been shown that the affinity of pertechnetate towards uranyl in water is significantly smaller than that of nitrate. It is thus unlikely that uranyl-pertechnetate complexes, believed to be responsible for the poor separability of uranium and technetium, can already be formed in the aqueous phase during reprocessing of nuclear waste. With this MD-based methodology it is now possible to compute and reliably predict structures, stabilities, and reactivities of uranyl complexes in aqueous solution, taking a significant step toward the virtual actinide lab.

Publications resulting from this research area: 24, 25, 26, 27, 28, 68, 134, 135, 236, 237, 238, 239, 240, 241, 242, 243, 286, 289, 308, 359, 389, 419, 420, 421, 422, 423, 424, 431, 457, 515, 543, 545, 546, 547

External Funding: DFG (Ph.D. position for F. R. G., postdoc positions for V. G., S. G., H. K., and M. P. W.); Humboldt Foundation (Research Fellowships for R. S. and V.V.); DAAD

Cooperations: M. Biruš (Zagreb, HR), J. W. de M. Carneiro (Niteroi, BR), J. D. Figueroa-Villar (Rio de Janeiro, BR), D. Hnyk (Rez, CZ), R. A. Layfield (Cambridge, UK), W.-W. du Mont (Braunschweig, DE), K. Pörschke (Mülheim/Ruhr, DE), W. Thiel (Mülheim/Ruhr, DE), G. Wipff (Strasbourg, FR).

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 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.

3.1 Technical Laboratories (N. Theyssen)

Involved: A. Brinkmann, T. Scholl, L. Winkel

The "Technikum" of the Max-Planck-Institut für Kohlenforschung includes the central high pressure laboratories, central solvent purification and drying distillation apparatus, large-scale synthesis facilities, and the central treatment of waste chemicals. The involved co-workers have specific skills for the execution of the associated tasks. The service for the scientific departments is mainly provided by one chemical engineer (A. Brinkmann) and one chemical technician (L. Winkel).

The high pressure laboratory offers equipment and support to all groups of the institute to carry out chemical reactions under elevated pressure. It comprises 27 especially designed high pressure boxes built of ferroconcrete and massive steel plates. High pressure stainless steel reactors of various designs are available from 50-5000 ml volume for batch-wise synthesis and exploratory studies. The central facility was intensively used in the reporting period as the utilization ratio was 100% for the larger and medium size boxes and between 40 and 80% for the small boxes.
In 2005 the central gas supply for carbon monoxide, ethylene and hydrogen was fundamentally modified: A new and modern filling station was built in a walk-in fume cupboard. A *continuous* gas supply was established by the installed combination of (i) gas discharging devices with an automatic switching for redundant gas cylinders, (ii) an optic and acoustic status indication, and (iii) double contact manometers (to maintain the pressure level automatically at a certain level by connected compressors). Thereby the number of gas cylinder could be reduced significantly. This diminishes the leasing costs, ensures a maximum utilization of each gas cylinder, and increases the operational safety substantially. The latter was further improved by the installation of a central gas warning device with optic and acoustic alerting and automatic cut-off valves for the ring line system. Due to the continuously growing demand for hydrogen supply, the respective compressor was rebuilt in 2006 to achieve an increased performance and to add a membrane-break-securing device in order to exclude a contamination of the connected plants with compressor oil.
A high level of job safety is also maintained by a variety of organisational measures. First of all a checklist for weekly inspections in the high pressure laboratory was developed to ensure the adherence to safety rules (since 2005). Secondly about 15 instruction sessions are held every year with first-time users of the high pressure facilities. Finally, as legally required, the large pressure vessels, large-scale reactors,

and pressure cylinders are regularly controlled by the external Technical Inspection Agency (TÜV) whereas the remaining smaller ones are checked by especially trained co-workers of the Institute's mechanical workshop (K. Gräfenstein and W. Kersten). This workshop is also essential for the maintenance or adaptation of existing as well as the development and production of new high pressure equipment.

In comparison to the last reporting period the demand for purified solvents has increased by 80%. Nowadays about 2.900 L of ethyl acetate and about 10.000 L of a mixture of hexane isomers are purified by simple distillation every year. In addition about 1.300 L of *n*-pentane are rectified annually. To circumvent supply shortfalls and to ensure a complete separation from contained plasticizers, a further rectification plant is being installed for the hexane fraction. In the course of this work the measuring and control technology of both rectification plants is currently renewed to meet safety regulations. This includes the detection of solvent vapour at the outer part and of oxygen at the inner part of the plants (explosion precaution). Further solvents that are distilled and dried include diethyl ether, *n*-pentane, THF and toluene. The remaining water content of each charge is steadily controlled by coulometric Karl Fischer titration before handing them out to the scientific groups.
To reduce operating costs, both processing sites – the central solvent treatment facility and the hall where the two rectification plants and the drying unit for dichloromethane are located – were connected to the central cooling circuit at the end of 2007. In addition, the electric sub-distributions were renewed completely in both parts of the building. This activity included the installation of ground fault circuit interrupters and emergency stop switches so that the complete building now possesses a uniform security level from this perspective.

Finally, every year about 25.000 L of non-halogenated solvents, 3.000 L of halogenated solvents, and 2.700 kg of sorted solid waste were accepted and applied to an appropriate and environmental benign waste disposal by the personnel of the technical laboratories.

Research: The joint research activities with W. Leitner are summarized in sections 2.1.7 and 2.1.8.

3.2 Chromatography and Separation Science (D. Belder)

The chromatography group serves as a central facility for the analysis and isolation of compounds in chemical mixtures. A section of the group was also engaged in independent research projects in electrophoresis and lab-on-a-chip technology. The head of the group left the institute in June 2006 to become professor for Analytical Chemistry at the University of Regensburg. He has meanwhile been appointed as a full professor at the University of Leipzig.
The service group is divided in four sections according to the different separation techniques applied in the respective laboratories:

Liquid Chromatography and Electrophoresis: The laboratory offers nearly the full range of modern liquid phase separation techniques such as liquid chromatography, electrophoresis and capillary electrophoresis (CE). Besides routine analysis and method development, the team has been involved in several long-term projects such as chiral high-throughput-screening in HPLC (with M. T. Reetz).
Gas Chromatography (GC): The laboratory is equipped with various modern automated instruments in manifold configurations. Besides routine analyses the team has especially been engaged in the development of new methods and instrumental configurations for subsequent transfer to decentralized facilities.
Multidimensional Large Scale Gas Chromatography (Preparative GC)*:* With the unique technical equipment, which has been developed in this group, it is possible to isolate volatile compounds present in very complex mixtures.
Distillation*:* The distillation laboratory equipped with a wide variety of different columns completes the array of available separation techniques.

Research Area "Microfluidics and Chip-Electrophoresis" (D. Belder)

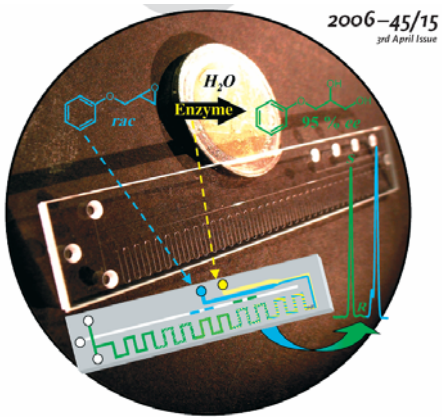
Involved: F. Kohler, M. Ludwig, N. Piehl, P. Schulze, K.M. Tolba, U. Häusig, P. Hoffmann

Objective: We aim at the development of techniques and instrumental configurations to realize integrated micro-machined devices for fast analyses and multiplexed high throughput screening. One of our foci is microchip-electrophoresis (MCE), which is currently the most successful microfluidic “lab-on-a-chip” technique. We worked on the following research topics: Integrating chemical synthesis and analysis on chip, native

fluorescence detection, chip/mass-spectrometry coupling, microfluidic devices of hydrophilic materials, surface chemistry and soft lithography.
Results from two of these several projects will be presented in short.

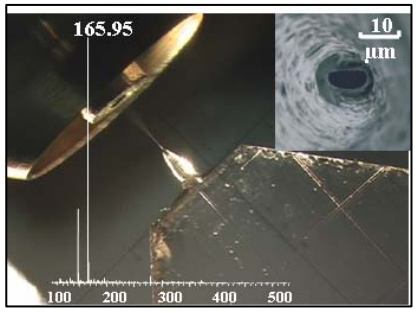
Catalysis / Analysis Chip

In cooperation with Prof. Reetz, we developed the first example of an integrated chip-based system applied in synthetic chemistry and catalysis which integrates a microfluidic reactor with chemical analysis. The device was successfully applied for testing enantioselective biocatalysts created by directed evolution of enzymes. Integration of chemical reaction and analysis on a single chip results in reduced reagent consumption and allows unsurpassed speed of the whole screening process. For a schematic drawing of the approach, as displayed on the cover page of the respective issue of the Angewandte Chemie, see right figure.



Chip / Mass Spectrometry-Coupling

The first example of a microfluidic glass chip having a monolithically integrated nanospray tip was developed. Such chips were used to study biochemical reactions with online MS-monitoring, as well as for coupling chip-electrophoresis with mass spectrometry. The device was successfully applied for on-chip digestion of proteins followed by mass-spectrometric detection and peptide mapping. A microscopic image of the device in front of a mass spectrometer is shown, together with a respective mass spectrum, on the right figure.



Publications: 11, 12, 163, 225, 226, 227, 228, 459

External funding: DFG: BE 1922/1-1, BE 1922/1-3, BE 1922/1-5, BE 1922/3-1, BE 1922/ 5-1; Egyptian Government scholarship (stipend to K.M. Tolba); BMBF: FKZ 01 RI 0643 B

Cooperations: M. T. Reetz (Mülheim/Ruhr, DE)

3.3 Mass Spectrometry (W. Schrader)

The work of the mass spectrometry group is divided into service and research. The major task is the service for both institutes (Kohlenforschung and Bioanorganische Chemie) on the campus. Here, emphasis is placed on utilizing the modern analytical capabilities of the group to solve analytical problems through mass spectrometry. This is being done by providing full support for identifying unknown 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 fast enough to proceed with their work. The Institute's own data base and software package (MassLib) were modernized by incorporating high resolution data. Between 6000-8000 samples were measured 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: The FT-ICR mass spectrometer is now utilized fully for demanding research tasks. A new triple quadrupole mass spectrometer was purchased that can be used to acquire MS/MS data. The group has started to generate a new data base obtained from MS/MS measurements which should allow us to obtain structural information of polar and non-volatile components in the near future.

The **research interests** are focusing on the investigation of complex reactions. Here, three projects were carried out during the reporting period. The first one is a continuing investigation into nucleation in solution together with the group of Prof. Schüth (see section 2.3.1).

The second project concerns the study of organocatalytic reactions with mass spectrometry to gain mechanistic information. Two cooperations (within the DFG Priority Program Organocatalysis) were carried out successfully that adressed complex cascade reactions (with B. List) and a "conjugate" umpolung reaction to convert α,β-unsaturated aldehydes into nucleophiles (with F. Glorius). Very helpful in this connection is the use of the MS/MS technique, where a specifically selected ion can be subjected to fragmentation with gas molecules by using collision activated dissociation (CAD). The fragment spectrum gives information about structural aspects of the investigated ion and thus allows mechanistic insights.

The combination with accurate FT-ICR MS measurements further corroborates the obtained data. Using this approach the conjugate umpolung reaction could be studied and a mechanism was suggested (see Figure 1).

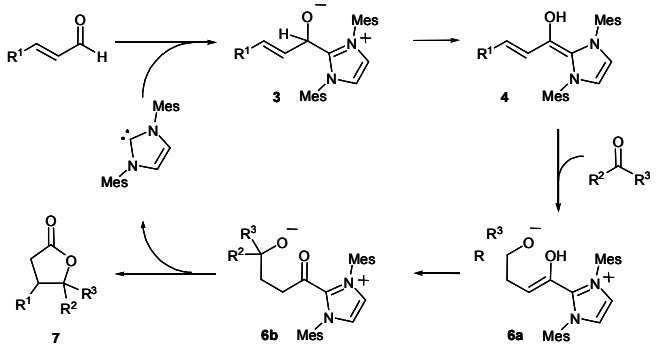


Figure 1: Proposed mechanism of organocatalytic umpolung reaction

The third project deals with the investigation of complex crude oil samples, especially with regard to the content of non-polar heteroaromatic compounds. A high amount of sulfur in the crude oil fraction applied as transportation fuels can cause environmental harm, which has led to more drastic emission regulation worldwide. The most widely used catalytic process to remove sulfur from crude oil fractions – hydrodesulfurization – is currently optimized by using the overall content of sulfur as a parameter. We have developed a strategy to characterize sulfur heterocycles in the complex crude oil fraction with more than 5000 different components using different chromatographic separation methods and mass spectrometry, for a better optimization of complex catalytic systems. An important tool is the sulfur selective derivatization of sulfur species that form a thiophenium salt, which dissociates in solution and thus can more easily be subjected to electrospray MS measurements. This derivatization allows us to study non-polar components like sulfur heterocycles by using electrospray ionization which would not be possible otherwise, due to the lack of polarity.

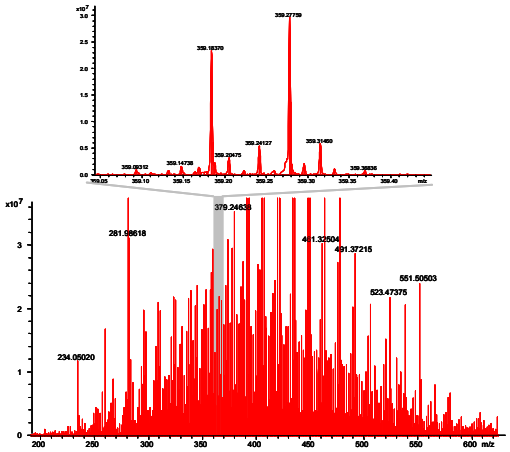


Figure 2: MS spectrum of a crude oil fraction

Publications: 126, 154, 155, 333, 336, 410, 494, 495, 497, 498, 499, 523

External funding: DFG SCHR 8-1, SCHR 8-2; Shell Global Solutions

Cooperations: F. Schüth (Mülheim/Ruhr, DE); B. List (Mülheim/Ruhr, DE); J.T. Andersson, F. Glorius (Münster, DE)

3.4 Nuclear Magnetic Resonance (R. Mynott)

The NMR department is equipped with five NMR spectrometers with magnetic field strengths from 7.05 to 14.1 Tesla (corresponding to ^{1}H resonance frequencies of 300 to 600 MHz) for analyses in solution and two NMR spectrometers with magnetic field strengths of 7.05 and 11.7 Tesla (^{1}H: 300 and 500 MHz, respectively) used exclusively for solid state studies.

Fully automatic measurements (open access). Basic NMR measurements can be carried out by scientific and technical staff on two NMR spectrometers with proton frequencies of 400 and 300 MHz, respectively, that are available round the clock for measurements at room temperature. The NMR data are acquired, processed and plotted fully automatically. 2D NMR spectra (^{1}H COSY and ^{1}H,^{13}C correlated spectra) can be run on the 400 MHz spectrometer. A high throughput is achieved by offering a limited selection of standard experiments with predefined measurement parameters that cannot be altered by the users: the number of NMR spectra measured in automatic mode rose in 2006 to almost 38,000 (^{1}H, 62%; ^{13}C, 31.5%; ^{31}P, 5.1%; ^{11}B, 1.9%).

Routine measurements. Samples requiring special treatment are measured by our operators on two further 300 and 400 MHz spectrometers. Typical applications are analyses for which the acquisition parameters need to be adjusted to optimize the spectra, measurements are required at low temperature, experiments are needed that are not available on the automatic mode, or reactions are to be followed in the NMR tube.

Special Studies are carried out on selected compounds in close cooperation with the chemical research groups. The NMR group selects the techniques most appropriate for solving the analytical problems posed by each sample, carries out the experiments on 600 and 400 MHz NMR spectrometers and interprets the results in detail. Any new analytical questions that may have arisen are addressed by further experiments.

- The main emphasis of this analytical work is the characterization of organic and organometallic compounds using a wide range of 1D and 2D NMR techniques to determine or confirm their structures, stereochemistries and conformations. Most of the samples are submitted by the groups of A. Fürstner, B. List, and M. Haenel. In addition to pentalene complexes of cobalt, other types of organometallic compounds of transition metals including Mo, Pd, Pt, Ru, and Zr have been characterized.
- Further studies of reaction mechanisms by analysis of mixtures of partially deuterated organic compounds by ^{1}H, ^{2}D and ^{13}C NMR and high resolution 2D NMR, which provide a powerful means of assigning the spectra of mixtures containing several isotopomers fully and unambiguously, have been carried out (cooperation with M. Haenel, W. Leitner).

- Nitrogen NMR data obtained from 2D $^{1}H,^{15}N$ HMBC and HSQC NMR spectra is proving to be valuable for determining the structures of nitrogen heterocycles and for the conformational analysis of cyclohexanes and other systems with nitrogen-containing substituents.

Not only have the amounts of materials available for analysis tended to become smaller, but the analytical problems themselves have tended to become more demanding, placing ever greater demands upon the sensitivity of the NMR spectrometers. Therefore, in November 2007 the 600 MHz NMR spectrometer was equipped with a cryoprobe and a new console. This increased the sensitivity of the instrument by a factor of about 8, not only allowing in many cases the full characterization of materials when the amounts are severely limited but also lowering the practical limits of powerful but less sensitive NMR experiments such as 2D-INADEQUATE and proton-detected 2D-INADEQUATE, so that these have become accessible for many more samples.

Solid State NMR spectroscopy is one of the most important techniques for the characterization of solid catalysts and other new materials synthesized in the Institute.

- In continuation of earlier work, ^{29}Si MAS and ^{13}C CP/MAS NMR has been used extensively to follow the changes occurring during the various steps of the preparation of the ready-to-use catalysts from the as-synthesized mesoporous silicas in order to optimize the whole procedure (Department of Heterogeneous Catalysis; B. Zibrowius).
- ^{29}Si MAS NMR has been used to study the effects of ion exchange on the framework of zeolites and the microporous titanosilicate ETS-10 (Department of Heterogeneous Catalysis; B. Zibrowius).
- ^{27}Al MAS NMR has been applied to follow structural changes during the dehydrogenation and rehydrogenation of alkaline earth aluminium hydrides *ex situ* (Department of Heterogeneous Catalysis; B. Zibrowius).
- Further studies of the structures and structural dynamics of organometallic compounds, in particular of five-coordinate Ni-allyl complexes, have been carried out (A. Rufińska).

Investigations carried out in cooperation with groups at universities include ^{13}C and ^{109}Ag MAS NMR of homoleptic propynyloargentates (B. Zibrowius with Prof. U. Ruschewitz, Universität zu Köln;), ^{13}C CP/MAS NMR of insoluble CO/ethylene copolymers and the dependence of their composition upon the reaction parameters (A. Rufińska with Prof. Kläui, Uni Düsseldorf) and ^{13}C CP/MAS NMR studies of the structure and molecular dynamics of Ru(II) imidazol complexes that have anti-tumour properties (A. Rufińska with A. Arion, Uni Wien).

3.5 Chemical Crystallography (C. W. Lehmann)

Introduction: The Chemical Crystallography group provides a service for solid state characterization and structure determination, and combines these service tasks with research activities in high-throughput crystallography, X-ray diffraction instrumentation and chemical crystallography. The research activities focus primarily on high resolution electron density studies, but also include developments towards new methods.

Service Activities: 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.

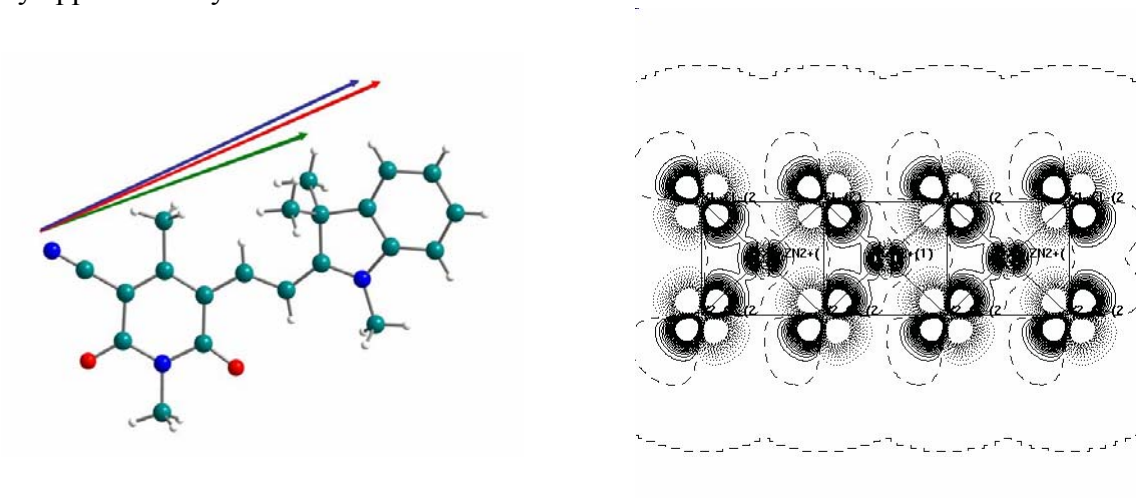
For single crystal structure analysis state-of-the-art technology is employed, comprising three area detector systems (including two 4k CCD detectors) in combination with Mo- and Cu-rotating anode X-ray generators. A broad variety of samples, ranging from inorganic via organometallic and organic to macromolecular protein crystals comprise the approximately 450 data sets collected each year. The requirement for determination of the structures of compounds from very small samples resulting from multi-step synthesis and/or preparative gas chromatography has necessitated the development of techniques for growing crystals from very small amounts of sample. One example (originating from the group of O. Trapp) is the allocation of isomers to the peaks from the HPLC by crystallization and determination crystal structures of separated samples. Small crystals (Ø < 50 μm) were measured at the ANKA synchrotron source at the Forschungszentrum Karlsruhe. It was explored whether the longer wavelengths (> 1.7 Å) available at the synchrotron together with the high intensities could be used to determine the absolute configuration of a small crystal of unknown chirality. Application of this technique was the determination of the crystal structure and of the absolute configuration of a chiral phosphine oxide from a very small crystal (Ø ca. 20 μm), which was subsequently used to allocate the enantiomeric peak obtained on a chiral column (R. Goddard in collaboration with the department of B. List).

For the routine phase identification of polycrystalline materials three powder diffractometers are available. 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. In one project (C. Weidenthaler in cooperation with K. R. Pörschke and C. Creusen) novel ionic pentacoordinate Ni^{II}-π-allyl complexes $[(\eta^3\text{-}C_3H_5)Ni(PMe_3)_3]Y$ and $[(3\text{-}C_3H_5)Ni\{P(OMe)_3\}_3]Y$ (with Y = SO_3CF_3,PF_6, Br, and I) have been synthesized and were investigated by DSC, solid-state NMR, X-ray single-crystal and *in situ* low temperature XRD. The calorimetric

measurements indicate phase transformations in the range between 100 K and the melting temperature. However, heating single crystals mostly results in decomposition into domains preventing further analysis by single crystal diffractometry. *In situ* XRD investigations allowed to identify the nature of these phase transformations in the temperature range between 100 K and 400 K. Patterns collected at 100 K correspond to the single crystal structures. Depending on the anion some of the solid-state structures transform at higher temperatures (250-350K) into highly mobile, plastically crystalline mesophases, whereas some of the compounds pass through conventional structural phase transformations .

Research Projects:

Electron Density Studies (E. Duman, R. Wang). Electron density studies of push-pull chromophores used in photo refractive and non-linear optic materials were intensified within a DFG priority program. Novel chromophores synthesized in the group of F. Würthner (Würzburg) were investigated by electro-optical absorption spectroscopy (H.-G. Kuball, Kaiserslautern) and their one electron properties studied, based on multipole least-squares refinement of high resolution diffraction data. The results (in particular molecular in-crystal dipole moments) were compared with high level *ab-initio* calculations to reveal the magnitude of dipole moment enhancements in the solid state. Together with solution based measurements the effect of the reaction field could be shown. Calculation of theoretical structure factors and subsequent application of the multipole formalism also revealed an overestimation of the in-crystal dipole moments by approximately 4 D.



Experimentally determined molecular dipole moments (red and blue) and theoretical dipole moment (green, B3LYP/D95) shown on the left, on the right deformation density in the metal-halogen plane of a Zn-Cl coordination polymer.

In cooperation with U. Englert (Aachen) the electron density distribution in metal organic coordination polymers was studied. These compounds of formal composition $[MX_2py_2]$, show a subtle balance between the nature of the divalent cation M (zinc and cadmium), the metal-bonded halides X and the halogen-functionalized pyridine ligands py. In particular those analogs based on cadmium and bromine require the use of short X-ray wavelength (~ 0.5 Å) only available at high energy synchrotrons. Through the detailed analysis of the topological properties of the electron density non-bonding halogen-halogen interactions are studied.

Hydrogen Storage Project (C. Weidenthaler, F. Schüth, M. Felderhoff). As a continuation of detailed crystallographic investigations of metal doped sodium alanate ($NaAlH_4$) (see report 2004), powder diffraction studies were extended to alkali and alkaline earth aluminum hydrides. Major focus was on the decomposition of complex alanates and the formation of intermediate compounds which were studied by means of *in situ* high temperature X-ray diffraction. This method provides helpful insights into the dehydrogenation behavior of the different alanates and gives possible explanations why the compounds cannot be reversibly rehydrogenated. The investigations revealed the formation of alloys for both, the $Mg(AlH_4)_2$ and the $Ca(AlH_4)_2$ system. The formation of aluminum-containing intermetallic compounds seems to hinder the hydrogenation of Al to AlH_3 and is therefore responsible for the irreversibility.

X-ray photoelectron spectroscopy (XPS) investigations of surface modified zeolites (C. Weidenthaler, W. Schmidt, U. Wilczok). Surface modification with alkyl chlorosilanes and methoxy silanes is a suitable method for fine-tuning of the molecular sieve properties of zeolites. The surface of large silanized MFI crystals was investigated by means of infra red (IR) and *in situ* XPS to get insight in the silanization of the surfaces and thermal stability of the surface modification. The experimental setup used for the *in situ* XPS studies allows to heat the sample in the analysis chamber and to collect spectra directly after the heating step without changing the sample position.

Publications: 7, 41, 42, 43, 44, 67, 100, 102, 109, 125, 127, 189, 190, 231, 251, 259, 260, 321, 322, 329, 359, 363, 409, 438, 443, 451, 458, 469, 470, 471, 474, 517

External Funding: DFG priority program 1178 “Experimental Electron Densities”

Cooperations: F. Würthner (Würzburg, DE), G. Punte (La Plata, AR), H. Willner (Wuppertal, DE), U. Scherf (Wuppertal, DE), U. Englert (Aachen, DE), J.-F. Carpentier (Rennes, FR), H.-G. Kuball (Kaiserslautern, DE)

3.6 Electron Microscopy (B. Tesche)

The department's activity developed along the lines indicated in the previous report. In general terms these endeavors can be classified as analytical and structural studies of supported catalysts and mesoporous materials by means of HRTEM and SEM. The work in the reporting period has addressed the structure of surfaces and isolated colloidal clusters, elemental mapping in porous supports, and the elucidation of activities of metal-supported catalysis. Optimum use of different preparation procedures and different electron microscopy techniques is needed to cover such a wide range of topics.

Selected research project: "Characterization of Catalytic Supports by means of High-Resolution TEM and SEM in Combination with Shadow-Casting and Decoration Procedures"

Introduction: For a better understanding of the support structure and the activity of heterogenous catalysts we applied electrochemical studies and high-resolution TEM and SEM investigations in combination with shadow casting and decoration procedures on Pt/C catalysts with various carbon supports. In order to study the influence of the surface structure on the preservation of the particle size and distribution, tungsten was evaporated under a flat angle on different types of carbon support. The tungsten deposited catalysts were studied by means of HRTEM (Hitachi HF 2000) and HRSEM (Hitachi S-5200). Results are summarized in HRSEM micrographs of Fig. 1.

Results: The surface roughness depends on the preparation of the carbon black supports. Vulcan XC72 (Carbot Corp.) reveals a quite smooth surface whereas Printex XE2 (Degussa) shows a rough texture. In order to prove the existence of differences in the surface roughness between the carbon blacks we carried out gold-decoration experiments, Fig 2. The smallest Au cluster and the highest particle density were achieved in case of Printex XE2.

We observed that the surface roughness influences the particle size, distribution and preservation of carbon supported Pt nanoparticles. The HRTEM studies of the various carbon blacks before and after platinum oxide loading and after electrochemical reduction to platinum confirmed the results obtained by the roughness studies: Under operating conditions, undesired sintering of Pt nanoparticles is much less pronounced in case of the Printex XE2 support, compared to the Vulcan XE72 support, because Printex XE2 has a much rougher surface (Fig. 3).

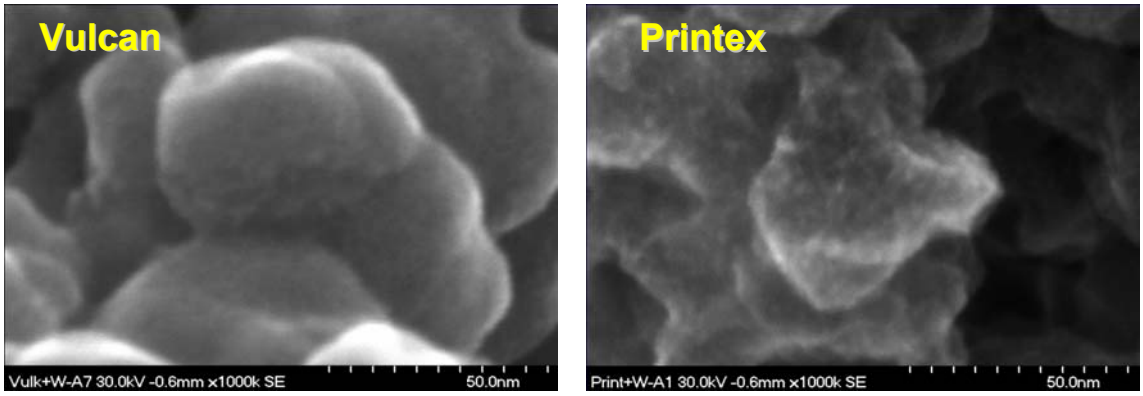


Fig. 1: HRSEM images from carbon supports Vulcan XC72 and Printex XE2 after shadow casting with tungsten.

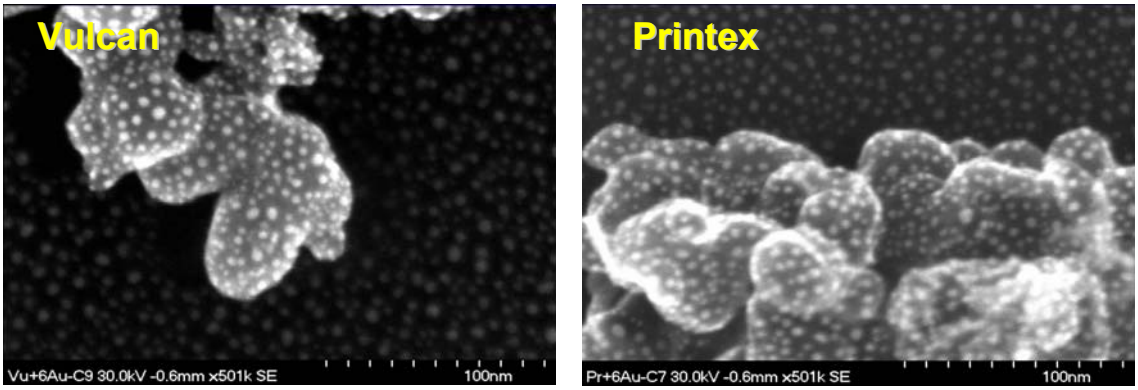


Fig. 2: HRSEM images from gold decorated carbon supports Vulcan XC72 and Printex XE2.

Fig. 3: Influence of smooth (left) and rough surface structure (right) on the fixation of particles (schematic).

Conclusion: In our investigations the Pt/Printex XE2 material proves to be the best electrocatalyst for the oxygen reduction reaction.

Publications: 130, 254, 334, 337, 338, 377, 391, 404, 405, 533

External funding: none

Cooperations: M.T. Reetz (Mülheim/Ruhr, DE); F. Schüth (Mülheim/Ruhr, DE); K. Kleinermanns (Düsseldorf, DE); H. Knözinger (München, DE); D. Gerthsen (Karlsruhe, DE); P. Albers (Degussa, Hanau, DE)

3.7 Library and Information Management (W. Richter, R. Barabasch)

The “Grundversorgung” within the Max Planck Society (see report 2002-2004) allows online access to most of the core journals which are of interest for our scientists. The financing though direct transfer from the global budget leads to a substantially lower budget of the library. A list of all relevant publishers is part of the start-up page of our institute. Generally, this service works well – except for journals from the Springer group. Since no financial agreement between the MPG and Springer Information Group was reached for 2008, Springer electronic journals are no longer covered by the “Grundversorgung”. This decision does not affect our institute much since we keep seven journals as print editions in our library.

The “Grundversorgung” 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 at a low price, since it is by no means obvious how the long-term electronic storage will work – either by the publishers themselves or by the Max-Planck-Society. In addition we subscribe several other print journals, which are not included in the “Grundversorgung” bringing the number to 95 journals. Not all scientific articles are available either in our library or within other MPG libraries, so we heavily rely on loans through the SUBITO, British Library and Chemical Abstracts Service. Consequently, our in-house book bindery was closed in early 2007.

All digital activities of the Max Planck Society are now concentrated in the so called Max Planck Digital Library (MPDL) under the leadership of Laurent Romary. The MPDL which now manages the “Grundversorgung” requires a library team like ours to mirror and select locally from the projects offered according to the needs of our scientists. So new management qualities are required from the library.

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 expanded to 75 in 2007. SciFinder enables users to run their own structural and bibliographic inquiries; the introduction to updated versions and the more intricate questions are handled by the library. The BEILSTEIN files from Elsevier are also accessible via a special licence paid by the library; from July 2007 it was included in the “Grundversorgung” as a two year test version.

Despite the large effort of publishing companies like Wiley or Elsevier to promote their e-books neither the licence 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 storage seems to be solved only for printed media. A central digital book archive is being discussed within the MPG but without clear perspectives. Printed books still are of major importance for our library, and its number is constantly growing by ~200 titles per year. However, due to a strong scientific diversification many additional books are ordered from other libraries.

Open Access to the scientific literature is a major theme in the MPDL, 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 do not support the idea of using the eDoc server as a substitute for open access, but just as the data source for the MPG Yearbook.

3.8 Computer Group (A. Koslowski)

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 the 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.

Server room: The server room in the second floor of the physics building had reached the limit of its capacity with respect to space, air conditioning, uninterruptible power supply (UPS), and load bearing of the floor. After a sufficiently large room (ca. 200 m^2 usable area supporting 2500 kg/m^2) had become available in the basement of the main laboratory building, the server room was relocated (early 2007) and the area in the physics building was turned into urgently needed office space. A modularly extensible integrated infrastructure system (InfraStruXure by APC-MGE) for cooling, UPS, management and monitoring of the servers was installed. A separate room for the installation and configuration of devices is present.

Local area network: The common hierarchically structured LAN of both Mülheim institutes was upgraded significantly with respect to bandwidth and security using HP ProCurve core components and a central CISCO ASA firewall. The lowest level of the main laboratory building (with the new server room) and the floor of the Department of Homogeneous Catalysis, the physics building (with the Department of Theory), and the MPI-BAC (Max-Planck-Institut für Bioanorganische Chemie) now share a common 10 Gbit/s backbone. The other parts of our institute are connected to the backbone with a bandwidth of 1 Gbit/s. The link to the German science network (WiN) was upgraded from 34 to 75 Mbit/s. Incoming email is scanned for viruses and undesired messages (spam) by the content scanning module in our central firewall. All computers (and other network devices) except three central servers have private IP addresses that cannot be

reached directly from outside the institute, and in addition the devices of the Department of Theory are separated in their own virtual network (VLAN).

Server computers: The IT group operates the central UNIX and Windows servers, and manages the application, compute and file servers of the Department of Theory. The central UNIX servers include four machines with Alpha architecture running the Tru64 operating system, which host the central services (external and internal logins, email dispatch and receipt, internet and intranet web pages, web cache, DNS, DHCP, RADIUS etc.). The backup system which started operation in 2005 consists of a HP-UX/Itanium backup server, a 2 TB RAID system, and a HP ESL 712e tape library with 700 slots and three LTO3 tape drives which has a maximum storage capacity of ca. 280 TB (uncompressed data). Both Mülheim institutes share a common hierarchically structured Windows Server 2003 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. Since 2006 the Department of Theory uses a Citrix application server to access Windows programs on Linux workstations. Data is stored centrally on a highly redundant EMC Celerra NS80 network attached storage (NAS) server acquired in 2007. Linux clusters with a total of 57 dual-Xeon nodes (32 bit), 20 dual-Opteron nodes, 59 quad-Opteron nodes (42 acquired since the last evaluation), and 27 eight-way Opteron systems (24 acquired in 2007) 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. 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.

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.

Research projects: The GUGA-CI module of the MNDO program is being maintained. The entire MNDO program is kept up to date concerning new developments of operating systems and compilers of supported platforms (A. Koslowski).

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 100 (cf Fig. 1 – The ratio of funding by the Institute's standard research budget and third party funds depends upon their relative contributions).

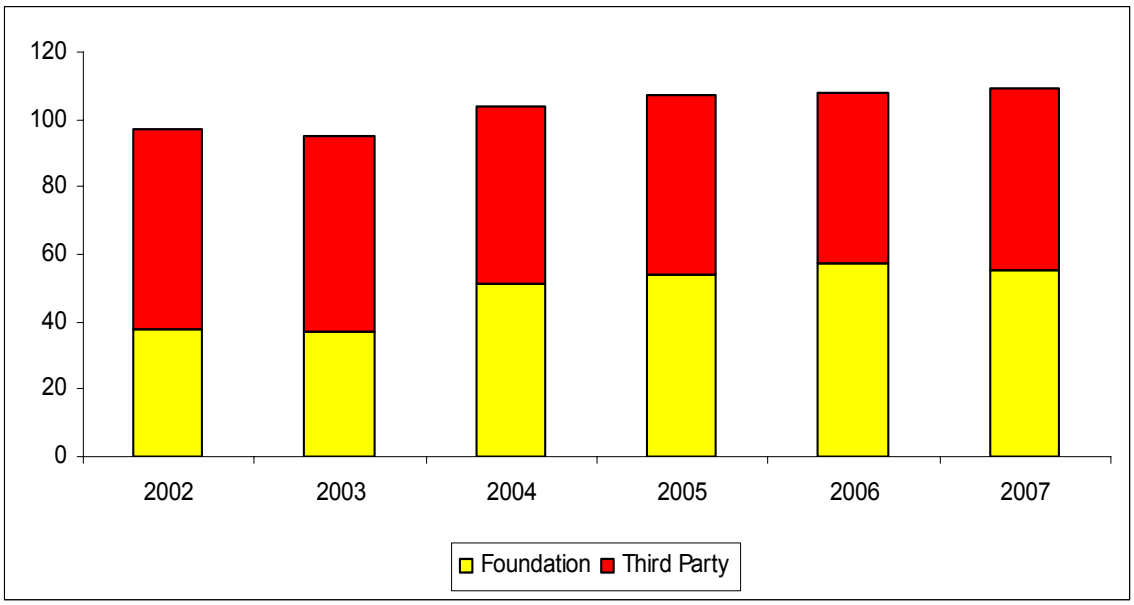


Fig. 1 Support for young scientists

The financial resources of the Institute allow for the support of 8 such positions in the group of each Scientific Member and a further position for every research group assigned to them. The remaining positions are financed by third party funds and by support grants awarded to individual scientists. During 2005 till 2007 the latter category includes 24 scholarship awardees (1 Emmy-Noether, 11 Alexander-von-Humboldt, 5 Deutscher Akademischer Austauschdienst, 1 Fulbright, 5 Kekulé, 1 Cusanus) and in addition 15 similar awards from abroad (China, Spain, Canada, Japan, Belgium, Austria, Switzerland, Denmark, Taiwan, Brasil, Egypt).

Status 31.12.2005	Total	MPG and Foundation Funds	Third Party Funds	national (n) internat. (i)	female (f) male (m)
Diploma students	1	1		1 n	1 m
PhD students	60	33	27	32 n 27 i	15 f 45 m
Post-docs	46	20	26	46 i	9 f 37 m
Status 31.12.2006					
Diploma students	3	2	1	3 n	1 f 2 m
PhD students	55	23	32	34 n 21 i	17 f 38 m
Post-docs	50	32	18	1 n 49i	11 f 39 m
Status 30.11.2007					
Diploma students	3		3	2 n	1 f 1 m
PhD students	60	26	34	39 n 21 i	18 f 42 m
Post-docs	46	29	17	46 i	7 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, Cologne, Dortmund, Duisburg/Essen, Düsseldorf, Münster, Siegen, and Wuppertal.

PhD	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**
Bochum	5	5	7	4	3	11
Dortmund	1	4	4	3	4	4
Düsseldorf		5	5	2	2	2
Aachen	1	2				1
Berlin				1	1	1
Wuppertal		1				
Frankfurt			1			
Saarbrücken		1				
Siegen			1			
Istanbul			1			
Graz			1			
Zürich		1				
Dalian (China)				1		
Total	7	19	20	11	10	19

Postdocs (country of origin)	2002	2003	2004	2005	2006	30.11.2007
Germany	1	1				
Europe	13	16	23	22	24	23
USA / Canada	1	3	5	5	3	4
Asia	13	16	20	18	20	17
Africa / Australia	1		1	1	3	2
Total	29	36	46	46	50	46

The preceding table specifies, 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 quarterly held interdisciplinary colloquia including poster sessions. The latter are open to the whole Institute and held by the young scientists themselves. The doctoral students themselves organize an internal program of lectures on catalysis to which all the group leaders from the various chemical and analytical groups contribute. Every November there is a 3-day long workshop for young scientists held by an internationally renowned scientist as part of the duties of the Ziegler Professor. The daily lectures are supplemented by discussions. Special emphasis was laid on active participation of the young scientists. Beginning in 2000 a four-semester cycle of lectures for the doctoral students and postdocs of the Institute took place, covering homogeneous and heterogeneous catalysis, organocatalysis, biocatalysis, aspects of chemical engineering, and theory. In spring 2006 the latest repetition of this lecture cycle was started. Lecturers, students and postdocs from the Institute also participate in the “Ruhr-Lehrverbund Catalysis”, which brings together the Universities of Dortmund, Bochum, Aachen, Forschungszentrum Jülich, and the Max-Planck-Institut für Kohlenforschung. 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 University 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 (SFB 558, Metal-Surface Interactions in Heterogeneous Catalysis; SFB 663, Molecular Response After Electronic Excitation) and two Max Planck

Research Initiatives (Enerchem with 5 participating MPIs; multiscale materials modeling with 7 participating MPIs).

A survey of the diploma and doctoral theses completed in the reporting period is summarized at the end of this chapter. Students finishing their doctoral studies between 2005 and 2007 had, on average, received financial support for 3.4 years and were awarded their doctorates at the age of 29.5 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 of a possible twenty-two by students from the MPI für Kohlenforschung.

During the period 2005-2007 six Junior Scientists of the Institute have received calls from universities.

Name	Year	University
Belder	2005	Regensburg
Kleitz	2005	Laval University, Canada
Hecht	2006	Humboldt University, Berlin
Hou	2006	Research Institute of Industrial Catalysis, Shanghai, VR China
Li	2006	Dalian, VR China
Bühl	2007	St. Andrews, Scotland

On the other hand, Lisbet Kvaerno from Harvard has joined the Institute in September 2007, after being selected by the Max Planck Society as a leader of an Independent Junior Research Group.

Habilitations 2006 / 2007

Hecht, S.: Design of Folding Macromolecular Architectures: Synthesis, Structural Characterization and Function. FU Berlin 2006.

Schrader, W.: Untersuchung komplexer Reaktionen mit analytischen Kopplungs-methoden. Münster 2007.

Doctoral Theses 2005

Ferrari, D.: Videomikroskopische Einzelkornanalyse der Olefinhomo- und Copolymerisation mit heterogenen Katalysatoren. Düsseldorf 2005.

Jensen, J. T.: The Total Synthesis of Latrunculin A and Latrunculin B. Dortmund 2005.

Khan, A. U. H.: Phenylene Ethynylene Foldamers: From Synthesis to Tubular Scaffolding and Photoswitchable Helices. FU Berlin 2005.

Koley, D.: Density Functional Studies of Transition-Metal Catalyzed Reactions. Düsseldorf 2005.

Kruppa, T.: Gasphasenepoxidierung von Propen mit Wasserstoffperoxid. Bochum 2005.

Maywald, M.: Methodenentwicklung zur Anwendung genetischer Optimierungsstrategien auf semisynthetische Enzyme. Bochum 2005.

Ritzkopf, I.: Kupfer-Katalysatoren für die Methanol-Dampfreformierung. Bochum 2005.

Scheiper, B.: Eisen-katalysierte Kreuzkupplungen und Synthese biologisch aktiver Naturstoffe. Dortmund 2005.

Schneider, T.: Gerichtete Evolution als Methode zur Erzeugung enantioselektiver Cyclohexanonmonooxygenasen (CHMOs) für die Katalyse von Baeyer-Villinger-Reaktionen. Bochum 2005.

Wen, F.: Nanoscopic Transition Metals – Colloidal Precursors, Networks, and Catalysts. Dalian 2005.

Wuchrer, M: Studien zur Totalsynthese von Hikizimycin. Dortmund 2005.

Doctoral Theses 2006

Altenhoff, A. G.: Ibiox – Eine neue Klasse von Carbenliganden für Kreuzkupplungen. Dortmund 2006.

Arnal, P. M.: The synthesis of monodisperse colloidal core@shell spheres and hollow particles. Bochum 2006.

Balbo Block, M. A.: Folding Architectures Containing Phenylene Ethynylene Oligomers and Polymers. FU Berlin 2006.

Bellosta von Colbe, J. M.: Hydrogen Storage in Light Metal Hydrides. Bochum 2006

Bonnekessel, M.: Eisen-katalysierte Kreuzkupplungen und Totalsynthese von Myxovirescin A. Dortmund 2006.

Hannen, P.: Metall-katalysierte Umlagerungsreaktionen. Dortmund 2006.

Jantsch, A. E.: Studien zur Totalsynthese von (-)-Papuamin. Dortmund 2006.

Otte, A.-N.: Combined Quantum Mechanical / Molecular Mechanical Investigation of Enantioselective Reactions in Lipases. Düsseldorf 2006.

Sedlatzek, F.: Übergangsmetallkomplexe mit dreizähnigen (NCP)- und (SCS)-Pincer- sowie (SNS)-Chelat-Liganden: Thermostabile homogene Palladiumkatalysatoren zur Knüpfung von C-C-Bindungen. Düsseldorf 2006.

Wang, L.-W.: Directed Evolution of the *Aspergillus niger* Epoxide Hydrolase. Bochum 2006.

Doctoral Theses 2007

Baltes, C.: Hochdurchsatz-Untersuchungen der Synthese/Struktur/Aktivitäts-Beziehungen bei $Cu/ZnO/Al_2O_3$-Katalysatoren für die Methanolsynthese. Bochum 2007.

Chernyshova, E. S.: Über M(0)-Olefin-Komplexe (M = Ni, Pd, Pt) und einkernige Palladium-Allyl-Carben-Ionenkomplexe mit schwach koordinierenden Anionen. Düsseldorf 2007.

Comotti, M.: „Nano-design“ as a Powerful Tool in Gold Catalyzed Oxidation Reactions. Bochum 2007.

Fasching, B.: Studien zur Totalsynthese von Spirastrellolide A. Dortmund 2007.

Graf, D.: Dichtefunktionalrechnungen zur homogenen Katalyse mit Übergangs-metallen: Olefinpolymerisation und asymmetrische Hydrierung. Düsseldorf 2007.

Greß, T. S. K.: Synthese von Heterocyclen und gespannten Ringen durch Gold- und Platin-katalysierte Umlagerungen. Dortmund 2007.

Kattnig, E.: Totalsynthese von Amphidinolid X und Y. Dortmund 2007.

Konjhodzic, D.: Structure and properties of mesoporous silica films for optical applications. FU Berlin 2007.

Müller, C.: Studien zur Olefinmetathese und deren Anwendung in der Synthese mittlerer Ringe. Dortmund 2007.

Muratova, N.: Highly distributed copper nanoparticles on carbon supports for methanol steam reforming. Bochum 2007.

Olejnik, S.: Entwicklung einer Anlage zur Herstellung von Metalloxiden mit hoher spezifischer Oberfläche. Bochum 2007.

Palkovits, R.: Anwendungen von geordnetem mesoporösem Siliciumdioxid in der heterogenen Katalyse. Bochum 2007.

Pelster, S. A.: Untersuchung der Festkörperbildung von Silicaten mittels Massenspektrometrie. Bochum 2007.

Prechtl, M.: Novel Ruthenium Dihydrogen Complexes and their Application in Catalysis. Aachen 2007.

Rumplecker, A.: Host-Guest Chemistry of Mesoscopically Ordered Porous Materials. Bochum 2007.

Schulz, F.: Monooxygenases – Experiments to Turn a Class of Enzymes into a Toolbox for Biocatalysis. Bochum 2007.

Stempniewicz, M.: Release Studies on Mesoporous Microcapsules for New Corrosion Protection Systems. Bochum 2007.

Streukens, G.: Thermodynamische und katalytische Eigenschaften von Titan- und Cer-dotierten komplexen Aluminiumhydriden. Bochum 2007.

Taglieber, A.: New Reactivities of Old Enzymes. Bochum 2007.

Diploma Theses 2005

Bazula, P. A.: Selective surface functionalization of ordered mesoporous carbons. FH Münster 2005.

Döring, J.: Fixierung von Aminosäuren auf porösen Siliciumdioxidträgern. FH Recklinghausen 2005.

Meudtner, R. M.: Synthese von Polypeptiden alternierender Stereochemie ausgehend von α-Oligoaminosäure-N-carboxyanhydriden. FU Berlin 2005.

Stark, A. H.: Hydriding kinetics of catalyst doped sodium alanate. Freiberg 2005.

Diploma Thesis 2006

Engels, V.: Untersuchungen zu 1,8-Dialkylphosphinoanthracen-Ruthenium-Komplexes. Düsseldorf 2006.

Diploma Theses 2007

Alfs, S.: Neue mondentate P-Liganden für die asymmetrische Übergangsmetall-Katalyse. FH Gelsenkirchen/Recklinghausen 2007.

Gobin, O. C.: High-Throughput Reactor Automatization and Multi-objective Optimization of deNOx Catalysts. TU München 2007.

Scholz, P.: Beiträge zur Rhodium katalysierten asymmetrischen Olefinhydrierung. Bochum 2007.

CHAPTER 5

Technology Transfer

5 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, the Studiengesellschaft Kohle mbH (SGK), was founded decades ago.

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 cooperations with industrial partners.

10 new patent applications in 2005, 6 in 2006 and 2 in 2007 were filed (see list of patent applications below). For 8 applications from earlier years patents were issued in 2005-2007 in Europe and USA.

License contracts exist for the electrochemical coating with aluminum and with aluminum/magnesium alloys, the production of coated chromatographic columns, the process for the production of monodispersible magnetic nanocolloides, chiral monodentate phosphorus ligands as well as ferrocene-based diphosphonites for asymmetrical catalysis, the production of chiral phophorus compounds ("Quinaphos") and their use as catalysts or catalyst components for the preparation of optically active products. The contract for the distribution of software (MassLib) developed in the Institute has been extended.

Over the period 2005-2007 12 direct cooperations with industrial partners were in operation. Such cooperative projects are partially financed by the partner, who in return is granted an option to a licence 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.

General manager ("Geschäftsführer") of the Studiengesellschaft is Professor Dr. Manfred T. Reetz. Operational functions are performed by Dr. Ruth Christophersen, a patent lawyer, who works for the Institute for about 7 days/month on a freelance contract, and who has per pro for SGK.

Patent Applications 2005

1. Verfahren zur reversiblen Speicherung von Wasserstoff
   (Bogdanović, Felderhoff, Pommerin, Schüth)

2. Method for Synthesizing Compounds
   (Schüth, Bogdanović, Felderhoff, Bellosta von Colbe)

3. Verfahren zur Entfernung von bei der Verbrennung entstehenden Verbindungen
   (Schüth, Schmidt, Schwickardi)

4. Method for the Production of Olefins from Carbonyl Compounds
   (List, Hechavarria-Fonseca, Döhring, Job)

5. Method for Decarboxylating C-C-Bond Formation of Carboxylic Acid with Carbon Electrophiles
   (Goossen, Deng)

6. Chiral Diphosphonites as Ligands in the Ruthenium-catalyzed Enantioselective Reduction of Ketones, β-Ketoesters, and Ketimines
   (Reetz, Li)

7. Chirale Phosphoramidite
   (Reetz, Mehler)

8. Verfahren zur organokatalytischen Transferhydrierung von Iminen
   (List, Hoffmann)

9. Analyse von Stoffgemischen
   (Trapp)

10. Verfahren zur Herstellung von α,β-ungesättigten Carbonsäurederivaten
    (List, Ozores Viturro, Rios Torres, Rodefeld)

Patent Applications 2006

1. Organische Salze sowie Verfahren zur Herstellung von chiralen organischen Verbindungen
   (List, Mayer)

2. Verfahren zur Herstellung von N-Acyl-α-Aminonitrilen
   (List, Pan)

3. Verfahren zur Herstellung von chiralen Aminocarbonylverbindungen
   (List, Yang, Stadler)

4. Lösungsmittelfreie Hydrierung/Hydrogenolyse von hochinkohlten Steinkohlen mit Boran- und Jod-Katalysatoren
   (Haenel, Rufinska, Richter)

5. Microfluidische Glas-Chips mit monolithischem Elektrospray-Emitter für die Chips-MS Kopplung
   (Belder, Schulze, Häusig, Hoffmann)

6. Photoschaltbare Katalysatoren
   (Hecht, Peters, Stoll)

Patent Applications 2007

1. Iejimalides Analogues and Uses thereof
   (Fürstner, Nevado, Waser, Moulin, Aïssa)

2. Process for the Synthesis of 3,6-Dihydro-1,3,5-Triazine Derivatives for the Treatment of Disorders Associated with Insulin-Resistance Syndrom
   (List)

CHAPTER 6

Appendices

6.1 List of Publications 2005 - 2007

2005

1. *Abuhamdah, S., A. Fürstner, G. Lees and P.L. Chazot:* Radioligand binding studies of caloporoside and novel congeners with contrasting effects upon [^{35}S] TBPS binding to the mammalian $GABA_A$ receptor. Biochem. Pharmacol. **70**, 1382-1388 (2005).

2. *Alberti, D., R. Goddard and K.-R. Pörschke:* Dinuclear [{(π-C_3H_5)M(PR_3)}$_2$(μ-X]Y Complexes of Nickel and Palladium. Organometallics **24**, 3907-3915 (2005).

3. *Alfredsson, V., H. Amenitsch, K. Flodstrom, M. Lindén, C.V. Teixeira and H. Wennerstrom:* In-situ studies of the formation mechanism of SBA-15. In: Nanoporous Materials IV. (Eds.) A. Sayari, M. Jaroniec. Stud. Surf. Sci. Catal. **156**, 69-74 (2005).

4. *Alfredsson, V., H. Amenitsch, F. Kleitz, M. Lindén, P. Linton and C.V. Teixeira:* Formation mechanism of mesoporous silica formed with triblock copolymers; effect of salt addition. In: Molecular Sieves: From Basic Research to Industrial Applications. (Ed.) J. Cejka. Stud. Surf. Sci. Catal. **158**, 97-104 (2005).

5. *Altun, A. and W. Thiel:* Combined Quantum Mechanical/Molecular Mechanical Study on the Pentacoordinated Ferric and Ferrous Cytochrome $P450_{cam}$ Complexes. J. Phys. Chem. B **109**, 1268-1280 (2005).

6. *Andersson, J., S. Areva, B. Spliethoff and M. Lindén:* Sol-gel synthesis of a multifunctional, hierarchically porous silica/apatite composite. Biomaterials **26**, 6827-6835 (2005).

7. *Balaban, T.S., M. Linke-Schaetzel, A.D. Bhise, N. Vanthuyne, C. Roussel, C.E. Anson, G. Buth, A. Eichhöfer, K. Foster, G. Garab, H. Gliemann, R. Goddard, T. Javorfi, A.K. Powell, H. Rösner and T. Schimmel:* Structural Characterization of Artificial Self-Assembling Porphyrins That Mimic the Natural Chlorosomal Bacteriochlorophylls *c, d,* and *e.* Chem.-Eur. J. **11**, 2267-2275 (2005).

8. *Balbo Block, M.A. and S. Hecht:* Umwickeln von Peptidröhren – Konvergenz von biologischer Selbstorganisation und Polymersynthese. Angew. Chem. **117**, 7146-7149 (2005); Angew. Chem. Int. Ed. **44**, 6986-6989 (2005).

9. *Balbo Block, M.A., C. Kaiser, A. Khan and S. Hecht:* Discrete Organic Nanotubes Based on a Combination of Covalent and Non-Covalent Approaches. In: Functional Molecular Nanostructures. (Ed.) A.D. Schlüter. Top. Curr. Chem. **245**, 89-150 (2005)

10. *Bandyopadhyay, M., A. Birkner, M.W.E. van den Berg, K.V. Klementiev, W. Schmidt, W. Grünert and H. Gies:* Synthesis and characterization of mesoporous MCM-48 containing TiO_2 nanoparticles. Chem. Mater. **17**, 3820-3829 (2005).

11. *Belder, D.:* Mikrofluidik mit Tröpfchen. Angew. Chem. **117**, 3587-3588 (2005); Angew. Chem. Int. Ed. **44**, 3521-3522 (2005).

12. *Belder, D.:* Auf dem Weg zum Chip-Labor. Jahrb. MPG (Tätigkeitsbericht des MPI für Kohlenforschung) **2005**, 321-325.

13. *Bellosta von Colbe, J.M., M. Felderhoff, B. Bogdanović, F. Schüth and C. Weidenthaler:* One-step direct synthesis of a Ti-doped sodium alanate hydrogen storage material. Chem. Commun. (Cambridge, U. K.) **2005**, 4732-4734.

14. *Bernsmann, H., M. van den Berg, R. Hoen, A.J. Minnaard, G. Mehler, M.T. Reetz, J.G. De Vries and B.L. Feringa:* PipPhos and MorfPhos: Privileged Monodentate Phosphoramidite Ligands for Rhodium-Catalyzed Asymmetric Hydrogenation. J. Org. Chem. **70**, 943-951 (2005).

15. *Beşev, M., C. Brehm and A. Fürstner:* Formal Total Syntheses of Crocacin A-D. Collect. Czech. Chem. Commun. **70**, 1696-1708 (2005).

16. *Bhriain, N.N., H.-H. Brintzinger, D. Ruchatz and G. Fink:* Polymeryl Exchange between *ansa*-Zirconocene Catalysts for Norbornene–Ethene Copolymerization and Aluminum or Zinc Alkyls. Macromolecules **38**, 2056-2063 (2005).

17. *Bocola, M., F. Schulz, F. Leca, A. Vogel, M.W. Fraaije and M.T. Reetz:* Converting Phenylacetone Monooxgenase into Phenylcyclohexanone Monooxygenase by Rational Design: Towards Practical Baeyer-Villinge Monooxygenases. Adv. Synth. Catal. **347**, 979-986 (2005).

18. *Böing, C., G. Franciò and W. Leitner:* Nickel catalysed asymmetric cycloisomerisation of diethyl diallylmalonate. Chem. Commun. (Cambridge, U. K.) **2005**, 1456-1458.

19. *Böing, C., G. Franciò and W. Leitner:* Cationic Nickel Complexes with Weakly Coordinating Counterions and Their Application in the Asymmetric Cycloisomerisation of 1,6-Dienes. Adv. Synth. Catal. **347**, 1537-1541 (2005).

20. *Bönnemann, H., S.S. Botha, B. Bladergroen and V.M. Linkov:* Monodisperse copper- and silver-nanocolloids suitable for heat-conductive fluids. Appl. Organomet. Chem. **19**, 768-773 (2005).

21. *Bönnemann, H., R.A. Brand, W. Brijoux, H.-W. Hofstadt, M. Frerichs, V. Kempter, W. Maus-Friedrichs, N. Matoussevitch, K.S. Nagabhushana, F. Voigt and V. Caps:* Air stable Fe and Fe-Co magnetic fluids – synthesis and characterization. Appl. Organomet. Chem. **19**, 790-796 (2005).

22. *Boukis, N., U. Galla, H. Bönnemann u. E. Dinjus:* Vergasung organischer Substanzen in überkritischem Wasser. Nasse Biomasse liefert Energie für Brennstoffzellen. H_2 Tec August, 14-16 (2005).

23. *Brendebach, B., S. Bucher, J. Hormes, H. Bönnemann, K.S. Nagabhushana, R. Brinkmann and H. Modrow: In-Situ* X-Ray Absorption Near Edge Structure (Xanes) Spectroscopy of PtRu Colloid Catalysts at Operating Temperature. Phys. Scr. **115**, 773-775 (2005).

24. *Bühl, M.:* Molecular Dynamic of a Vanadate-Dipeptide Complex in Aqueous Solution. Inorg. Chem. **44**, 6277-6283 (2005).

25. *Bühl, M., A. Chaumont, R. Schurhammer and G. Wipff:* Ab Initio Molecular Dynamics of Liquid 1,3-Dimethylimidazolium Chloride. J. Phys. Chem. B **109**, 18591-18599 (2005).

26. *Bühl, M., R. Diss and G. Wipff:* Coordination Environment of Aqueous Uranyl(VI) Ion. J. Am. Chem. Soc. **127**, 13506-13507 (2005).

27. *Bühl, M. and S. Grigoleit:* Molecular Dynamics of Neutral and Protonated Ferrocene. Organometallics **24**, 1516-1527 (2005).

28. *Bühl, M., D. Hnyk and J. Macháček:* Computational Study of Structures and Properties of Metallaboranes: Cobalt Bis(dicarbollide). Chem.-Eur. J. **11**, 4109-4120 (2005).

29. *Burgemeister, K., G. Franciò, H. Hugl and W. Leitner:* Enantioselective hydrogenation of polar substrates in inverted supercritical CO_2/aqueous biphasic media. Chem. Commun. (Cambridge, U. K.) **2005**, 6026-6028.

30. *Burk, S., G. Franciò and W. Leitner:* Ruthenium-catalysed asymmetric hydrogenation of ketones using QUINAPHOS as the ligand. Chem. Commun. (Cambridge, U. K.) **2005**, 3460-3462.

31. *Burstein, C., C.W. Lehmann and F. Glorius:* Imidazol[1,5-*a*]pyridine-3-ylides—derived N-heterocyclic carbene ligands. Tetrahedron **61**, 6207-6217 (2005).

32. *Canè, E., G. Di Lonardo, L. Fusina, W. Jerzembeck, H. Bürger, J. Breidung and W. Thiel:* The Rotation Spectrum and Infrared Fundamental Bands of $^{123}SbD_3$. Determination of the Molecular Geometry, and *Ab Initio* Calculations of Spectroscopic Parameters. Mol. Phys. **103**, 557-577 (2005).

33. *Derat, E., S. Cohen, S. Shaik, A. Altun and W. Thiel:* Principal Active Species of Horseradish Peroxidase, Compound I: A Hybrid Quantum Mechanical/Molecular Mechanical Study. J. Am. Chem. Soc. **127**, 13611-13621 (2005).

34. *Dichtel, W.R., S. Hecht and J.M.J. Fréchet:* Functionally Layered Dendrimers: A New Building Block and Its Application to the Synthesis of Multichromophoric Light-Harvesting Systems. Org. Lett. **7**, 4451-4454 (2005).

35. *Ding, Y., R. Goddard and K.-R. Pörschke:* Cationic Dinuclear Pd-Allyl-Halide Complexes with N-Heterocyclic Carbenes. Organometallics **24**, 439-445 (2005).

36. *Eggert, T., S.A. Funke, N.M. Rao, P. Acharya, H. Krumm, M.T. Reetz and K.-E. Jaeger:* Multiplex-PCR-Based Recombination as a Novel High-Fidelity Method for Directed Evolution. ChemBioChem **6**, 1062-1067 (2005).

37. *Farrusseng, D., C. Klanner, L. Baumes, M. Lengliz, C. Mirodatos and F. Schüth:* Design of Discovery Libraries for Solids Based on QSAR Models. QSAR-Comb. Sci. **24**, 78-93 (2005).

38. *Fenster, M.D.B. and G.R. Dake:* An Asymmetric Formal Synthesis of Fasicularin. Chem.-Eur. J. **11**, 639-649 (2005).

39. *Ferrari, D. and G. Fink:* Video Microscopy for the Investigation of Gas Phase Copolymerization. Macromol. Mater. Eng. **290**, 1125-1136 (2005).

40. *Fink, G., C. Karafilidis, K. Angermund, G. Breitenbruch, B. Gabor, H. Hermann, W. Joppek, R.J. Mynott, A. Rufińska, J. Rust and W. Thiel:* Metallocenkatalysierte C7-Verknüpfung bei der Hydrooligomerisierung von Norbornen durch σ-Bindungs-Metathese: Endlich Einblick in die Mikrostruktur von Polynorbornen. Macromol. Rapid Commun. **26**, F45-F46 (2005).

41. *Finze, M., E. Bernhardt, H. Willner and C.W. Lehmann:* Haloacyl Complexes of Boron, $[(CF_3)_3BC(O)Hal]^-$ (Hal=F, Cl, Br, I). Chem.-Eur. J. **11**, 6653-6665 (2005).

42. *Finze, M., E. Bernhardt, H. Willner and C.W. Lehmann:* Cyano- and Isocyanotris(trifluoromethyl)borates: Syntheses, Spectroscopic Properties, and Solid State Structures of $K[(CF_3)_3BCH]$ and $K[(CF_3)_3BNC]$. J. Am. Chem. Soc. **127**, 10712-10722 (2005).

43. *Finze, M., E. Bernhardt, H. Willner, C.W. Lehmann and F. Aubke:* Homoleptic, σ-Bonded Octahedral Superelectrophilic Metal Carbonyl Cations of Iron(II), Ruthenium(II), and Osmium(II). Part 2: Synthesis and Characterizations of $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, OS). Inorg. Chem. **44**, 4206-4212 (2005).

44. *Flanagan, S.P., R. Goddard and P.J. Guiry:* The preparation and resolution of 2-(2-pyridyl)- and 2-(2-pyrazinyl)-Quinazolinap and their application in palladium-catalysed allylic substitution. Tetrahedron **61**, 9808-9821 (2005).

45. *Fu, A., H. Li, D. Du and Z. Zhou:* Density Functional Study on the Reaction Mechanism of Proton Transfer in 2-Pyridone: Effect of Hydration and Self-Association. J. Phys. Chem. A **109**, 1468-1477 (2005).

46. *Fürstner, A.:* Reflections upon Olefin Metathesis in Carbohydrate Chemistry. In: Glycomimetics: Modern Synthetic Methodologies. (Ed.) R. Roy. ACS Symp. Ser. **896**, 1-22 (2005).

47. *Fürstner, A. and P.W. Davies:* Alkyne metathesis. Chem. Commun. (Cambridge, U. K.) **2005**, 2307-2320.

48. *Fürstner, A. and P.W. Davies:* Heterocycles by $PtCl_2$-Catalyzed Intramolecular Carboalkoxylation or Carboamination of Alkynes. J. Am. Chem. Soc. **127**, 15024-15025 (2005).

49. *Fürstner, A., P.W. Davies and T. Gress:* Cyclobutenes by Platinum-Catalyzed Cycloisomerization Reactions of Enynes. J. Am. Chem. Soc. **127**, 8244-8245 (2005).

50. *Fürstner, A., P.W. Davies and C.W. Lehmann:* Bidentate Ruthenium Vinylcarbene Catalysts Derived from Enyne Metathesis. Organometallics **24**, 4065-4071 (2005).

51. *Fürstner, A., M.M. Domostoj and B. Scheiper:* Total Synthesis of Dictyodendrin B. J. Am. Chem. Soc. **127**, 11620-11621 (2005).

52. *Fürstner, A., D. Kirk, M.D.B. Fenster, C. Aïssa, D. De Souza and O. Müller:* Diverted total synthesis: Preparation of a focused library of latrunculin analogues and evaluation of their actin-binding properties. Proc. Natl. Acad. Sci. USA **102**, 8103-8108 (2005).

53. *Fürstner, A., A. Leitner and G. Seidel:* 4-Nonylbenzoic Acid. Org. Synth. **81**, 33-41 (2005).

54. *Fürstner, A. and R. Martin:* Advances in Iron Catalyzed Cross Coupling Reactions. Chem. Lett. **34**, 624-629 (2005).

55. *Fürstner, A., R. Martin and K. Majima:* Cycloisomerization of Enynes Catalyzed by Iron(0)–Ate Complexes. J. Am. Chem. Soc. **127**, 12236-12237 (2005).

56. *Fürstner, A. and C. Müller:* Total synthesis of aspercyclide C. Chem. Commun. (Cambridge, U. K.) **2005**, 5583-5585.

57. *Fürstner, A., K. Radkowski and H. Peters:* Chasing a Phantom by Total Synthesis: The Butylcycloheptylprodigiosin Case. Angew. Chem. **117**, 2837-2841 (2005); Angew. Chem. Int. Ed. 44, 2777-2781 (2005).

58. *Fürstner, A. and L. Turet:* Concise and Practical Synthesis of Latrunculin A by Ring-Closing Enyne-Yne Metathesis. Angew. Chem. **117**, 3528-3532 (2005); Angew. Chem. Int. Ed. **44**, 3462-3466 (2005).

59. *Funke, S.A., N. Otte, T. Eggert, M. Bocola, K.-E. Jaeger and W. Thiel:* Combination of Computational Prescreening and Experimental Library Construction can Accelerate Enzyme Optimization by Directed Evolution. Protein Eng. Des. Sel. **18**, 509-514 (2005).

60. *Ghalit, N., A.J. Poot, A. Fürstner, D.T.S. Rijkers and R.M.J. Liskamp:* Ring-Closing Alkyne Metathesis Approach toward the Synthesis of Alkyne Mimics of Thioether A-, B-, C-, and DE-Ring Systems of the Lantibiotic Nisin Z. Org. Lett. **7**, 2961-2964 (2005).

61. *Gooßen, L.J. and M.K. Dezfuli:* Practical Protocol for the Palladium-Catalyzed Synthesis of Arylphosphonates from Bromoarenes and Diethyl Phosphite. Synlett **2005**, 445-448.

62. *Gooßen, L.J., D. Koley, H.L. Hermann and W. Thiel:* Mechanistic Pathways for Oxidative Addition of Aryl Halides to Palladium(0) Complexes: A DFT Study. Organometallics **24**, 2398-2410 (2005).

63. *Gooßen, L.J., D. Koley, H.L. Hermann and W. Thiel:* The Palladium-Catalyzed Cross-Coupling Reaction of Carboxylic Anhydrides with Arylboronic Acids: A DFT Study. J. Am. Chem.. Soc. **127**, 11102-11114 (2005).

64. *Gooßen, L.J., J. Paetzold, O. Briel, A. Rivas-Nass, R. Karch and B. Kayser:* Buchwald-Hartwig Aminations of Aryl Chlorides: A Practical Protocol Based on Commercially Available Pd(0)-NHC Catalysts. Synlett **2005**, 275-278.

65. *Gooßen, L.J., J.E. Rauhaus and G. Deng:* Ru-Catalyzed Anti-Markovnikov Addition of Amides to Alkynes: A Regio- and Stereoselective Synthesis of Enamides. Angew. Chem. **117**, 4110-4113 (2005); Angew. Chem. Int. Ed. **44**, 4042-4045 (2005).

66. *Gregersen, B.A., J. Khandogin, W. Thiel and D.M. York:* Smooth Solvation Method for d-Orbital Semiempirical Calculations of Biological Reactions. 2. Application to Transphosphorylation Thio Effects in Solution. J. Phys. Chem. B **109**, 9810-9817 (2005).

67. *Grevels, F.-W., J. Jacke, R. Goddard, C.W. Lehmann, S. Özkar and S. Saldamli:* Bis(trimethylsilyl)ethyne as a Two-Electron Alkyne Ligand in Group 6 Carbonylmetal(0) Complexes: Photochemical Syntheses and Comprehensive

Characterization of $M(CO)_5(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (M = W, Mo, Cr) and *trans*-$Mo(CO)_4(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)_2$. Organometallics **24**, 4613-4623 (2005).

68. *Grigoleit, S. and M. Bühl:* Computational ^{59}Co NMR Spectroscopy: Beyond Static Molecules. J. Chem. Theory Comput. **1**, 181-193 (2005).

69. *Grunwaldt, J.D., C. Kiener, F. Schüth and A. Baiker:* X-ray Absorption Spectroscopy on CuZnO Catalysts Selected by High Throughput Experimentation Techniques. Phys. Scr. **115**, 819-822 (2005).

70. *Hashimoto, S., M. Saitoh, N. Taira, W. Schmidt, K. Hirai and H. Tomioka:* Emission Spectroscopic Investigation of Triplet Diarylcarbene Generated in Molecular Sieve VPI-5. J. Phys. Chem. B **109**, 20407-20414 (2005).

71. *Hecht, S.:* Construction with macromolecules. Mater. Today **8**, (3) 48-55 (2005).

72. *Hecht, S.:* Optical Switching of Hierarchical Self-Assembly: Towards "Enlightened" Materials. Small **1**, 26-29 (2005).

73. *Hirao, H., D. Kumar, W. Thiel and S. Shaik:* Two States and Two More in the Mechanisms of Hydroxylation and Epoxidation by Cytochrome P450. J. Am. Chem. Soc. **127**, 13007-13018 (2005).

74. *Hoffmann, S., A.M. Seayad and B. List:* A Powerful Brønsted Acid Catalyst for the Organocatalytic Aymmetric Transfer Hydrogenation of Imines. Angew. Chem. **117**, 7590-7593 (2005); Angew. Chem. Int. Ed. **44**, 7424-7427 (2005).

75. *Hollmann, F., K. Hofstetter, T. Habicher, B. Hauer and A. Schmid:* Direct Electrochemical Regeneration of Monooxygenase Subunits for Biocatalytic Asymmetric Epoxidation. J. Am. Chem. Soc. **127**, 6540-6541 (2005).

76. *Hormes, J., H. Modrow, H. Bönnemann and C.S.S.R. Kumar:* The influence of various coatings on the elecronic, magnetic, and geometric properties of cobalt nanoparticles (invited). J. App. Phys. **97**, 10R102 (2005).

77. *Hou, Z., N. Theyssen, A. Brinkmann and W. Leitner:* Biphasic Aerobic Oxidation of Alcohols Catalyzed by Poly(ethylene glycol)-Stabilized Palladium Nanoparticles in Supercritical Carbon Dioxide. Angew. Chem. **117**, 1370-1373 (2005); Angew. Chem. Int. Ed. **44**, 1346-1349 (2005)

78. *Huang, S., Z. Xiao, F. Wang, J. Zhou, G. Yuan, S. Zhang, Z. Chen, W. Thiel, P. von Rague Schleyer, X. Zhang, X. Hu, B. Chen and L. Gan:* Preparation of [5,6] and [6,6] Oxa-homofullerene Derivates and their Interconversion through Lewis Acid Assisted Reactions of Fullerene-mixed Peroxides. Chem.-Eur. J. **11**, 5449-5456 (2005).

79. *Hussain, Z., D. Koley and H. Hopf:* Synthesis and Stereochemical Aspects of Ethyl 1,1a2,3,4,5,6,6a-Octahydro-4-octylcyclopropa[*f*]indene-1-carboxylate. Helv. Chim. Acta **88**, 3263-3273 (2005).

80. *Jang, Y.-J., K. Bieber, C. Naundorf, N. Nenov, M. Klapper, K. Müllen, D. Ferrari, S. Knoke and G. Fink:* Optical methods to study the behaviour of supported metallocene catalysts during olefin polymerisation. E-Polymers **2005**, No. 13, 1-13 (http://www.e-polymers.org).

81. *Jensen, V.R., M. Graf and W. Thiel:* Unusual Temperature Effects in Propene Polymerization Using Stereorigid Zirconocene Catalysts. ChemPhysChem **6**, 1929-1933 (2005).

82. *Jensen, V.R.; D. Koley, M.N. Jagadeesh and W. Thiel:* DFT Investigation of the Single-Center, Two-State Model for the Broken Rate Order of Transition Metal Catalyzed Olefin Polymerization. Macromolecules **38**, 10266-10278 (2005).

83. *Kästner, J., S. Hemmen and P.E. Blöchl:* Activation and protonation of dinitrogen at the FeMo cofactor of nitrogenase. J. Chem. Phys. **123**, 074306-1-8 (2005).

84. *Kästner, J. and W. Thiel:* Bridging the gap between thermodynamic integration and umbrella sampling provides a novel analysis method: "Umbrella integration". J. Chem. Phys. **123**, 144104/1-5 (2005).

85. *Kaskel, S., G. Chaplais and K. Schlichte:* Synthesis, Characterization, and Catalytic Properties of High-Surface-Area Aluminum Silicon Nitride Based Materials. Chem. Mater. **17**, 181-185 (2005).

86. *Khan, A. and S. Hecht:* Photocontrolling the helix-coil transition: azobenzene-containing foldamers. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **46**, 161 (2005).

87. *Khan, A., S. Müller and S. Hecht:* Practical Synthesis of an amphiphilic, non-ionic poly(*para*)phenyleneethynylene) derivative with a remarkable quantum yield in water. Chem. Commun. (Cambridge, U. K.) **2005**, 584-586.

88. *Khandogin, J., B.A. Gregersen, W. Thiel and D.M. York:* Smooth Solvation Method for d-Orbital Semiempirical Calculations of Biological Reactions. 1. Implementation. J. Phys. Chem. B **109**, 9799-9809 (2005).

89. *Kimmel, J.R., O.K. Yoon, I.A. Zuleta, O. Trapp and R.N. Zare:* Peak Height Precision in Hadamard Transform Time-of-Flight Mass Spectra. J. Am. Soc. Mass Spectrom. **16**, 1117-1130 (2005).

90. *Kinge, S. and H. Bönnemann:* Optimization of colloidal nanoparticle synthesis via $NR_4(BEt_3H)$ reduction. Appl. Organomet. Chem. **19**, 750-758 (2005).

91. *Kirchhoff, M., U. Specht and G. Veser:* Engineering high-temperature stable nanocomposite materials. Nanotechnol. **16**, S401-S408 (2005).

92. *Koch, O., M. Bocola and G. Klebe:* Cooperative Effects in Hydrogen-Bonding of Protein Secondary Structure Elements: A Systematic Analysis of Crystal Data Using Secbase. Proteins: Struct., Funct., Bioinf. **61**, 310-317 (2005).

93. *Konjhodzic, D., H. Bretinger, U. Wilczok, A. Dreier, A. Ladenburger, M. Schmidt, M. Eich and F. Marlow:* Low-*n* mesoporous silica films: structure and properties. Appl. Phys. A **81**, 425-432 (2005).

94. *Kornatowski, J.:* Expressiveness of Adsorption Measurements for Characterization of Zeolitic Materials—A Review. Adsorption **11**, 275-293 (2005).

95. *Kornatowski, J.:* Adsorption isotherms of water as a tool for characterization of metal substituted aluminophosphate molecular sieves. C. R. Chim. **8**, 561-568 (2005).

96. *Kornatowski, J.:* Relationship between adsorption properties, synthesis conditions, and morphology of the AFI type crystals. In: Molecular Sieves: From Basic Research to Industrial Applications. (Ed.) J. Cejka. Stud. Surf. Sci. Catal. **158**, 303-310 (2005)

97. *Kornatowski, J., J.O. Barth and J.A. Lercher:* New modifications of layered MCM-36 molecular sieve pillared with various mixed oxides: facts and perspectives. In: Nanoporous Materials IV. (Eds.) A. Sayari, M. Jaroniec. Stud. Surf. Sci. Catal. **156**, 349-356 (2005).

98. *Kremzow, D., G. Seidel, C.W. Lehmann and A. Fürstner:* Diaminocarbene- and Fischer-Carbene Complexes of Palladium and Nickel by Oxidative Insertion: Preparation, Structure, and Catalytic Activity. Chem.-Eur. J. **11**, 1833-1853 (2005).

99. *Kubanek, P., H.-W. Schmidt, B. Spliethoff and F. Schüth:* Parallel IR spectroscopic characterization of CO chemisorption on Pt loaded zeolites. Microporous Mesoporous Mater. **77**, 89-96 (2005).

100. *Kubik, S., R. Goddard, S. Otto, S. Pohl, C. Reyheller and S. Stüwe:* Optimization of the binding properties of a synthetic anion receptor using rational and combinatorial strategies. Biosens. Bioelectron. **20**, 2364-2375 (2005).

101. *Kumar, D., H. Hirao, S.P. de Visser, J. Zheng, D. Wang, W. Thiel and S. Shaik:* New Features in the Catalytic Cycle of Cytochrome P450 during the Formation of Compound I from Compound 0. J. Phys. Chem. B **109**, 19946-19951 (2005).

102. *Lavanant, L., L. Toupet, C.W. Lehmann and J.-F. Carpentier:* Group 4 Metal Complexes of Nitrogen-Bridged Dialkoxide Ligands: Synthesis, Structure, and Polymerization Activity Studies. Organometallics **24**, 5620-5633 (2005).

103. *Li, H.-L., W. Dong, H.-J. Bongard and F. Marlow:* Improved Controllability of Opal Film Growth Using Capillaries for the Deposition Process. J. Phys. Chem. B **109**, 9939-9945 (2005).

104. *Li, H.-L. and F. Marlow:* Controlled Arrangement of Colloidal Crystal Strips. Chem. Mater. **17**, 3809-3811 (2005); featured in: MRS Bull. **30**, 632 (2005).

105. *Li, W.-C., A.-H. Lu, R. Palkovits, W. Schmidt, B. Spliethoff and F. Schüth:* Hierarchically Structures Monolithic Silicalite-1 Consisting of Crystallized Nanoparticles and Its Performance in the Beckmann Rearrangement of Cyclohexanone Oxime. J. Am. Chem. Soc. **127**, 12595-12600 (2005).

106. *Li, W.-C., A.-H. Lu, W. Schmidt and F. Schüth:* High Surface Area, Mesoporous, Glassy Alumina with a Controllable Pore Size by Nanocasting from Carbon Aerogels. Chem.-Eur. J. **11**, 1658-1664 (2005).

107. *Li, W.-C., A.-H. Lu and F. Schüth:* Preparation of Monolithic Carbon Aerogels and Investigation of Their Pore Interconnectivity by a Nanocasting Pathway. Chem. Mater. **17**, 3620-3626 (2005).

108. *Li, W.-C., A.-H. Lu, C. Weidenthaler, R. Godard, H.-J. Bongard and F. Schüth:* Growth of single crystal α-Al_2O_3 nanofibers on a carbon aerogel substrate. J. Mater. Chem. **15**, 2993-2996 (2005).

109. *Lian, B., C.W. Lehmann, C. Navarro and J.-F. Carpentier:* Model Studies of Methacrylate Chain Transfer Polymerization Mediated by Cationic Zirconocene *tert*-Butyl Enolate. Organometallics **24**, 2466-2472 (2005).

110. *List, B., A. Döhring, M.T. Hechavarria Fonseca, K. Wobser, H. van Thienen, R. Rios Torres and P. Llamas Galilea:* Practical Synthesis of (*E*)-α,β-Unsaturated Esters from Aldehydes. Adv. Synth. Catal. **347**, 1558-1560 (2005).

111. *Lu, A.-H., W.-C. Li, N. Matoussevitch, B. Spliethoff, H. Bönnemann and F. Schüth:* Highly stable carbon-protected cobalt nanoparticles and graphite shells. Chem. Commun. (Cambridge, U. K.) **2005,** 98-100.

112. *Lu, A.-H., W.-C. Li, N. Muratova, B. Spliethoff and F. Schüth:* Evidence for C-C bond cleavage by H_2O_2 in a mesoporous CMK-5 type carbon at room temperature. Chem. Commun. (Cambridge, U. K.) **2005**, 5184-5186.

113. *Lu, A.-H., W.-C. Li, W. Schmidt and F. Schüth:* Template synthesis of large pore ordered mesoporous carbon. Microporous Mesoporous Mater. **80**, 117-128 (2005).

114. *Lu, A.-H., W. Schmidt, W. Kiefer and F. Schüth:* High surface area mesoporous SiC synthesized via nanocasting and carbothermal reduction process. J. Mater Sci. **40**, 5091-5093 (2005).

115. *Lu, A.-H., W. Schmidt, S. Tatar, B. Spliethoff, J. Popp, W. Kiefer and F. Schüth:* Formation of amorphous carbon nanotubes on ordered mesoporous silica support. Carbon **43**, 1811-1814 (2005).

116. *Lu, A.-H. and F. Schüth:* Nanocasting pathways to create ordered mesoporous solids. C. R. Chim. **8**, 609-620 (2005).

117. *Lu, A.-H., J.-H. Smått and M. Lindén:* Combined Surface and Volume Templating of Highly Porous Nanocast Carbon Monoliths. Adv. Funct. Mater. **15**, 865-871 (2005).

118. *Manger, M., M. Scheck, H. Prinz, J.P. von Kries, T. Langer, K. Saxena, H. Schwalbe, A. Fürstner, J. Rademann and H. Waldmann:* Discovery of Mycobacterium Tuberculosis Protein Tyrosine Phosphatase A (MptpA) Inhibitors Based on Natural Products and a Fragment-Based Approach. ChemBioChem **6**, 1749-1753 (2005).

119. *Marlow, F., F. Kleitz, U. Wilczok, W. Schmidt and I. Leike:* Texture Effects of Circularly Ordered Fibers. ChemPhysChem **6**, 1269-1275 (2005).

120. *Marlow, D. Konjhodzic, H. Bretinger and H. Li:* Sol-Gel Approaches to Photonic Crystal Systems. Adv. Solid State Phys. **45**, 149-160 (2005).

121. *Mayr, M., D. Wang, R. Kröll, N. Schuler, S. Prühs, A. Fürstner and M.R. Buchmeiser:* Monolithic Disk-Supported Metathesis Catalysts for Use in Combinatorial Chemistry. Adv. Synth. Catal. **347**, 484-492 (2005).

122. *Milosevic, P. and S. Hecht:* Design of Branched and Chiral Solvatochromic Probes: Toward Quantifying Polarity Gradients in Dendritic Macromolecules. Org. Lett. **7**, 5023-2026 (2005).

123. *Modrow, H., G. Köhl, J. Hormes, H. Bönnemann, U. Endruschat and R. Mörtel: In-situ* X-ray Absorption Spectroscopy Investigations During the Conditioning Procedure of PtRu Colloid Catalysts. Phys. Scr. **115**, 671-674 (2005).

124. *Modrow, H., S. Modrow, J. Hormes, N. Waldöfner and H. Bönnemann:* "Contact Voltage" in Nanoparticle/Molecule Connections. J. Phys. Chem. B **109**, 900-906 (2005).

125. *Mroginski, M.-A., K. Németh, T. Bauschlicher, W. Klotzbücher, R. Goddard, O. Heinemann, P. Hildebrandt and F. Mark:* Calculation of Vibrational Spectra of Linear Tetrapyrroles. 3. Hydrogen-Bonded Hexamethylpyrromethene Dimers. J. Phys. Chem. A **109**, 2139-2150 (2005).

126. *Müller, H., J.T. Andersson and W. Schrader:* Characterization of High-Molecular-Weight Sulfur-Containing Aromatics in Vacuum Residues Using Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Anal. Chem. **77**, 2536-2543 (2005).

127. *Nehls, B.S., F. Galbrecht, A. Bilge, D.J. Brauer, C.W. Lehmann, U. Scherf and T. Farrell:* Synthesis and Spectroscopy of an oligophenyl based cruciform with remarkable π–π assisted folding. Org. Biomol. Chem. **3**, 3213-3219 (2005).

128. *Neumann, D. and G. Veser:* Catalytic Partial Oxidation of Methane in a High-Temperature Reverse-Flow Reactor. AIChE J. **51**, 210-223 (2005).

129. *Ould-Ely, T., J.H. Thurston, A. Kumar, M. Respaud, W. Guo, C. Weidenthaler and K.H. Whitmire:* Wet-Chemistry Synthesis of Nickel-Bismuth Bimetallic Nanoparticles and Nanowires. Chem. Mater. **17**, 4750-4754 (2005).

130. *Palkovits, R., H. Althues, A. Rumplecker, B. Tesche, A. Dreier, U. Holle, G. Fink, C.H. Cheng, D.F. Shantz and S. Kaskel:* Polymerization of w/o Microemulsions for the Preparation of Transparent SiO_2/PMMA Nanocomposites. Langmuir **21**, 6048-6053 (2005).

131. *Palkovits, R., Y. Ilhan, W. Schmidt, C.-M. Yang, A. Erdem-Sentalar and F. Schüth:* Beckmann Rearrangement on microporous and mesoporous silica. In: Molecular Sieves: From Basic Research to Industrial Applications. (Ed.) J. Cejka. Stud. Surf. Sci. Catal. **158**, 1255-1262 (2005).

132. *Patchkovskii, S., A. Koslowski and W. Thiel:* Generic Implementation of Analytical CI Gradients for NDDO-Type Methods. Theor. Chem. Acc. **114**, 84-89 (2005).

133. *Pop, L.M., S. Odenbach, A. Wiedenmann, N. Matoussevitch, H. Bönnemann:* Mirostructure and rheology of ferrofluids. J. Magn. Magn. Mater. **289**, 303-306 (2005).

134. *Ramalho, T.C. and M. Bühl:* Probing NMR Parameters, Structure, and Dynamics of 5-Nitroimidazole Derivatives. Density Functional Study of Prototypical Radiosensitizers. Magn. Reson. Chem. **43**, 139-146 (2005).

135. *Ramalho, T.C., M. Bühl, J.D. Figueroa-Villar and R. Bicca de Alencastro:* Computational NMR Spectroscopy of Transition-Metal/Nitroimidazole

Complexes: Theoretical Investigation of Potential Radiosensitizers. Helv. Chim. Acta **88**, 2705-2721 (2005).

136. *Reetz, M.T.:* Evolution im Reagenzglas: Neue Perspektiven für die Weiße Biotechnology. Jahrb. MPG (Tätigkeitsbericht des MPI für Kohlenforschung) **2005**, 327-331.

137. *Reetz, M.T., M. Bocola, J.D. Carballeira, D. Zha and A. Vogel:* Expanding the Range of Substrate Acceptance of Enzymes: Combinatorial Active-Site Saturation Test. Angew. Chem. **117**, 4264-4268 (2005); Angew. Chem. Int. Ed. **44**, 4192-4196 (2005).

138. *Reetz, M.T., O.G. Bondarev, H.-J. Gais and C. Bolm:* BINOL-Derived N-Phosphino Sulfoximines as Ligands for Asymmetric Catalysis. Tetrahedron Lett. **46**, 5643-5646 (2005).

139. *Reetz, M.T. and H. Guo:* Mixtures of Monodentate P-Ligands as a Means to Control the Diastereoselectivity in Rh-Catalyzed Hydrogenation of Chiral Alkenes. Beilstein J. Org. Chem. **1**:3, (2005) doi:10.1186/1860-5397-1-3.

140. *Reetz, M.T. and M. Hermes:* Gelenkte in vitro-Evolution enantioselektiver Enzyme. Eine Automationslösung für Hochdurchsatz-Screening von Enzymbibliotheken. BIOspektrum **2005**, 681-682.

141. *Reetz, M.T. and X. Li:* Mischungen konfigurationsstabiler and fluxionaler atropisomerer einzähniger P-Liganden in der asymmetrischen Rh-katalysierten Olefin-Hydrierung. Angew. Chem. **117**, 3019-3021 (2005); Angew. Chem. Int. Ed. **44**, 2959-2962 (2005).

142. *Reetz, M.T. and X. Li:* Der Einfluss von Mischungen achiraler einzähniger Liganden auf die Regioselektivität der übergangsmetallkatalysierten Hydroformylierung. Angew. Chem. **117**, 3022-3024 (2995); Angew. Chem. Int. Ed. **44**, 2962-2964 (2005).

143. *Reetz, M.T. and X. Li:* Rhodium-Catalyzed Enantioselective Hydrogenation of β,β-Disubstituted α-Acetamido Acrylates Using Cheap Monodentate P-Ligands. Synthesis **2005**, 3183-3185.

144. *Reetz, M.T., J.-A. Ma and R. Goddard:* Binol-Derived Monodentate Phosphites and Phosphoramidites with Phosphorus Stereogenic Centers: Novel Ligands for

Transition-Metal Catalysis. Angew. Chem. **117**, 416-419 (2005); Angew. Chem. Int. Ed. **44**, 412-415 (2005).

145. *Reetz, M.T., A. Meiswinkel, G. Mehler, K. Angermund, M. Graf, W. Thiel, R. Mynott and D.C. Blackmond:* Why Are BINOL-Based Monophosphites Such Efficient Ligands in Rh-Catalyzed Asymmetric Olefin Hydrogenation? J. Am. Chem. Soc. **127**, 10305-10313 (2005).

146. *Reetz, M.T.and K. Sommer:* Gold-catalyzed Hydroarylation of Alkynes. In: Handbook of C-H Transformations, Vol. 1 (Applications in Organic Synthesis). (Ed.) G. Dyker. Wiley-VCH, Weinheim 2005, 157-166, 268-269.

147. *Reisner, E., V.B. Arion, A. Rufińska, I. Chiorescu, W.F. Schmid and B.K. Keppler:* Isomeric $[RuCl_2(dmso)_2(indazole)_2]$ complexes: ruthenium(II)-mediated coupling reaction of acetonitrile with 1*H*-indazole. Dalton Trans. **2005**, 2355-2364

148. *Rozwadowski, M., J. Datka, M. Lezanska, J. Wloch, K. Erdmann and J. Kornatowski:* Detailed characterisation of Al-grafted MCM-48. In: Molecular Sieves: From Basic Research to Industrial Applications. (Ed.) J. Cejka. Stud. Surf. Sci. Catal. **158**, 703-710 (2005).

149. *Sarazin, Y., G. Fink, K. Hauschild and M. Bochmann:* Copolymerization of Propene and 5-Vinyl-2-Norbornene: A Simple Route to Polar Poly(propylene)s. Macromol. Rapid Commun. **26**, 1208-1213 (2005).

150. *Schilling, O., B. Späth, B. Kostelecky, A. Marchfelder, W. Meyer-Klaucke and A. Vogel:* Exosite Modules Guide Substrate Recognition in the ZiPD/ElaC Protein Family. J. Biol. Chem. **280**, 17857-17862 (2005).

151. *Schmidt, W.:* Synthetische Zeolithe. In: Chemische Technologie (Winnacker-Küchler) Bd. 3. (Eds.) R. Dittmeyer, W. Keim, G. Kreysa, A. Oberholz. Wiley-VCH, Weinheim 2005, 834-849.

152. *Schmidt, W.:* Synthetische Silicate. In: Chemische Technologie (Winnacker-Küchler) Bd. 3. (Eds.) R. Dittmeyer, W. Keim, G. Kreysa, A. Oberholz. Wiley-VCH, Weinheim 2005, 849-850.

153. *Schöneboom, J.C., F. Neese and W. Thiel:* Toward Identification of the Compound I Reactive Intermediate in Cytochrome P450 Chemistry: A QM/MM

Study of Its EPR and Mössbauer Parameters. J. Am. Chem. Soc. **127**, 5840-5853 (2005).

154. *Schrader, W.:* Atmosphäre – ein chemischer Reaktor: Bildungsmechanismus sekundärer organischer Aerosole. Angew. Chem. **117**, 1468-1470 (2005); Angew. Chem. Int. Ed. **44**, 1444-1446 (2005).

155. *Schrader, W., J. Geiger and M. Godejohann:* Studies of complex reactions using modern hyphenated methods: α-Pinene ozonolysis as a model reactions. J. Chromatogr. A **1075**, 185-196 (2005).

156. *Schüth, F.:* Hydrogen and hydrates. Nature (London) **434**, 712-713 (2005).

157. *Schüth, F.:* Neue Materialien für die Heterogene Katalyse. Chem. Ing. Tech. **77**, 1399-1416 (2005).

158. *Schüth, F.:* Engineered Porous Catalytic Materials. Annu. Rev. Mater. Res. **35**, 209-238 (2005).

159. *Schüth, F.:* High-throughput experiments for synthesis and applications of zeolites. In: Zeolites and Ordered Mesoporous Materials: Progress and Prospects. (Eds.) J. Cejka, H. van Bekkum, Stud. Surf. Sci. Catal. **157**, 161-180 (2005).

160. *Schüth, F. and S. Schunk:* Combinatorial Approaches to Design Complex Metal Oxides. In: Metal Oxides: Chemistry and Applications. (Ed.) J.L. Fierro. CRC Press, Boca Raton 2005, 391-412.

161. *Schüth, F., Y. Wang, C.-M. Yang and B. Zibrowius:* Mesostructured Silica and Organically Functionalized Silica – Status and Perspectives. In: Organosilicon Chemistry VI, Vol. 2. (Eds.) N. Auner, J. Weis. Wiley-VCH, Weinheim 2005, 860-868.

162. *Schulz, F., F. Leca, F. Hollmann and M.T. Reetz:* Towards practical biocatalytic Baeyer-Villinger reactions: applying a themostable enzyme in the gram-scale synthesis of optically active lactones in a two-liquid-phase system. Beilstein J. Org. Chem. **1**:10, (2005) doi:10.1186/1860-5397-1-10.

163. *Schulze, P., M. Ludwig, F. Kohler and D. Belder:* Deep UV Laser-Induced Fluorescence Detection of Unlabeled Drugs and Proteins in Microchip Electrophoresis. Anal. Chem. **77**, 1325-1329 (2005).

164. *Schunk, S.A., C. Baltes and J. Klein:* How High Throughput Technology Can Facilitate Better Hydrocarbon Processing. Oil, Gas (Hamburg, Ger.) **31**, 77-82 (2005).

165. *Schwickardi, M., B. Spliethoff, W. Schmidt and F. Schüth:* Direct Synthesis of Supported Noble Metal Catalysts via the Activated Carbon Route. Z. Phys. Chem. **219**, 939-948 (2005).

166. *Seayad, J. and B. List:* Asymmetric organocatalysis. Org. Biomol. Chem. **3**, 719-724 (2005).

167. *Senn, H.M., D. O'Hagan and W. Thiel:* Insight into Enzymatic C-F Bond Formation from QM and QM/MM Calculations. J. Am. Chem. Soc. **127**, 13643-13655 (2005).

168. *Senn, H.M., S. Thiel and W. Thiel:* Enzymatic Hydroxylation in *p*-Hydroxybenzoate Hydroxylase: A Case Study for QM/MM Molecular Dynamics. J. Chem. Theory Comput. **1**, 494-505 (2005).

169. *Seth, M., H.M. Senn and T. Ziegler:* The Influence of Solvation and Finite Temperatures on the Wittig Reactions: A Theoretical Study. J. Phys. Chem. A **109**, 5136-5143 (2005).

170. *Shaik, S., D. Kumar, S.P. de Visser, A. Altun and W. Thiel:* Theoretical Perspective on the Structure and Mechanism of Cytochrome P450 Enzymes. Chem. Rev. **105**, 2279-2328 (2005).

171. *Söhnel, T., H. Hermann and P. Schwerdtfeger:* Solid State Density Functional Calculations for the Group 11 Monohalides. J. Phys. Chem. B **109**, 526-531 (2005).

172. *Solinas, M., J. Jiang, O. Stelzer and W. Leitner:* Ein Kartuschen-System für die metallorganische Katalyse: sequenzielle Katalyse und Stofftrennung mit überkritischem CO_2 zur Kontrolle der Löslichkeit. Angew. Chem. **117**, 2331-2335 (2005); Angew. Chem. Int. Ed. **44**, 2291-2295 (2005).

173. *Späth, B., S. Kirchner, A. Vogel, S. Schubert, P. Meinlschmidt, S. Aymanns, J. Nezzar and A. Marchfelder:* Analysis of the Functional Modules of the tRNA 3' Endonuclease (tRNase Z). J. Biol. Chem. **280**, 35440-35447 (2005).

174. *Steiger, R., C.H. Bischof, B. Lang and W. Thiel:* Using Automatic Differentiation to Compute Derivatives for a Quantum-Chemical Computer Program. Future Gener. Comput. Syst. **21**, 1324-1332 (2005).

175. *Taguchi, A. and F. Schüth:* Ordered mesoporous materials in catalysis. Microporous Mesoporous Mater. **77**, 1-45 (2005).

176. *Theyssen, N.:* State of the Art – Applications of Supercritical Fluids other than Catalysis. In: Multiphase Homogeneous Catalysis. Vol. 2. (Eds.) B. Cornils u.a.. Wiley-VCH, Weinheim 2005, 630-643.

177. *Thiel, W.:* Semiempirical Quantum-Chemical Methods in Computational Chemistry. In: Theory and Applications of Computational Chemistry: The First 40 Years. (Eds.) C.E. Dykstra, K.S. Kim, G. Frenking, G.E. Scuseria. Elsevier, Amsterdam 2005, 559-580.

178. *Tiemann, M., Ö. Weiß, J. Hartikainen, F. Marlow and M. Lindén:* Early Stages of ZnS Nanoparticle Growth Studied by In-Situ Stopped-Flow UV Absorption Spectroscopy. ChemPhysChem **6**, 2113-2119 (2005).

179. *Trapp, O.:* Direct calculation of interconversion barriers in dynamic chromatography and electrophoresis: Isomerization of captopril. Electrophoresis **26**, 487-493 (2005).

180. *Trapp, O., E.W. Pearce, J.R. Kimmel, O.K. Yoon, I.A. Zuleta and R.N. Zare:* A soft on-column metal coating procedure for robust sheathless electrospray emitters used in capillary electrophoresis-mass spectrometry. Electrophoresis **26**, 1358-1365 (2005).

181. *Tsoncheva, T., J. Rosenholm, H. Huwe, D. Paneva, M. Dimitrov, I. Mitov, F. Kleitz, M. Lindén, N. Froba and C. Minchev:* Pore design in view adsorption, reductive and catalytic properties of Fe or Cu oxide modified large mesoporous silicas. In: Molecular Sieves: From Basic Research to Industrial Applications. (Ed.) J. Cejka. Stud. Surf. Sci. Catal. **158**, 773-780 (2005).

182. *Vedder, C., F. Schaper, H.-H. Brintzinger, M. Kettunen, S. Babik and G. Fink:* Chiral Iron(II) and Cobalt(II) Complexes with Biphenyl-Bridged Bis(pyridylimine) Ligands – Syntheses, Structures and Reactivities. Eur. J. Inorg. Chem. **2005**, 1071-1080.

183. *Veser, G.:* Process intensification through heat-integration for high-temperature catalysis. In: Microreactor Technology and Process Intensification. (Eds.) Y. Wang, J.D. Holladay. ACS Symp. Ser. **914**, 145-161 (2005).

184. *Vogel, A., O. Schilling, B. Späth and A. Marchfelder:* The tRNase Z family of proteins: physiological functions, substrate specificity and structural properties. Biol. Chem. **386**, 1253-1264 (2005).

185. *Vukojević, S., O. Trapp, J.-D. Grunwaldt, C. Kiener and F. Schüth:* Quasi-Homogeneous Methanol Synthesis Over Highly Active Copper Nanoparticles. Angew. Chem. **117**, 8192-8195 (2005); Angew. Chem. Int. Ed. **44**, 7978-7981 (2005).

186. *Vyboishchikov, S.F. and W. Thiel:* Ring-Closing Olefin Metathesis on Ruthenium Carbene Complexes: Model DFT Study of Stereochemistry. Chem.-Eur. J. **11**, 3921-3935 (2005).

187. *Wang, Y., Yang, C.-M., W. Schmidt, B. Spliethoff, E. Bill and F. Schüth:* Weakly Ferromagnetic Ordered Mesoporous Co_3O_4 Synthesized by Nanocasting from Vinyl-Functionalized Cubic *Ia*3*d* Mesoporous Silica. Adv. Mater. **17**, 53-56 (2005).

188. *Wanko, M., M. Hoffmann, P. Strodel, A. Koslowski, W. Thiel, F. Neese, T. Frauenheim and M. Elstner:* Calculating Absorption Shifts for Retinal Proteins: Computational Challenges. J. Phys. Chem. B **109**, 3606-3615 (2005).

189. *Weidenthaler, C., Y. Mao and W. Schmidt:* Mixed CoNiAl spinels synthesized from ion-exchanged zeolites A and X. In: Molecular Sieves: From Basic Research to Industrial Applications. (Ed.) J. Cejka. Stud. Surf. Sci. Catal. **158**, 415-422 (2005).

190. *Weidenthaler, C., A. Pommerin, M. Felderhoff, W. Schmidt, B. Bogdanović and F. Schüth:* Evidence for the existence of β-Na_3AlH_6: Monitoring the phase

transformations from α-Na_3AlH_6 by in situ methods. J. Alloys Compd. **398**, 228-234 (2005).

191. *Weidenthaler, C., B. Zibrowius, J. Schimanke, Y. Mao, B. Mienert, E. Bill and W. Schmidt:* Oxidation behavior of ferrrous cations during ion exchange under atmospheric conditions. Microporous Mesoporous Mater. **84**, 302-317 (2005).

192. *Wen, F. and H. Bönnemann:* A facile one-pot synthesis of [(COD)Pt(CH_3)$_2$]. Appl. Organomet. Chem. **19**, 94-97 (2005).

193. *Wen, F., H. Bönnemann, J. Jiang, D. Lu, Y. Wang and Z. Jin:* Evidence of colloidal rhodium formation during the biphasic hydroformylation of 1-octene with thermoregulated phase-transfer phosphine rhodium(I) catalyst. Appl. Organomet. Chem. **19**, 81-89 (2005).

194. *Wen, F., H. Bönnemann, R. Mynott, B. Spliethoff, C. Weidenthaler, N. Palina, S. Zinoveva and H. Modrow:* Preparation of Pt_{13} clusters in the presence of trialkylaluminium. Appl. Organomet. Chem. **19**, 827-829 (2005).

195. *Wen, F., N. Waldöfner, W. Schmidt, K. Angermund, H. Bönnemann, S. Modrow, S. Zinoveva, H. Modrow, J. Hormes, L. Beuermann, S. Rudenkiy, W. Maus-Friedrichs, V. Kempter, T. Vad and H.G. Haubold:* Formation and Characterization of Pt Nanoparticle Networks. Eur. J. Inorg. Chem. **2005**, 3625-3640.

196. *Woodman, T.J., Y. Sarazin, G. Fink, K. Hauschild and M. Bochmann:* Heterogenized "Ligand-Free" Lanthanide Catalysts for the Homo- and Copolymerization of Ethylene and 1,3-Butadiene. Macromolecules **38**, 3060-3067 (2005).

197. *Woodman, T.J., Y. Sarazin, S. Garratt, G. Fink and M. Bochmann:* Chromium allyl and alkyl catalysts for the vinyl polymerization of norbornene and ethylene-norbornene copolymerizations. J. Mol. Catal. A: Chem. **235**, 88-97 (2005).

198. *Yang, C.-M., W. Schmidt and F. Kleitz:* Pore topology control of three-dimensional large pore cubic silica mesophases. J. Mater. Chem. **15**, 5112-5114 (2005).

199. *Yang, C.-M., C. Weidenthaler, B. Spliethoff, M. Mamatha and F. Schüth:* Facile Template Synthesis of Ordered Mesoporous Carbon with Polypyrrole as Carbon Precursor. Chem. Mater. **17**, 355-358 (2005).

200. *Yang, J.W., M.T. Hechavarria Fonseca and B. List:* Catalytic Asymmetric Reductive Michael Cyclization. J. Am. Chem. Soc. **127**, 15036-15037 (2005).

201. *Yang, J.W., M.T. Hechavarria Fonseca, N. Vignola and B. List:* Metal-Free, Organocatalytic Asymmetric Transfer Hydrogenation of α,β-Unsaturated Aldehydes. Angew. Chem. **117**, 110-112 (2005); Angew. Chem. Int. Ed. **44**, 108-110 (2005).

202. *Yurchenko, S.N., J. Breidung and W. Thiel:* Vibrational Spectrum of BiH_3: Six-Dimensional Variational Calculations on High Level *ab Initio* Potential Energy Surfaces. Theor. Chem. Acc. **144**, 333-340 (2005).

203. *Yurchenko, S.N., M. Carvajal, H. Lin, J. Zheng, W. Thiel and P. Jensen:* Dipole moment and rovibrational intensities in the electronic ground state of NH_3: Bridging the gap between *up initio* theory and spectroscopic experiment. J. Chem. Phys. **122**, 104317/1-14 (2005).

204. *Yurchenko, S.N., M. Carvajal, P. Jensen, H. Lin, J. Zheng and W. Thiel:* Rotation-Vibration Motion of Pyramidal XY_3 Molecules Described in the Eckart Frame: Theory and Applications to NH_3. Mol. Phys. **103**, 359-378 (2005).

205. *Yurchenko, S.N., W. Thiel, M. Carvajal, H. Lin and P. Jensen:* Rotation-Vibration Motion of Pyramidal XY_3 Molecules Described in the Eckart Frame: The Calculation of Intensities with Application to NH_3. Adv. Quantum Chem. **48**, 209-238 (2005).

206. *Yurchenko, S.N., W. Thiel, S. Patchkovskii and P. Jensen:* Theoretical Evidence for the Formation of Rotational Energy Level Clusters in the Vibrational Ground State of PH_3. Phys. Chem. Chem. Phys. **7**, 573-582 (2005).

207. *Yurchenko, S.N., J. Zheng, H. Lin, P. Jensen and W. Thiel:* Potential-energy surface for the electronic ground state of NH_3 up to 20 000 cm^{-1} above equilibrium. J. Chem. Phys. **123**, 134308/1-14 (2005).

2006

208. *Aïssa, C.:* Improved Julia-Kocienski Conditions for the Methylenation of Aldehydes and Ketones. J. Org. Chem. **71**, 360-363 (2006).

209. *Alemani, M., M.V. Peters, S. Hecht, K.-H. Rieder, F. Moresco and L. Grill:* Electric Field-Induced Isomerization of Azobenzene by STM. J. Am. Chem. Soc. **128**, 14446-14447 (2006).

210. *Althues, H., R. Palkovits, A. Rumplecker, P. Simon, W. Sigle, M. Bredol, U. Kynast and S. Kaskel:* Synthesis and Characterization of Transparent Luminescent ZnS:Mn/PMMA Nanocomposites. Chem. Mater. **18**, 1068-1072 (2006).

211. *Altun, A., V. Guallar, R.A. Friesner, S. Shaik and W. Thiel:* The Effect of Heme Environment on the Hydrogen Abstraction Reaction of Camphor in $P450_{cam}$ Catalysis: A QM/MM Study. J. Am. Chem. Soc. **128**, 3924-3925 (2006).

212. *Altun, A., S. Shaik and W. Thiel:* Systematic QM/MM Investigation of Factors that Affect the Cytochrome $P450_{cam}$-Catalyzed Hydrogen Abstraction of Camphor. J. Comput. Chem. **27**, 1324-1337 (2006).

213. *Arnal, P.M., M. Comotti and F. Schüth:* High-Temperature-Stable Catalysts by Hollow Sphere Encapsulation. Angew. Chem. **118**, 8404-8407 (2006); Angew. Chem. Int. Ed. **45**, 8224-8227 (2006).

214. *Arnal, P.M., F. Schüth and F. Kleitz:* A versatile method for the production of monodisperse spherical particles and hollow particles: Templating from binary core-shell structures. Chem. Commun. (Cambridge, U. K.) **2006**, 1203-1205.

215. *Arnal, P.M., C. Weidenthaler and F. Schüth:* Highly monodisperse zirconia coated silica spheres and zirconia/silica hollow spheres with remarkable textural properties. Chem. Mater. **18**, 2733-2739 (2006).

216. *Baca, S.G., M.T. Reetz, R. Goddard, I.G. Filippova, Y.A. Simonov, M. Gdaniec and N. Gerbeleu:* Coordination polymers constructed from *o*-phthalic acid and diamines: Syntheses and crystal structures of the phthalate-imidazole complexes $\{[Cu(Pht)(Im)_2]\cdot 1.5H_2O\}_n$ and $[Co(Pht)(Im)_2]_n$ and their application in oxidation catalysis. Polyhedron **25**, 1215-1222 (2006).

217. *Baker, R.T., S. Kobayashi and W. Leitner:* Divide at Impera – Multiphase, Green Solvent and Immobilization Strategies for Molecular Catalysis. Adv. Synth. Catal. **348**, 1337-1340 (2006).

218. *Balbo Block, M.A., S. Hecht:* Influence of chirality on conformation and aggregation behavior of poly(propylene oxide)-poly(phenylene ethynylene) copolymers. PMSE Prepr. **95**, 110-111 (2006).

219. *Baltes, C., S. Vukojević and F. Schüth:* Real Condition High Throughput Screening of $Cu/ZnO/Al_2O_3$ Catalysts for Methanol Synthesis. DGMK-Tagungsber. **2006-4**, 19-26 (2006).

220. *Bandyopadhyay, M., O. Korsak, M.W.E. van den Berg, W. Grünert, A. Birkner, W. Li, F. Schüth and H. Gies:* Gold nano-particles stabilized in mesoporous MCM-48 as active CO-oxidation catalyst. Microporous Mesoporous Mater. **89**, 158-163 (2006).

221. *Baumes, L.A.:* MAP: An Iterative Experimental Design Methodology for the Optimization of Catalytic Search Space Structure Modeling. J. Comb. Chem. **8**, 304-314 (2006).

222. *Beale, A.M., D. Grandjean, J. Kornatowski, P. Glatzel, F.M.F. de Groot and B.M. Weckhuysen:* Unusual Coordination Behavior of Cr^{3+} in Microporous Aluminophosphates. J. Phy. Chem. B **110**, 716-722 (2006).

223. *Behrens, S., H. Bönnemann, N. Matoussevitch, E. Dinjus, H. Modrow, N. Palina, M. Frerichs, V. Kempter, W. Maus-Friedrichs, A. Heinemann, M. Kammel, A. Wiedenmann, L. Pop, S. Odenbach, E. Uhlmann, N. Bayat, J. Hesselbach and J.M. Guldbakke:* Air-stable Co-, Fe-, and Fe/Co-Nanoparticles and Ferrofluids. Z. phys. Chem. **220**, 3-40 (2006).

224. *Behrens, S., H. Bönnemann, N. Matoussevitch, A. Gorschinski, E. Dinjus, W. Habicht, J. Bolle, S. Zinoveva, N. Palina, J. Hormes, H. Modrow, S. Bahr and V. Kempter:* Surface engineering of Co and FeCo nanoparticles for biomedical applications. J. Phys.: Condens. Matter **18**, S2543-S2561 (2006).

225. *Belder, D.:* Integrating Chemical Synthesis and Analysis on a Chip. Anal. Bioanal. Chem. **385**, 416-418 (2006).

226. *Belder, D.:* Chiral separations in microfluidic devices. In: Chiral Analysis (Eds.) K. Busch, M. Busch. Elsevier, Amsterdam 2006, 277-295.

227. *Belder, D., F. Kohler, M. Ludwig, K. Tolba and N. Piehl:* Coating of powder-blasted channels for high-performance microchip electrophoresis. Electrophoresis **27**, 3277-3283 (2006).

228. *Belder, D., M. Ludwig, L.-W. Wang und M.T. Reetz:* Enantioselektive Katalyse und Analyse auf einem Mikrochip. Angew. Chem. **118**, 2523-2526 (2006); Angew. Chem. Int. Ed. **45**, 2463-2466 (2006).

229. *Bellosta von Colbe, J.M., W. Schmidt, M. Felderhoff, B. Bogdanović and F. Schüth:* Hydrogen-Isotope Scrambling on Doped Sodium Alanate. Angew. Chem. **118**, 3745-3747 (2006); Angew. Chem. Int. Ed. **45**, 3663-3665 (2006).

230. *Berlier, G., F. Meneau, G. Sankar, C.R.A. Catlow, J.M. Thomas, B. Spliethoff, F. Schüth and S. Coluccia:* Synthesis and characterisation of small ZnS particles. Res. Chem. Intermed. **32**, 683-693 (2006).

231. *Bernhardt, E., M. Finze, H. Willner, C.W. Lehmann and F.* Aubke*:* Salts of the Cobalt(I) Complexes $[Co(CO)_5]^+$ and $[Co(CO)_2(NO)_2]^+$ and the Lewis Acid-Base Adduct $[Co_2(CO)_7CO–B(CF_3)_3]$. Chem.-Eur. J. **12**, 8276-8283 (2006).

232. *Bönnemann, H. and K.S. Nagabhushana:* Colloidal Nanoparticles in Catalysis. In: Surface and Nanomolecular Catalysis. (Ed.) R. Richards. CRC/Taylor & Francis, Boca Raton 2006, 63-94.

233. *Bogdanović, B., M. Felderhoff, A. Pommerin, F. Schüth and N. Spielkamp:* Advanced Hydrogen-Storage Materials Based on Sc-, Ce-, and Pr-Doped $NaAlH_4$. Adv. Mater. **18**, 1198-1201 (2006).

234. *Bondarev, O.G. and R. Goddard:* New modular P-chiral ligands for Rh-catalyzed asymmetric hydrogenation. Tetrahedron Lett. **47**, 9013-9015 (2006).

235. *Breidung, J. and W. Thiel:* Thermochemistry of the Fluoroformyloxyl Radical: A Computational Study Based on Coupled Cluster Theory. J. Phys. Chem. A **110**, 1575-1585 (2006).

236. *Bühl, M.:* Density Functional Computation of ^{53}Cr NMR Chemical Shifts. Magn. Reson. Chem. **44**, 661-668 (2006).

237. *Bühl, M., S. Grigoleit, H. Kabrede and F.T. Mauschick:* Simulation of ^{59}Co NMR Chemical Shifts in Aqueous Solution. Chem.-Eur. J. **12**, 477-488 (2006).

238. *Bühl, M., J. Holub, D. Hnyk and J. Machacek:* Computational Study of Structures and Properties of Metallaboranes, Part 2: Transition-Metal Dicarbollide Complexes. Organometallics **25**, 2173-2181 (2006).

239. *Bühl, M. and H. Kabrede:* Geometrics of Transition-Metal Complexes from Density Functional Theory. J. Chem. Theory Comput. **2**, 1282-1290 (2006).

240. *Bühl, M. and H. Kabrede:* Acidity of Uranyl(VI) Hydrate Studied with First-Principles Molecular Dynamics Simulations. ChemPhysChem **7**, 2290-2293 (2006).

241. *Bühl, M. and H. Kabrede:* Mechanism of Water Exchange in Aqueous Uranyl(VI) Ion. A Density Functional Molecular Dynamics Study. Inorg. Chem. **45**, 3834-3836 (2006).

242. *Bühl, M., H. Kabrede, R. Diss and G. Wipff:* Effect of Hydration on Coordination Properties of Uranyl(VI) Complexes. A First-Principles Molecular Dynamics Study. J. Am. Chem. Soc. **128**, 6357-6368 (2006).

243. *Bühl, M. and W. Thiel:* Molekulardynamik-Simulationen für Reaktionen in Lösung und in Enzymen. Jahrb. MPG (Tätigkeitsbericht des MPI für Kohlenforschung) **2006**, 6 Seiten.

244. *Bunker, P.R., R. Guérot, Z.J. Jakubek, P. Jensen and S.N. Yurchenko:* The rovibronic energies of the SiNSi radical in its $\widetilde{X}\,^2\Pi_g$ electronic state. J. Mol. Struct. **795**, 9-13 (2006).

245. *Canè, E., G. Di Lonardo, F. Fusina, W. Jerzembeck, H. Bürger, J. Breidung and W. Thiel:* Rotation Spectrum and High Resolution Infrared Spectra of the Fundamental Bands of $^{121}SbD_3$. Determination of the Ground State and Equilibrium Structures. *Ab Initio* Calculations of the Spectroscopic Parameters. J. Mol. Struct. **780**, 98-110 (2006).

246. *Claeyssens, F., J.N. Harvey, F.R. Manby, R.A. Mata, A.J. Mulholland, K.E. Ranaghan, M. Schütz, S. Thiel, W. Thiel and H.-J. Werner:* High Accuracy Computation of Reaction Barriers in Enzymes. Angew. Chem. **118**, 7010-7013 (2006); Angew. Chem. Int Ed. **45**, 6856-6859 (2006).

247. *Clouthier, C.M., M.M. Kayser and M.T. Reetz:* Designing New Baeyer-Villiger Monooxygenases Using Restricted CASTing. J. Org. Chem. **71**, 8431-8437 (2006).

248. *Colmenares, L., Z. Jusys, S. Kinge, H. Bönnemann and R.J. Behm:* Synthesis, characterization and electrocatalytic performance of W surface modified, carbon supported Pt anode catalysts for low-temperature fuel cell applications. J. New Mater. Electrochem. Syst. **9**, 107-120 (2006).

249. *Comotti, M., W.-C. Li, B. Spliethoff u. F. Schüth:* Support Effect in High Activity Gold Catalysts for CO Oxidation. J. Am. Chem. Soc. **128**, 917-924 (2006).

250. *Dobrov, A., V.B. Arion, N. Kandler, W. Ginzinger, M.A. Jakupec, A. Rufińska, N.G. von Keyserlingk, M. Galanski, C. Kowol and B.K. Keppler:* The first metal-based paullone derivative with high anti proliferative activity in vitro. Inorg. Chem. **45**, 1945-1950 (2006).

251. *Döpp, D., A.A. Hassan, A.M. Nour El-Din, A.-F. E. Mourad, C.W. Lehmann and J. Rust:* Reaction of (1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile with *N*-arylisoindolines. Tetrahedron **62**, 11618-11626 (2006).

252. *Dröge, M.J., Y.L. Boersma, L. Ykelien, G. van Pouderoyen, T.E. Vrenken, C.J. Rüggeberg, M.T. Reetz, B.W. Dijkstra and W.J. Quax:* Directed evolution of Bacillus subtilis lipase A by use of enantiomeric phosphonate inhibitors: Crystal structures and phage diplay selection. ChemBioChem **7**, 149-157 (2006).

253. *Elend, C., C. Schmeisser, C. Leggewie, P. Babiak, J.D. Carballeira, H.L. Steele, J.-L. Reymond, K.-E. Jaeger and W.R. Streit:* Isolation and Biochemical Characterization of Two Novel Metagenome-Derived Esterases. Appl. Environ. Microbiol. **72**, 3637-3645 (2006).

254. *Ferrari, D., S. Knoke, B. Tesche and G. Fink:* Microkinetic Videomicroscopic Analysis of the Olefin-Copolymerization with Heterogeneous Catalysts. Macromol. Symp. **236**, 78-87 (2006).

255. *Fidale, L.C., S. Köhler, M.H.G. Prechtl, T. Heinze and O.A. El Seoud:* Simple, expedient methods for the determination of water and electrolyte contents of cellulose solvent systems. Cellulose **13**, 581-592 (2006).

256. *Fink, G.:* Styrolpolymere. In: Kunststoffe. (Ed.) W. Keim. Wiley-VCH, Weinheim 2006, 102-127.

257. *Fink, G. and S.T. Babik:* Propylene Bulk Phase Oligomerization with Bisiminepyridine Iron Catalysts: Mechanistic Investigation of 1,2- versus 2,1-Propylene Insertion. Kinet. Catal. **47**, 198-206 (2006).

258. *Fink, G. and H.-H. Brintzinger:* Polymerization Reactions. In: Metal-Catalysis in Industrial Organic Processes. (Eds.) G.P. Chiusoli, P.M. Maitlis. RSC Publ., Cambridge 2006, 218-254.

259. *Finze, M., E. Bernhardt, H. Willner and C.W. Lehmann:* $(PPh_3)_3RhCNB(CF_3)_3$ and $(PPh_3)_3RhNCB(CF_3)_3$: Isocyano- and Cyanoborate Complexes of Tris(triphenylphosphine)rhodium(I). Organometallics **25**, 3070-3075 (2006).

260. *Finze, M., E. Bernhardt, H. Willner and C.W. Lehmann:* Reactions of $(CF_3)_3BCO$ with amines and Phosphines. Inorg. Chem. **45**, 669-678 (2006).

261. *Fu, A., B. List and W. Thiel:* Density Functional Study of Enantioselectivity in the 2-Methylproline-Catalyzed α-Alkylation of Aldehydes. J. Org. Chem. **71**, 320-326 (2006).

262. *Fu, A. and W. Thiel:* Density Functional Study of Noncovalent Catalysis of the Diels-Alder Reaction by the Neutral Hydrogen Bond Donors Thiourea and Urea. J. Mol. Struct. (THEOCHEM) **765**, 45-52 (2006).

263. *Fürstner, A. and C. Aïssa:* $PtCl_2$-Catalyzed Rearrangement of Methylenecyclopropanes. J. Am. Chem. Soc. **128**, 6306-6307 (2006).

264. *Fürstner, A., C. Aïssa, C. Chevrier, F. Teplý, C. Nevado and M. Tremblay:* Studies on Iejimalide B: Preparation of the Seco Acid and Identification of the Molecule's "Achilles Heel". Angew. Chem. **118**, 5964-5969 (2006); Angew. Chem. Int. Ed. **45**, 5832-5837 (2006).

265. *Fürstner, A., M. Alcarazo, V. César and C.W. Lehmann:* Convenient, Scalable and Flexible Method for the Preparation of Imidazolium Salts with Previously Inaccessible Substitution Patterns. Chem. Commun. (Cambridge, U. K.) **2006**, 2176-2178.

266. *Fürstner, A., M.M. Domostoj and B. Scheiper:* Total Syntheses of the Telomerase Inhibitors Dictyodendrin B, C, and E. J. Amer. Chem. Soc. **128**, 8087-8094 (2006).

267. *Fürstner, A., M.D.B. Fenster, B. Fasching, C. Godbout and K. Radkowski:* Toward the Total Synthesis of Spirastrellolide A. Part 1: Strategic Considerations and Preparation of the Southern Domain. Angew. Chem. **118**, 5632-5636 (2006); Angew. Chem. Int. Ed. **45**, 5506-5510 (2006).

268. *Fürstner, A., M.D.B. Fenster, B. Fasching, C. Godbout and K. Radkowski:* Toward the Total Synthesis of Spirastrellolide A. Part 2: Conquest of the Northern Hemisphere. Angew. Chem. **118**, 5636-5641 (2006); Angew. Chem. Int. Ed. **45**, 5510-5515 (2006).

269. *Fürstner, A. and P. Hannen:* Platinum- and Gold-Catalyzed Rearrangement Reactions of Propargyl Acetates: Total Syntheses of (–)-α-Cubebene, (–)-Cubebol, Sesquicarene and Related Terpenes. Chem.-Eur. J. **12**, 3006-3019 (2006).

270. *Fürstner, A., E. Kattnig and O. Lepage:* Total Syntheses of Amphidinolide X and Y. J. Am. Chem. Soc. **128**, 9194-9204 (2006).

271. *Fürstner, A. and J.W.J. Kennedy:* Total Syntheses of the Tylophora alkaloids Cryptopleurine, (-)-Antofine,(-)-Tylophorine, and (-)-Ficuseptine C. Chem.-Eur. J. **12**, 7398-7410 (2006)

272. *Fürstner, A., H. Krause and C.W. Lehmann:* Unusual Structure and Reactivity of a Homoleptic "Super-Ate" Complex of Iron: Implications for Grignard Additions, Cross-Coupling Reactions, and the Kharasch Deconjugation. Angew. Chem. **118**, 454-458 (2006); Angew. Chem. Int. Ed. **45**, 440-444 (2006).

273. *Fürstner, A., V. Mamane, G. Seidel and D. Laurich:* Indium-Catalyzed Cycloisomerization: Preparation of 4-Methylpyrrolo[1,2-a]quinoline. Org. Synth. **83**, 103-110 (2006).

274. *Fürstner, A., C. Nevado, M. Tremblay, C. Chevrier, F. Teplý, C. Aïssa and M. Waser:* Total Synthesis of Iejimalide B. Angew. Chem. **118**, 5969-5974 (2006); Angew. Chem. Int. Ed. **45**, 5837-5842 (2006).

275. *Fürstner, A. and M. Wuchrer:* Concise Approach to the "Higher Sugar" Core of the Nucleoside Antibiotic Hikizimycin. Chem.-Eur. J. **12**, 76-89 (2006).

276. *Gausepohl, R., P. Buskens, J. Kleinen, A. Bruckmann, C.W. Lehmann, J. Klankermayer and W. Leitner:* Hoch enantioselektive Aza-Baylis-Hillman-Reaktionen in einem chiralen Reaktionsmedium. Angew. Chem. **118**, 3772-3775 (2006); Angew. Chem. Int. Ed. **45**, 3689-3692 (2006).

277. *Gavrilov, K.N., V.N. Tsarev, M.G. Maksimova, I.G. Bondarev, E.A. Rastorguev, S.E. Lyubimov, P.V. Petrovskii and V.A. Davanko:* Iminoarylphosphites with ferrocenylidene and cymantrenylidene fragments: Coordination properties and the use in palladium-catalysed asymmetric allylic substitution. J. Mol. Catal. A: Chem. **259**, 267-274 (2006).

278. *Goossen, L.J., D. Koley, H.L. Hermann and W. Thiel:* Palladium Monophosphine Intermediates in Catalytic Cross-Coupling Reactions: A DFT Study. Organometallics **25**, 54-67 (2006).

279. *Graf, M., K. Angermund, G. Fink, W. Thiel u. V.R. Jensen:* Site epimerization in *ansa*-zirconocene polymerization catalysts. J. Organomet. Chem. **691**, 4367-4378 (2006).

280. *Guo, H.-C. and J.-A. Ma:* Katalytische asymmetrische Tandemumwandlungen mit einer konjugierten Addition als einleitendem Schritt. Angew. Chem. **118**, 362-375 (2006); Angew. Chem. Int. Ed. **45**, 354-366 (2006).

281. *Guo, Y.Z., W. Meyer-Zaika, M. Muhler, S. Vukojevic and M. Epple:* Cu/Zn/Al xerogels and aerogels prepared by a sol-gel reaction as catalysts for methanol synthesis. Eur. J. Inorg. Chem. **23**, 4774-4781 (2006).

282. *Haenel, M.W.:* 80 Jahre Fischer-Tropsch-Synthese. Renaissance eines Klassikers der Kohleverflüssigung. Erdöl Erdgas Kohle **122**, 78-80 (2006).

283. *Haenel, M.W., J. Narangerel, U.-B. Richter und A. Rufińska:* Verflüssigung von Hoch-inkohlten Steinkohlen nach Hydrierung in Gegenwart von Boran- oder Iod-Homogenkatalysatoren. Angew. Chem. **118**, 1077-1082 (2006); Angew. Chem. Int. Ed. **45**, 1061-1066 (2006).

284. *Haenel, M.W., J. Narangerel, U.-B. Richter und A. Rufińska:* Liquefaction of high-rank bituminous coals by preceding hydrogenation with homogeneous

borane and iodine catalysts. Prepr. Symp. – Am. Chem. Soc., Div. Fuel Chem. **51**, 741-742 (2006).

285. *Heegaard, N.H.H., T.J.D. Jørgensen, L. Cheng, C. Schou, M.H. Nissen and O. Trapp:* Interconverting Conformations of Variants of the Human Amyloidogenic Protein β_2-Microglobulin Quantitatively Characterized by Dynamic Capillary Electrophoresis and Computer Simulation. Anal. Chem. **78**, 3667-3673 (2005).

286. *Hnyk, D., M. Bühl, J. Holub, S.A. Hayes, D.A. Wann, I.D. Mackie, K.B. Borisenko, H.E. Robertson, D.W.H. Rankin:* Molecular Structures of *arachno*-Decarborane Derivatives 6,9-$X_2B_8H_{10}$(X=CH_2, NH, Se) Including a Gas-Phase Electron-Diffraction Study of 6,9-$C_2B_8H_{14}$. Inorg. Chem. **45**, 6014-6019 (2006).

287. *Hoffmann, M., M. Wanko, P. Strodel, P.H. König, T. Frauenheim, K. Schulten, W. Thiel, E. Tajkhorshid and M. Elstner:* Color Tuning in Rhodopsins: The Mechanism for the Spectral Shift Between Bacteriorhodopsin and Sensory Rhodopsin II. J. Am. Chem. Soc. **128**, 10808-10818 (2006).

288. *Hoffmann, S., M. Nicoletti and B. List:* Catalytic Asymmetric Reductive Amination of Aldehydes via Dynamic Kinetic Resolution. J. Am. Chem. Soc. **128**, 13074-13075 (2006).

289. *Hrib, C.G., F. Ruthe, E. Seppälä, M. Bätcher, C. Druckenbrodt, C. Wismach, P.G. Jones, W.-W. du Mont, V. Lippolis, F.A., F.A. Devillanova and M.Bühl:* The Bromination of Bulky Trialkylphosphane Selenides $R_2R'PSe$ (R, R' = *i*Pr or *t*Bu) Studied by physical and Computational Methods. Eur. J. Inorg. Chem. **2006**, 88-100.

290. *Jakubek, Z.J., P.R. Bunker, M. Zachwieja, S.G. Nakhate, B. Simard, S.N. Yurchenko, W. Thiel and P. Jensen:* A dispersed fluorescence and *ab initio* investigation of the $\tilde{X}\,^2B_1$ and $\tilde{A}^2A_1$ electronic states of the PH_2 molecule. J. Chem. Phys. **124**, 094306/1-5 (2006).

291. *Jobic, H., W. Schmidt, C.B. Krause and J. Karger:* PFG NMR and QENS diffusion study of *n*-alkane homologues in MFI-type zeolites. Microporous Mesoporous Mater. **90**, 299-306 (2006).

292. *Kabrede, H.:* Using vibrational modes in the search for global minima of atomic and molecular clusters. Chem. Phys. Lett. **430**, 336-339 (2006).

293. *Kästner, J., H.M. Senn, S. Thiel, N. Otte and W. Thiel:* QM/MM Free-Energy Perturbation Compared to Thermodynamic Integration and Umbrella Sampling: Application to an Enzymatic Reactions. J. Chem. Theory Comput. **2**, 452-461 (2006).

294. *Kästner, J. and W. Thiel:* Analysis of the Statistical Error in Umbrella Sampling Simulations by Umbrella Integration. J. Chem. Phys. **124**, 234106/1-7 (2006).

295. *Kaiser, J., L. Colmenares, Z. Jusys, R. Mörtel, H. Bönnemann, G. Kohl, H. Modrow, J. Hormes and R.J. Behm:* On the role of reactant transport and (surface) alloy formation for the CO tolerance of carbon supported PtRu polymer electrolyte fuel cell catalysts. Fuel Cells **6**, 190-202 (2006).

296. *Kammel, M., A. Wiedemann, A. Heinemann, H. Bönnemann and N. Matoussevitch:* Oxide coating of Co-ferrofluid studied by polarised SANS. Phys. B (Amsterdam, Neth.) **385**, 457-460 (2006).

297. *Kampen, D. and B. List:* Efficient Brønsted Acid Catalyzed Hosomi-Sakurai Reaction of Acetals. Synlett **2006**, 2589-2592.

298. *Khalil, A.S.G., D. Konhodzic and F. Marlow:* Hierarchy Selection, Position Control, and Orientation of Growing Mesostructures by Patterned Surfaces. Adv. Mater. **18**, 1055-1058 (2006).

299. *Khan, A. and S. Hecht:* Synthesis, tubular scaffolding, and photocontrolling the helix-coil transition in phenylene ethynylene foldamers. PMSE Prepr. **95**, 73-74 (2006).

300. *Khan, A. and S. Hecht:* Poly(*ortho*-phenylene ethynylene)s: Synthetic Accessibility and Optical Properties. J. Polymer. Sci., Part A: Polym. Chem. **44**, 1619-1627 (2006).

301. *Khan, A. and S. Hecht:* Towards Photocontrol over the Helix-Coil Transition in Foldamers: Synthesis and Photoresponsive Behavior of Azobenzene-Core Amphiphilic Oligo(*meta*-phenylene ethynylene)s. Chem.-Eur. J. **12**, 4764-4774 (2006).

302. *Khan, A., C. Kaiser und S. Hecht:* Prototyp eines photoschaltbaren Foldamers. Angew. Chem. **118**, 1912-1915 (2006); Angew. Chem. Int. Ed. **45**, 1878-1881 (2006).

303. *Khelashvili, G., S. Behrens, C. Weidenthaler, C. Vetter, A. Hinsch, R. Kern, K. Skupien, E. Dinjus and H. Bönnemann:* Catalytic platinum layers for dye solar cells: A comparative study. Thin Solid Films **511-512**, 342-348 (2006).

304. *Kinge, S. and H. Bönnemann:* One-pot dual size- and shape selective synthesis of tetrahedral Pt nanoparticles. Appl. Organomet. Chem. **20**, 784-787 (2006).

305. *Konjhodzic, D., H. Bretinger and F. Marlow:* Structure and properties of low-*n* mesoporous silica films for optical applications. Thin Solid Films **495**, 333-337 (2006)

306. *Kornatowski, J., J.O. Barth, K. Erdmann and M. Rozwadowski:* Effect of various pillaring oxides on adsorption behaviour of novel MCM-36 derivatives. Microporous Mesoporous Mater. **90**, 251-258 (2006).

307. *Krawiec, P., P.L. De Cola, R. Gläser, J. Weitkamp, C. Weidenthaler and S. Kaskel:* Oxide Foams for the Synthesis of High-Surface-Area Vanadium Nitride Catalysts. Adv. Mater. **18**, 505-508 (2006).

308. *Layfield, R.A., M. Bühl and J.M. Rawson:* Structure, Bonding, and Paramagnetism in the Manganese(II) Tris-Allyl Anions $[Mn\{\eta^x\text{-}(C_3H_3R_2)_3\}]^-$ (R=H, $SiMe_3$; *x*=1 or 3): Insight from Theory. Organometallics **25**, 3570-3575 (2006).

309. *Li, H.-L. and F. Marlow:* Solvent Effects in Colloidal Crystal Deposition. Chem. Mater. **18**, 1803-1810 (2006).

310. *Li, W.-C., M. Comotti, A.-H. Lu and F. Schüth:* Nanocast mesoporous $MgAl_2O_4$ spinel monoliths as support for highly active gold CO oxidation catalyst. Chem. Commun. (Cambridge, U. K.) **2006**, 1772-1774.

311. *Li, W.-C., M. Comotti and F. Schüth:* Highly reproducible syntheses of active Au/TiO_2 catalyst for CO oxidation by deposition-precipitation or impregnation. J. Catal. **237**, 190-196 (2006).

312. *List, B.:* The Ying and Yang of Asymmetric Aminocatalysis. Chem. Commun. (Cambridge, U. K.) **2006**, 819-824.

313. *List, B., A. Döhring, M.T. Hechavarria Foncseca, A. Job and R. Rios Torres:* A Practical, efficient, and atom economic alternative to the Wittig and Horner-

Wadsworth-Emmons reactions for the synthesis of (*E*)-α,β-unsaturated esters from aldehydes. Tetrahedron **62**, 476-482 (2006).

314. *List, B. and J.W. Yang:* The Organic Approach to Asymmetric Catalysis. Science **313**, 1584-1586 (2006).

315. *Lu, A.-H.:* A brief overview on the Carbon 2006 conference. New Carbon Mater. **21**, 285-288 (2006).

316. *Lu, A.-H., W.-C. Li, E.-L. Salabaş, B. Spliethoff and F. Schüth:* Low Temperature Catalytic Pyrolysis for the Synthesis of High Surface Area, Nanostructured Graphitic Carbon. Chem. Mater. **18**, 2086-2094 (2006).

317. *Lu, A.-H., W.-C. Li, W. Schmidt and F. Schüth*: Low temperature oxidative template removal from SBA-15 using MnO_4^- solution and carbon replication of the mesoporous silica product. J. Mater. Chem. **16**, 3396-3401 (2006).

318. *Lu, A.-H., W.-C. Li, W. Schmidt and F. Schüth:* Fabrication of hierarchically structured carbon monoliths via self-binding and salt templating. Microporous Mesoporous Mater. **95**, 187-192 (2006).

319. *Lu, A.-H. and F. Schüth:* Nanocasting: A versatile strategy to create nanostructured porous materials. Adv. Mater. **18**, 1793-1805 (2006).

320. *Maayan, G., B. Ganchegui, W. Leitner and R. Neumann:* Selective aerobic oxidation in supercritical carbon dioxide catalyzed by the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate. Chem. Commun. (Cambridge, U. K.) **2006**, 2230-2232.

321. *Mamatha, M., B. Bogdanović, M. Felderhoff, A. Pommerin, W. Schmidt, F. Schüth and C. Weidenthaler:* Mechanochemical preparation and investigation of properties of magnesium, calcium and lithium-magnesium alanates. J. Alloys Compd. **407**, 78-86 (2006).

322. *Mamatha, M., C. Weidenthaler, A. Pommerin, M. Felderhoff and F. Schüth:* Comparative studies of the decomposition of alanates followed by in situ XRD and DSC methods. J. Alloys Compd. **416**, 303-314 (2006).

323. *Marlow, F., A.S.G. Khalil, R. Brinkmann and M. Stempniewicz:* Hierarchische Silica-Strukturen: Wachstumssteuerung, Beschreibung und Eigenschaften. In:

Irreversible Prozesse und Selbstorganisation. (Eds.) T. Pöschel, H. Malchow, L. Schimansky-Geier. Logos Verlag, Berlin 2006, 113-129.

324. *Marlow, F. and M. Stempniewicz:* Comment on "Gas Diffusion and Microstructural Properties of Ordered Mesoporous Silica Fibers". J. Phys. Chem. B **110**, 11604-11605 (2006).

325. *Martin, N.J.A. and B. List:* Highly Enantioselective Transfer Hydrogenation of α,β-Unsaturated Ketones. J. Am. Chem. Soc. **128**, 13368-13369 (2006).

326. *Mayer, S. and B. List:* Asymmetrische Gegenanion-vermittelte Katalyse. Angew. Chem. **118**, 4299-4301 (2006); Angew. Chem. Int. Ed. **45**, 4193-4195 (2006).

327. *Mihovilovic, M.D., F. Rudroff, A. Winninger, T. Schneider, F. Schulz and M.T. Reetz:* Microbial Baeyer-Villinger Oxidation: Stereopreference and Substrate Acceptance of Cyclohexanone Monooxygenase Mutants Prepared by Directed Evolution. Org. Lett. **8**, 1221-1224 (2006).

328. *Nagabhushana, K.S., C. Weidenthaler, S. Hočevar, D. Strmčnik, M. Gaberšček, A.L. Antozzi and G.N. Martelli:* Preparation, Characterization and Properties of Pt-Cu Co-reduced and Pt-on-Cu Skin Type Bimetallic Carbon-Supported (Vulcan XC72) Electrocatalysts. J. New Mater. Electrochem. Syst. **9**, 73-81 (2006).

329. *Nehls, B.S., F. Galbrecht, D.J. Brauer, C.W. Lehmann, U. Scherf and T. Farrell:* Synthesis and Characterization of a Helical Step-Ladder Polyarylene. J. Polym. Sci., Part A: Polym. Chem. **44**, 5533-5545 (2006).

330. *Palkovits, R. and S. Kaskel:* Reverse micelle-mediated synthesis of zirconia with enhanced surface area using alcothermal treatment. J. Mater. Chem. **16**, 391-394 (2006).

331. *Palkovits, R., C.-M. Yang, S. Olejnik and F. Schüth:* Active sites SBA-15 in the Beckmann rearrangement of Cyclohexanone oximer to ε-caprolactam. J. Catal. **243**, 93-98 (2006).

332. *Pan, S.C., J. Zhou and B. List:* Catalytic acylcyanation of imines with acetylcyanide. Synlett **2006**, 3275-3276.

333. *Panda, S.K., W. Schrader and J.T. Andersson:* β-Cyclodextrin as a stationary phase for the group separation of polycyclic aromatic compounds in normal-phase liquid chromatography. J. Chromatogr., A **1122**, 88-96 (2006).

334. *Pavel, C.C., S.-H. Park, A. Dreier, B. Tesche and W. Schmidt:* Structural Defects Induced in ETS-10 by Postsynthesis Treatment with H_2O_2 Solution. Chem. Mater. **18**, 3813-3820 (2006).

335. *Pavel, C.C. and W. Schmidt:* Generation of hierarchical pore systems in the titanosilicate ETS-10 by hydrogen peroxide treatment under microwave irradiation. Chem. Commun. (Cambridge, U. K.) **2006**, 882-884.

336. *Pelster, S.A., W. Schrader and F. Schüth:* Monitoring Temporal Evolution of Silicate Species during Hydrolysis and Condensation of Silicates Using Mass Spectrometry. J. Am. Chem. Soc. **128**, 4310-4317 (2006).

337. *Peng, Z., L. Guo, Z. Zhang, B. Tesche, T. Wilke, D. Ogermann, S. Hu and K. Kleinermanns:* Micelle-Assisted One-Pot Synthesis of Water-Soluble Polyaniline-Gold Composite Particles. Langmuir **22**, 10915-10918 (2006).

338. *Peng, Z., B. Spliethoff, B. Tesche, T. Walther and K. Kleinermanns:* Laser-Assisted Synthesis of Au-Ag Alloy Nanoparticles in Solution. J. Phys. Chem. B **110**, 2549-2554 (2006).

339. *Peters, M.V., R. Goddard and S. Hecht:* Synthesis and Characterization of Azobenzene-Confined Porphyrins. J. Org. Chem. **71**, 7846-7849 (2006).

340. *Peters, M.V., R.S. Stoll, R. Goddard, G. Buth and S. Hecht:* On the Illusive Nature of *o*-Formylazobenzenes: Exploiting the Nucleophilicity of the Azo Group for Cyclization to Indazole Derivatives. J. Org. Chem. **71**, 7840-7845 (2006).

341. *Raballand, W., M. Rotger, V. Boudon, M. Loëte, J. Breidung and W. Thiel:* Stark Effect in X_2Y_4 Molecules: Application to Ethylene. J. Mol. Struct. **780**, 70-79 (2006).

342. *Reetz, M.T.:* High-throughput Screening Systems for Assaying the Enantioselectivity of Enzymes. In: Enzyme Assays – High-throughput Screening, Genetic Selection and Fingerprinting. (Ed.) J.-L. Reymond. Wiley-VCH, Weinheim 2006, 41-76.

343. *Reetz, M.T.:* Practical Protocols for Lipase Immobilization Via Sol-Gel Techniques. In: Immobilization of Enzymes and Cells. 2. Edition. Methods Biotechnol. Vol. 22. (Ed.) J.M. Guisan. Humana Press, Totowa 2006, 65-76.

344. *Reetz, M.T.:* Directed Evolution of Enantioselective Enzymes as Catalysts for Organic Synthesis. Adv. Catal. **49**, 1-69 (2006).

345. *Reetz, M.T., J.D. Carballeira, J. Peyralans, H. Höbenreich, A. Maichele and A. Vogel:* Expanding the Substrate Scope of Enzymes: Combining Mutations Obtained by CASTing. Chem.-Eur. J. **12**, 6031-6038 (2006).

346. *Reetz, M.T., J.D. Carballeira and A. Vogel:* Iterative Saturation Mutagenesis on the Basis of B Factors as a Strategy for Increasing Protein Thermostability. Angew. Chem. **118**, 7909-7915 (2006); Angew. Chem. Int. Ed. **45**, 7745-7751 (2006).

347. *Reetz, M.T., Y. Fu and A. Meiswinkel:* Nonlinear Effects in Rh-Catalyzed Asymmetric Olefin Hydrogenation Using Mixtures of Chiral Monodentate P Ligands. Angew. Chem. **118**, 1440-1443 (2006); Angew. Chem. Int. Ed. **45**, 1412-1415 (2006).

348. *Reetz, M.T. and H. Guo:* Transposition of Allylic Alcohols into Carbonyl Compounds Catalyzed by Rhodium-Phosphinine Complexes. Synlett **2006**, 2127-2129.

349. *Reetz, M.T. and N. Jiao:* Copper-Phthalocyanine Conjugates of Serum Albumins as Enantioselective Catalysts in Diels-Alder Reactions. Angew. Chem. **118**, 2476-2479 (2006); Angew. Chem. Int. Ed. **45**, 2416-2419 (2006).

350. *Reetz, M.T. and X. Li:* An Efficient Catalyst System for the Asymmetric Transfer Hydrogenation of Ketones: Remarkably Broad Substrate Scope. J. Am. Chem. Soc. **128**, 1044-1045 (2006).

351. *Reetz, M.T. and X. Li:* Asymmetric hydrogenation of quinolines catalyzed by iridium complexes of BINOL-derived diphosphonites. Chem. Commun. (Cambridge, U. K.) **2006**, 2159-2160.

352. *Reetz, M.T. and X. Li:* Asymmetric Hydrogenation of β-Keto Esters Using Chiral Diphosphonites. Adv. Synth. Catal. **348**, 1157-1160 (2006).

353. *Reetz, M.T., G. Mehler and O. Bondarev:* Chiral diphosphites and diphosphoramidites as cheap and efficient ligands in Rh-catalyzed asymmetric olefin hydrogenation. Chem. Commun (Cambridge, U. K.) **2006**, 2292-2294.

354. *Reetz, M.T., J. J.-P. Peyralans, A. Maichele, Y. Fu and M. Maywald:* Directed evolution of hybrid enzymes: Evolving enantioselectivity of an achiral Rh-complex anchored to a protein. Chem. Commun. (Cambridge, U. K.) **2000**, 4318-4320.

355. *Reetz, M.T. and M. Surowiec:* Extending the Concept of Mixtures of Chiral Monodentate P-Ligands in Asymmetric Rh-catalyzed Olefin-Hydrogenation: Use of Oxazaphospholidines. Heterocycles **67**, 567-574 (2006).

356. *Reetz, M.T., L.-W. Wang:* High-throughput selection system for assessing the activity of epoxide hydrolases. Comb. Chem. High Throughput Screening **9**, 295-299 (2006).

357. *Reetz, M.T., L.-W. Wang and M. Boccola:* Directed Evolution of Enantioselective Enzymes: Iterative Cycles of CASTing for Probing Protein-Sequence Space. Angew. Chem. **118**, 1258-1263 (2006); Angew. Chem. Int. Ed. **45**, 1236-1241(2006).
Erratum: Angew. Chem. **118**, 2556 (2006); Angew. Chem. Int. Ed. **45**, 2494 (2006).

358. *Ritzkopf, I., S. Vukojević, C. Weidenthaler, J.-D. Grunwaldt and F. Schüth:* Decreased CO production in methanol steam reforming over Cu/ZrO_2 catalysts prepared by the microemulsion technique. Appl. Catal. A **302**, 215-223 (2006).

359. *Rufińska, A., F. Goddard, C. Weidenthaler, M. Bühl and K.-R. Pörschke:* Structural Properties and Dynamics of Five-Coordinate Nickel(II)– π-Allyl Complexes Containing Monodentate Phosphorus Ligands. Organometallics **25**, 2308-2330 (2006).

360. *Salabaş, E.-L., A. Rumplecker, F. Kleitz, F. Radu and F. Schüth:* Exchange Anisotropy in Nanocasted Co_3O_4 Nanowires. Nano Lett. **6**, 2977-2981 (2006).

361. *Sauer, S.P.A., J. Oddershede and J.R. Sabin:* Directional Dependence of the Mean Excitation Energy and Spectral Moments of the Dipole Oscillator Strength

Distribution of Glycine and Its Zwitterion. J. Phys. Chem. A **110**, 8811-8817 (2006).

362. *Schmidt, W.:* Microporous and Mesoporous Catalysts. In: Surface and Nanomolecular Catalysis. (Ed.) R. Richards. CRC/Taylor & Francis, Boca Raton 2006, 95-139.

363. *Schneider, J.J., D. Spickermann, C.W. Lehmann, J. Magull, H.-J. Krüger, J. Ensling and P. Gütlich:* Decacyclene as Complexation Manifold: Synthesis, Structure and Properties of Its Fe_2 and Fe_4 Slipped Triple-Decker Complexes. Chem.-Eur. J. **12**, 1427-1435 (2006).

364. *Schüth, F.:* Mobile Wasserstoffspeicher mit Hydriden der leichten Elemente. Nachr. Chem. **54**, 24-28 (2006).

365. *Schüth, F.:* Schlüsseltechnologie der chemischen Industrie – Heterogene Katalyse. Chem. Unserer Zeit **40**, 92-103 (2006).

366. *Schüth, F., L. Baumes, F. Clerc, D. Demuth, D. Farrusseng, J. Llamas-Galilea, C. Klanner, J. Klein, A. Martinez-Joaristi, J. Procelewska, M. Saupe, S. Schunk, M. Schwickardi, W. Strehlau and T. Zech:* High throughput experimentation in oxidation catalysis: Higher integration and "intelligent" software. Catal. Today **117**, 284-290 (2006).

367. *Schüth, F., B. Bogdanović and M. Felderhoff:* Alanate Based Compounds for Hydrogen Storage. Prepr. Symp. – Am. Chem. Soc., Div. Fuel Chem. **51**, 513-514 (2006).

368. *Schüth, F. and D. Demuth:* High-Throughput-Experimentation in der heterogenen Katalyse. Chem. Ing. Tech. **78**, 851-861 (2006).

369. *Schulenburg, H., M. Hilgendorff, I. Dorbandt, J. Radnik, P. Bogdanoff, S. Fiechter, M. Bron and H. Tributsch:* Oxygen reduction at carbon supported ruthenium-selenium catalysts: Selenium as promoter and stabilizer of catalytic activity. J. Power Sources **155**, 47-51 (2006).

370. *Schunk, S.A., C. Baltes and A. Sundermann:* Exploring structure activity relationships in the acetoxylation of small olefins. Catal. Today **117**, 304-310 (2006).

371. *Schwickardi, M., S. Olejnik, E.-L. Salabaş, W. Schmidt and F. Schüth:* Scalable Synthesis of Activated Carbon with Superparamagnetic Properties. Chem. Commun (Cambridge, U. K.) **2006**, 3987-3989.

372. *Scurto, A.M. and W. Leitner:* Expanding the useful range of ionic liquids: melting point depression of organic salts with carbon dioxide for biphasic catalytic reactions. Chem. Commun. (Cambridge, U. K.) **2006**, 3681-3683.

373. *Seayad, J., A.M. Seayad and B. List:* Catalytic Asymmetric Pictet-Spengler Reaction. J. Am. Chem. Soc. **128**, 1086-1087 (2006).

374. *Smått, J.H., C. Weidenthaler, J.B. Rosenholm and M. Lindén:* Hierarchically Porous Metal Oxide Monoliths Prepared by the Nanocasting Route. Chem. Mater. **18**, 1443-1450 (2006).

375. *Stoll, R.S., N. Severin, J.P. Rabe and S. Hecht:* Synthesis of a Novel Chiral Squaraine Dye and Its Unique Aggregation Behavior in Solution and in Self-Assembled Monolayers. Adv. Mater. **18**, 1271-1275 (2006).

376. *Streukens, G., B. Bogdanović, M. Felderhoff and F. Schüth:* Dependence of dissociation pressure upon doping level of Ti-doped sodium alanate – a possibility for "thermodynamic tailoring" of the system. Phys. Chem. Chem. Phys. **8**, 2889-2892 (2006).

377. *Tesche, B., H. Schulenburg, B. Spliethoff and M.T. Reetz:* Characterization of Catalytic Supports by Means of High-Resolution TEM and SEM in Combination with Shadow-Casting and Decoration Procedures. In: Proc. Microsc. Microanal. Chicago, Ill., July 30-August 3, 2006, (Eds.) P. Kotula u.a., Cambridge University Press, Cambridge, 2006. Microsc. Microanal. **12**, (Suppl. 2) 806CD-807CD (2006).

378. *Theyssen, N., Z. Hou and W. Leitner:* Selective Oxidation of Alkanes with Molecular Oxygen and Acetaldehyde in Compressed (Supercritical) Carbon Dioxide as Reaction Medium. Chem.-Eur. J. **12**, 3401-3409 (2006).

379. *Tian, X., R. Goddard and K.-R. Pörschke:* (β-Diketiminato)palladium Complexes. Organometallics **25**, 5854-5862 (2006).

380. *Tiemann, M., F. Marlow, F. Brieler and M. Lindén:* Early Stages of ZnS Growth Studied by Stopped-Flow Absorption Spectroscopy: Effects of Educt

Concentration of the Nanoparticle Formation. J. Phys. Chem. B **110**, 23142-23147 (2006).

381. *Trapp, O.:* The Unified Equation for the Evaluation of First Order Reactions in Dynamic Electrophoresis. Electrophoresis **27**, 534-541 (2006).

382. *Trapp, O.:* Unified Equation for Access to Rate Constants of First-Order Reactions in Dynamic and On-Column Reaction Chromatography. Anal. Chem. **78**, 189-198 (2006).

383. *Trapp, O.:* Fast and Precise Access to Enantiomerization Rate Constants in Dynamic Chromatography. Chirality **18**, 489-497 (2006).

384. *Trapp, O.:* The unified equation for the evaluation of degenerated first-order reactions in dynamic electrophoresis. Electrophoresis **27**, 2999-3006 (2006).

385. *Trapp, O.:* Maximale Information bei minimaler Analysenzeit. Nachr. Chem. **54**, 1111-1114 (2006).

386. *Trapp, O.:* Neue Techniken zum Hochdurchsatzscreening von Katalysatoren. Jahrb. MPG (Tätigkeitsbericht des MPI für Kohlenforschung) **2006**, 5 Seiten.

387. *Tuttle, T., E. Keinan and W. Thiel:* Understanding the Enzymatic Activity of 4-Oxalocrotonate Tautomerase and its Mutant Analogs: A Computational Study. J. Phys. Chem. B **110**, 19685-19695 (2006).

388. *Tuttle, T., D. Wang, W. Thiel, J. Köhler, M. Hoffmann and J. Weis:* Mechanism of Olefin Hydrosilylation Catalyzed by $RuCl_2(CO)_2(PPh_3)_2$: A DFT Study. Organometallics **25**, 4504-4513 (2006).

389. *Vrcek, V. and M. Bühl:* Conformational Analysis of Ferrocene-Containing Alcohols. A Density Functional Study of Weak OH···Fe Interations. Organometallics **25**, 358-367 (2006).

390. *Wang, Y., Y. Wang, C.-M. Yang, G. Lu and F. Schüth:* Tuning the Mesostructures of Vinyl Silica by Adjusting the Micellar Curvature. Langmuir **22**, 5491-5496 (2006).

391. *Wanner, M., D. Bach, D. Gerthsen, R. Werner and B. Tesche:* Electron holography of thin amorphous carbon films: Measurement of the mean inner

potential and a thickness-independent phase shift. Ultramicroscopy **106**, 341-345 (2006).

392. *Weidenthaler, C., T.J. Frankcombe and M. Felderhoff:* First Crystal Structure Studies of $CaAlH_5$. Inorg. Chem. **45**, 3849-3851 (2006).

393. *Weidenthaler, C., A.-H. Lu, W. Schmidt and F. Schüth:* X-ray photoelectron spectroscopic studies of PAN-based ordered mesoporous carbons (OMC). Microporous Mesoporous Mater. **88**, 238-243 (2006).

394. *Weiss, R., Y. Guo, S. Vukojević, L. Khodeir, R. Boese, F. Schüth, M. Muhler and M. Epple:* Catalytic Activity of Copper Oxide/Zinc Oxide Composites Prepared by Thermolysis of Crystallographically Defined Bimetallic Coordination Compounds. Eur. J. Inorg. Chem. **2006**, 1796-1802.

395. *Weiss, R., S. Vukojevic, C. Baltes, R.N. d'Alnoncourt, M. Muhler and M. Epple:* Copper/zinc L-tartrates : Mixed crystals and thermolysis to a mixture of copper oxide and zinc oxide that is catalytically active in methanol synthesis. Eur. J. Inorg. Chem. **2006**, 4782-4786.

396. *Wilke, G., M.W. Haenel u.a. :* Die Energiewirtschaft sichern. Politische, technologische und wirtschaftliche Implikationen. Eine Denkschrift der Nordrhein-Westfälischen Akademie der Wissenschaften – unter Mitwirkung von G. Wilke und M.W. Haenel, 1-38, Mai (2006).

397. *Wistuba, D., O. Trapp, N. Gel-Moreto, R. Galensa and V. Schurig:* Stereoisomeric Separation of Flavanones and Flavanone-7-*O*-glycosides by Capillary Electrophoresis and Determination of Interconversion Barriers. Anal. Chem. **78**, 3424-3433 (2006).

398. *Yang, J.W. and B. List:* Catalytic Asymmetric Transfer Hydrogenation of α-Ketoesters with Hantzsch Esters. Org. Lett. **8**, 5653-5655 (2006).

399. *Yurchenko, S.N., M. Carvajal, W. Thiel and P. Jensen: Ab Initio* Dipole Moment and Theoretical Rovibrational Intensities in the Electronic Ground State of PH_3. J. Mol. Spectrosc. **239**, 71-87 (2006).

400. *Yurchenko, S.N., W. Thiel and P. Jensen:* Rotational Energy Cluster Formation in XY_3 Molecules: Excited Vibrational of BiH_3 and SbH_3. J. Mol. Spectrosc. **240**, 174-187 (2006).

401. *Yurchenko, S.N., W. Thiel, P. Jensen and P.R. Bunker:* Rotation-Vibration Energy Level Clustering in the $\widetilde{X}\,^2B_1$ Ground Electronic State of PH_2. J. Mol. Spectrosc. **239**, 160-173 (2006).

402. *Yurchenko, S.N., J. Zheng, W. Thiel, M. Carvajal, H. Lin and P. Jensen:* Theoretical Quantitative Spectroscopy: Computer Simulation of Molecular Spectra. In: Remote Sensing of the Atmosphere for Environmental Security. (Ed.) A. Perrin. Springer, Dordrecht 2006, 171-183.

403. *Zaikovskii, V.I., K.S. Nagabhushana, V.V. Kriventsov, K.N. Loponov, S.V. Cherepanova, R.I. Kvon, H. Bönnemann, D.I. Kochubey and E.R. Savinova:* Synthesis and Structural Characterization of Se-Modified Carbon-Supported Ru Nanoparticles for the Oxygen Reduction Reaction. J. Phys. Chem. B **110**, 6881-6890 (2006).

404. *Zaki, M.I., H. Knözinger and B. Tesche:* Structural and Morphological Consequences of High-Temperature Treatments of Hydroxyapatite in the Absence or Presence of HCl Vapor. Langmuir **22**, 749-755 (2006).

405. *Zhaki, M.I., H. Knözinger, B. Tesche and G.A.H. Mekhemer:* Influence of phosphonation and phosphation on surface acid-base and morphological properties of CaO as investigated by in situ FTIR spectroscopy and electron microscopy. J. Colloid Interface Sci. **303**, 9-17 (2006).

406. *Zheng, J., D. Wang, W. Thiel and S. Shaik:* QM/MM Study of Mechanisms for Compound I Formation in the Catalytic Cycle of Cytochrome $P450_{cam}$. J. Am. Chem. Soc. **128**, 13204-13215 (2006).

2007

407. *Aïssa, C. and A. Fürstner:* A Rhodium-Catalyzed C-H Activation/Cycloisomerization Tandem. J. Am. Chem. Soc. **129**, 14836-14837 (2007).

408. *Altun, A., S. Shaik and W. Thiel:* What is the Active Species of Cytochrome P450 during Camphor Hydroxylation? QM/MM Studies of Different Electronic States of Compound I and of Reduced and Oxidized Iron-Oxo Intermediates. J. Am. Chem. Soc. **129**, 8978-8987 (2007).

409. *Bernini, M.C., E.V. Brusau, G.E. Narda, G.E. Echeverria, C.G. Pozzi, G. Punte and C.W. Lehmann:* The Effect of Hydrothermal and Non-Hydrothermal Synthesis on the Formation of Holmium(III) Succinate Hydrate Frameworks. Eur. J. Inorg. Chem. **2007**, 684-693.

410. *Beutner, S., S. Frixel, H. Ernst, T. Hoffmann, I. Hernandez-Blanco, C. Hundsdoerfer, N. Kiesendahl, S. Kock, H.-D. Martin, B. Bayer, P. Noack, A. Perez-Galvez, G. Kock, R. Scherrers, W. Schrader, S. Sell and W. Stahl:* Carotenylflavonoids, a novel group of potent, dual-functional antioxidants. Arkivoc (Gainesville, FL, U. S.) **2007**, (viii) 279-295.

411. *Blackmond, D.G. and M. Klussmann:* Investigating the Evolution of Biomolecular Homochirality. AIChE J. **53**, 2-8 (2007).

412. *Blackmond, D.G. and M. Klussmann:* Spoilt for choice: assessing phase behavior models for the evolution of homochirality. Chem. Commun. (Cambridge, U. K.) **2007**, 3990-3996.

413. *Blum, K., E.S. Chernyshova, R. Goddard, K. Jonas and K.-R. Pörschke:* 4,9-Diazadodeca-1,*trans*-6,11-trienes as Ligands for Nickel(0), Palladium(0), and Platinum(0). Organometallics **26**, 5174-5178 (2007).

414. *Bönnemann, H., G. Khelashvili, S. Behrens, A. Hinsch, K. Skupien and E. Dinjus:* Role of the Platinum Nanoclusters in the Iodide/Triiodide Redox System of Dye Solar Cells. J. Cluster Sci. **18**, 141-155 (2007).

415. *Bönnemann, H. and K.S. Nagabhushana:* Metal Nanoclusters: Synthesis and Strategies for their Size-Control. In: Metal Nanoclusters in Catalysis and Materials Science: The Issue of Size Control. (Eds.) B. Corain, G. Schmid, N. Toshima. Elsevier, Amsterdam 2007, 21-48.

416. *Bönnemann, H., K.S. Nagabhushana and R.M. Richards:* Colloidal nanoparticles Stabilized by Surfactants or Al-organic Derivatives: Preparation and Use as Catalyst Precursors. In: Nanoparticles and Catalysis. (Ed.) D. Astruc. Wiley-VCH, Weinheim 2007, 49-91.

417. *Bogdanović, B., U. Eberle, M. Felderhoff and F. Schüth:* Complex aluminum hydrides. Scr. Mater. **56**, 813-816 (2007).

418. *Bogolowski, N., T. Nagel, B. Lanova, S. Ernst, H. Baltruschat, K.S. Nagabhushana and H. Bönnemann:* Activity of selenium modified ruthenium-electrodes and determination of the real surface area. J. Appl. Electrochem. **37**, 1485-1494 (2007).

419. *Bühl, M.:* Speciation of Peroxovanadium(V) Complexes Studied by First-Principles Molecular Dynamics Simulations and ^{51}V NMR Chemical Shift Computations. In: Vanadium: The Versatile Metal. (Eds.) K. Kustin, J. Costa Pessoa, D.C. Crans. ACS Symp. Ser. **974**, 2007, 312-322.

420. *Bühl, M., R. Diss and G. Wipff:* The Coordination Mode of Nitrate in Uranyl(VI) Complexes. A First-Principles Molecular Dynamics Study. Inorg. Chem. **46**, 5196-5206 (2007).

421. *Bühl, M. and V. Golubnychiy:* Binding of Pertechnetate to Uranyl(VI) in Aqueous Solution. A Density-Functional Molecular Dynamics Study. Inorg. Chem. **46**, 8129-8131 (2007).

422. *Bühl, M. and V. Golubnychiy:* On the Intermediacy of Chlorinated Alkylcobalt Complexes in the Reductive Dehalogenation of Chloroalkenes. A First-Principles Molecular Dynamics Study. Organometallics **26**, 6213-6218 (2007).

423. *Bühl, M., D. Hnyk and J. Macháček:* Computational Studies of Structures and Properties of Metallaboranes. Part 3: Protonated Iron Bis(dicarbollide), [3-Fe-[1,2-$C_2B_9H_{11}$)$_2$H]$^-$. Inorg. Chem. **46**, 1771-1777 (2007).

424. *Bühl, M., I. Vinković Vrček and H. Kabrede:* Dehalogenation of Chloroalkenes at Cobalt Centers. A Model Density Functional Study. Organometallics **26**, 1494-1504 (2007).

425. *Bunker, P.R., W. P. Kraemer, S. N. Yurchenko, W. Thiel, C. F. Neese, J. L. Gottfried and P. Jensen:* New Potential Energy Surfaces for the $\tilde{X}$ and $\tilde{A}$ States of CH_2^+. Mol. Phys. **105**, 1369-1376 (2007).

426. *Cao, Z., Y. Mo and W. Thiel:* Deprotonation Mechanism of NH_4^+ in the *Escherichia coli* Ammonium Transporter AmtB: Insight from QM and QM/MM Calculations. Angew. Chem. **119**, 6935-6939 (2007); Angew. Chem. Int. Ed. **46**, 6811-6815 (2007).

427. *Carballeira, J.D., P. Krumlinde, M. Bocola, A. Vogel, M.T. Reetz and J.-E. Bäckvall:* Directed Evolution and Axial Chirality: Optimization of the Enantioselectivity of *Pseudomonas aeruginosa* Lipase towards the Kinetic Resolution of a Racemic Allene. Chem. Commun. (Cambridge, U.K.) **2007**, 1913-1915.

428. *Chernyshova, E.S., R. Goddard and K.-R. Pörschke: cis,cis, cis*-1,5,9-Cyclododecatriene-Metal Complexes. Organometallics **26**, 4872-4880 (2007).

429. *Chernyshova, E.S., R. Goddard and K.-R. Pörschke:* Mononuclear NHC-Pd-π-Allyl Complexes Containing Weakly Coordinating Ligands. Organometallics **26**, 3236-3251 (2007).

430. *Comotti, M., C. Weidenthaler, W.-C. Li and F. Schüth:* Comparison of gold supported catalysts obtained by using different allotropic forms of titanium dioxide. Top. Catal. **44**, 275-284 (2007).

431. *de M. Cruz, M.T., J. W. de M. Carneiro, D.A.G. Aranda and M. Bühl:* DFT Study on Benzene Adsorption on Small Pd and Pt Clusters. J. Phys. Chem. C **111**, 11068-11076 (2007).

432. *Diez-Holz, C.J., C. Böing, G. Franciò, M. Hölscher and W. Leitner:* Phosphoramidite Quinaphos-Type Ligands for Highly Selective Ni-Catalysed Asymmetric C-C Bond Forming Reactions. Eur. J. Org. Chem. **2007**, 2995-3002.

433. *Dong, W. and F. Marlow:* Tuning of ordered porous skeleton structures. Microporous Mesoporous Mater. **99**, 236-243 (2007).

434. *Felderhoff, M., A. Pommerin, M. Mamatha, B. Bogdanović and F. Schüth:* Tribochemische Synthese von Hydriden durch Hochenergie-Kugelvermahlung. Chem. Ing.-Tech. **79**, 907-911 (2007).

435. *Felderhoff, M., C. Weidenthaler, R. von Helmolt and U. Eberle:* Hydrogen storage: the remaining scientific and technological challenges. Phys. Chem. Chem. Phys. **9**, 2643-2653 (2007).

436. *Fink, G.:* Polymerization on Molecular Catalysts. In: Handbook of Heterogeneous Catalysis, 2. Ed., (Eds.) G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Wiley-VCH, Weinheim 2007.

437. *Fürstner, A.:* Case Studies at the Metathesis/Asymmetric Synthesis Interface. In: Asymmetric Synthesis – The Essentials. (Eds.) M. Christmann, S. Bräse. Wiley-VCH, Weinheim 2007, 262-266.

438. *Fürstner, A., M. Alcarazo, H. Krause and C.W. Lehmann:* Effective Modulation of the Donor Properties of N-Heterocyclic Carbene Ligands by "Through-Space" Communication within a Planar Chiral Scaffold. J. Am. Chem. Soc. **129**, 12676-12677 (2007).

439. *Fürstner, A., M. Bindl and L. Jean:* Concise Total Synthesis of Cruentaren A. Angew. Chem. **119**, 9435-9438 (2007); Angew. Chem. Int. Ed. **46**, 9275-9278 (2007).

440. *Fürstner, A., M. Bonnekessel, J.T. Blank, K. Radkowski, G. Seidel, F. Lacombe, B. Gabor and R. Mynott:* Total Synthesis of Myxovirescin A_1. Chem.-Eur. J. **13**, 8762-8783 (2007).

441. *Fürstner, A., L.C. Bouchez, J.-A. Funel, V. Liepins, F.-H. Porée, R. Gilmour, F. Beaufils, D. Laurich and M. Tamiya:* Total Syntheses of Amphidinolide H and G. Angew. Chem. **119**, 9425-9430 (2007); Angew. Chem. Int. Ed. **46**, 9265-9270 (2007).

442. *Fürstner, A. and P.W. Davies:* Katalytische carbophile Aktivierung: Platin- und Gold-π-Säuren als Katalysatoren. Angew. Chem. **119**, 3478-3519 (2007); Angew. Chem. Int. Ed. **46**, 3410-3449 (2007).

443. *Fürstner, A., D. De Souza, L. Turet, M.D.B. Fenster, L. Parra-Rapado, C. Wirtz, R. Mynott and C.W. Lehmann:* Total Syntheses of the Actin-Binding Macrolides Latrunculin A, B, C, M, S and 16-*epi*-Latrunculin B. Chem.-Eur. J. **13**, 115-134 (2007).

444. *Fürstner, A., B. Fasching, G.W. O'Neil, M.D.B. Fenster, C. Godbout and J. Ceccon:* Toward the Total Synthesis of Spirastrellolide A. Part 3: Intelligence Gathering and Preparation of a Ring-Expanded Analogue. Chem. Commun. (Cambridge, U. K.) **2007**, 3045-3047.

445. *Fürstner, A., E.K. Heilmann and P.W. Davies:* Total Synthesis of the Antibiotic Erypoegin H and Cognates by a $PtCl_2$-Catalyzed Cycloisomerization Reaction.

Angew. Chem. **119**, 4844-4847 (2007); Angew. Chem. Int. Ed. **46**, 4760-4763 (2007).

446. *Fürstner, A., D. Kirk, M.D.B. Fenster, C. Aïssa, D. De Souza, C. Nevado, T. Tuttle, W. Thiel and O. Müller:* Latrunculin Analogues with Improved Biological Profiles by "Diverted Total Synthesis": Preparation, Evaluation, and Computational Analysis. Chem.-Eur. J. **13**, 135-149 (2007).

447. *Fürstner, A., O. Larionov and S. Flügge:* What is Amphidinolide V? Report on a Likely Conquest. Angew. Chem. **119**, 5641-5644 (2007); Angew. Chem. Int. Ed. **46**, 5545-5548 (2007).

448. *Fürstner, A. and T. Nagano:* Total Syntheses of Ipomoeassin B and E. J. Am. Chem. Soc. **129**, 1906-1907 (2007).

449. *Fürstner, A., T. Nagano, C. Müller, G. Seidel and O. Müller:* Total Synthesis and Evaluation of the Actin-Binding Properties of Microcarpalide and a Focused Library of Analogues. Chem.-Eur. J. **13**, 1452-1462 (2007).

450. *Fürstner, A., C. Nevado, M. Waser, M. Tremblay, C. Chevrier, F. Teplý, C. Aïssa, E. Moulin and O. Müller:* Total Synthesis of Iejimalide A-D and Assessment of the Remarkable Actin-Depolymerizing Capacity of These Polyene Macrolides. J. Am. Chem. Soc. **129**, 9150-9161 (2007).

451. *Fürstner, A., K. Radkowski, H. Peters, G. Seidel, C. Wirtz, R. Mynott and C.W. Lehmann:* Total Synthesis, Molecular Editing and Evaluation of a Tripyrrolic Natural Product: The Case of "Butylcycloheptylprodigiosin". Chem.-Eur. J. **13**, 1929-1945 (2007).

452. *Fürstner, A., A. Schlecker and C.W. Lehmann:* Facile Formation of Iodocyclobutenes by a Ruthenium-Catalyzed Enyne Cycloisomerization. Chem. Commun. (Cambridge, U. K.) **2007**, 4277-4279.

453. *Fürstner, A. and C.C. Stimson:* Two Manifolds for Metal-catalyzed Intramolecular Diels-Alder Reactions of Unactivated Alkynes. Angew. Chem. **119**, 9001-9005 (2007); Angew. Chem. Int. Ed. **46**, 8845-8849 (2007).

454. *Ganguly, B., D. Koley and W. Thiel:* Intra-annular Cyclophane Diamines as Proton Sponges: A Computational Study. Tetrahedron **63**, 7970-7976 (2007).

455. *Gavrilov, K.N., S.E. Lyubimov, O.G. Bondarev, M.G. Maksimova, S.V. Zheglov, P.V. Petrovskii, V.A. Davankov and M.T. Reetz:* Chiral Ionic Phosphites and Diamidophosphites: A Novel Group of Efficient Ligands for Asymmetric Catalysis. Adv. Synth. Catal. **349**, 609-616 (2007).

456. *Geerke, D.P., S. Thiel, W. Thiel and W. F. van Gunsteren:* Combined QM/MM Molecular Dynamics Study on a Condensed-Phase S_N2 Reaction at Nitrogen: The Effect of Explicitly Including Solvent Polarization. J. Chem. Theory Comp. **3**, 1499-1509 (2007).

457. *Geethalakshmi, K. R., M. P. Waller and M. Bühl*: The presumption of innocence? A DFT directed verdict on oxidized amavadin and vanadium catecholate complexes. Inorg. Chem. **46**, 11297-11307 (2007).

458. *Geier, J., H. Willner, C.W. Lehmann and F. Aubke:* Formation of Hexacarbonylmanganese(I) Salts, $[Mn(CO)_6]^+X^-$, in Anhydrous HF. Inorg. Chem. **46**, 7210-7214 (2007).

459. *Hoffmann, P., U. Häusig, P. Schulze and D. Belder:* Mikrofluidische Glas-Chips mit integriertem Nanospray-Emitter zur Kopplung mit der Massenspektrometrie. Angew. Chem. **119**, 5000-5003 (2007); Angew. Chem. Int. Ed. **46**, 4913-4916 (2007).

460. *Hollmann, F., A. Taglieber, F. Schulz and M.T. Reetz:* A Light-Driven Stereoselective Biocatalytic Oxidation. Angew. Chem. **119**, 2961-2964 (2007); Angew. Chem. Int. Ed. **46**, 2903-2906 (2007).

461. *Hou, Z., N. Theyssen and W. Leitner:* Palladium nanoparticles stabilised on PEG-modified silica as catalysts for the aerobic alcohol oxidation in supercritical carbon dioxide. Green Chem. **9**, 127-132 (2007).

462. *Jose, D.A., P. Kar, D. Koley, B. Ganguly, W. Thiel, G. Ramakrishna, D. K. Palit, H. N. Ghosh and A. Das:* Phenol and Catechol-Based Ruthenium(II) Polypyridyl Complexes as Colorimetric Sensors for Fluoride Ion. Inorg. Chem. **46**, 5576-5584 (2007).

463. *Kästner, J., S. Thiel, H. M. Senn, P. Sherwood and W. Thiel:* Exploiting QM/MM Capabilities in Geometry Optimization: A Microiterative Approach Using Electrostatic Embedding. J. Chem. Theory Comput. **3**, 1064-1072 (2007).

464. *Karafilidis, C., K. Angermund, B. Gabor, A. Rufińska, R.J. Mynott, G. Breitenbruch, W. Thiel and G. Fink:* Mikrostruktur von Polynorbornen. Angew. Chem. **119**, 3819-3823 (2007); Angew. Chem. Int. Ed. **46**, 3745-3749 (2007).

465. *Keal, T. W., A. Koslowski and W. Thiel:* Comparison of Algorithms for Conical Intersection Optimisation Using Semiempirical Methods. Theor. Chem. Acc. **118**, 837-844 (2007).

466. *Khelashvili, G., S. Behrens, A. Hinsch, W. Habicht, D. Schild, A. Eichhöfer, R. Sastrawan, K. Skupien, E. Dinjus and H. Bönnemann:* Preparation and Characterization of Low Platinum Loaded Pt:SnO_2 Electrocatalytic Films for Screen Printed Dye Solar Cell Counter Electrode. Thin Solid Films **515**, 4074-4079 (2007).

467. *Klussmann, M., T. Izumi, A.J.P. White, A. Armstrong, D.G. Blackmond:* The Emergence of Solution Phase Homochirality via Crystal Engineering of Amino Acids. J. Am. Chem. Soc. **129**, 7657-7660 (2007).

468. *Konjhodzic, D., S. Schröter and F. Marlow:* Ultra-low refractive index mesoporous substrates for waveguide structures. Phys. Status Solidi A **204**, 3676-3688 (2007).

469. *Küppers, T., E. Bernhardt, R. Eujen, H. Willner and C.W. Lehmann:* $[Me_3Si][RCB_{11}F_{11}]$ – Synthese und Eigenschaften. Angew. Chem. **119**, 6462-6465 (2007; Angew. Chem. Int. Ed. **46**, 6346-6349 (2007).

470. *Küppers, T., E. Bernhardt, C.W. Lehmann and H. Willner:* The Tetracyanoboronic Acids $H[B(CN)_4]\cdot n\ H_2O$, n = 0,1,2. Z. Anorg. Allg. Chem. **633**, 1666-1672 (2007).

471. *Lehmann, C.W. and F. Stowasser:* The Crystal Structure of Anhydrous β-Caffeine as Determined from X-ray Powder-Diffraction Data. Chem.-Eur. J. **13**, 2908-2911 (2007).

472. *Leitner, W.:* Supercritical and Compressed Carbon Dioxide as Reaction Medium and Mass Separating Agent for Hydrogenation Reactions Using Organometallic Catalysts. In: Handbook of Homogeneous Hydrogenation. (Ed.) J.G. de Vries. Wiley-VCH, Weinheim **2007**, 1361-1375.

473. *Li, X. and B. List:* Catalytic asymmetric hydrogenation of aldehydes. Chem. Commun. (Cambridge, U. K.) **2007**, 1739-1741.

474. *Lian, B., C.M. Thomas, O.L. Casagrande, C.W. Lehmann, T. Roisnel and J.-F. Carpentier:* Aluminium and Zinc Complexes Based on an Amino-Bis(pyrazol)Ligand: Synthesis, Structures, and Use in MMA and Lactide Polymerization. Inorg. Chem. **46**, 328-340 (2007).

475. *List, B.:* Biocatalysis and Organocatalysis: Asymmetric Synthesis Inspired by Nature. In: Asymmetric Synthesis – The Essentials. (Eds.) Christmann, M., S. Bräse. Wiley-VCH, Weinheim 2007, 161-165.

476. *Lu, A.-H., W.-C. Li, Z. Hou and F. Schüth:* Molecular level dispersed Pd clusters in the carbon walls of ordered mesoporous carbon as a highly selective alcohol oxidation catalyst. Chem. Commun. (Cambridge, U. K.) **2007**, 1038-1040.

477. *Lu, A.-H., E.-L. Salabaş and F. Schüth:* Magnetische Nanopartikel: Synthese, Stabilisierung, Funktionalisierung und Anwendung. Angew. Chem. **119**, 1242-1266 (2007); Angew. Chem. Int. Ed. **46**, 1222-1244 (2007).

478. *Marlow, F., A.S.G. Khalil and M. Stempniewicz:* Circular mesostructures: solids with novel symmetry properties. J. Mater. Chem. **17**, 2168-2182 (2007).

479. *Martin, N.J.A., L. Ozores and B. List:* Organocatalytic Asymmetric Transfer Hydrogenation of Nitroolefins. J. Am. Chem. Soc. **129**, 8976-8977 (2007).

480. *Matoussevitch, N., A. Gorschinski, W. Habicht, J. Bolle, E. Dinjus, H. Bönnemann and S. Behrens:* Surface Modification of Metallic Co Nanoparticles. J. Magn. Magn. Mater. **311**, 92-96 (2007).

481. *Meudtner, R.M., M. Ostermeier, R. Goddard, C. Limberg and S. Hecht:* Multifunctional "Clickates" as Versatile Extended Heteroaromatic Building Blocks: Efficient Synthesis via Click Chemistry, Conformational Preferences, and Metal Coordination. Chem.-Eur. J. **13**, 9834-9840 (2007).

482. *Mladenovic, M., T. Schirmeister, S. Thiel, W. Thiel and B. Engels:* About the Importance of the Active Site Histidine for the Activity of Epoxide or Aziridine Based Inhibitors of Cysteine Proteases. ChemMedChem **2**, 120-128 (2007).

483. *Mroginski, M.A., F. Mark, W. Thiel and P. Hildebrandt:* Quantum Mechanics/Molecular Mechanics Calculation of the Raman Spectra of the Phycocyanobilin Chromophore in α-C-Phycocyanin. Biophys. J. **93**, 1885-1894 (2007).

484. *Mukherjee, S. and B. List:* Radical Catalysis. Nature (London) **447**, 152-153 (2007).

485. *Mukherjee, S. and B. List:* Chiral Counteranions in Asymmetric Transition-Metal Catalysis: Highly Enantioselective Pd/Brønsted Acid-Catalyzed Direct α-Allylation of Aldehydes. J. Am. Chem. Soc. **129**, 11336-11337 (2007).

486. *Muller, J.-L., J. Klankermayer and W. Leitner:* Poly(ethylene glycol) stabilized Co nanoparticles as highly active and selective catalysts for the Pauson-Khand reactions. Chem. Commun. (Cambridge, U. K.) **2007**, 1939-1941.

487. *Muller, J.-L., A. Rickers and W. Leitner:* Raney Cobalt: An Effective and Recyclable Catalyst for the Pauson-Khand Reaction. Adv. Synth. Catal. **349**, 287-291 (2007).

488. *Nagabhushana, K. S., E. Dinjus, H. Bönnemann, V. Zaikovskii, C. Hartnig, G. Zehl, I. Dorbrandt, S. Fiechter and B. Bogdanoff:* Reductive Annealing for Generating Se Doped 20 wt% Ru/C Cathode Catalysts for the Oxygen Reduction Reaction. J. Appl. Electrochem. **37**, 1515-1522 (2007).

489. *Occhipinti, G., H.-R. Bjørsvik, K.W. Törnroos, A. Fürstner and V.R. Jensen:* The First Imidazolium-Substituted Metal Alkylidene. Organometallics **26**, 4383-4385 (2007).

490. *Otte, N., M. Scholten and W. Thiel:* Looking at Self-Consistent-Charge Density Functional Tight Binding from a Semiempirical Perspective. J. Phys. Chem. A **111**, 5751-5755 (2007).

491. *Pan, S.C. and B. List:* Catalytic One-Pot, Three-Component Acyl-Strecker Reaction. Synlett **2007**, 318-320.

492. *Pan, S.C. and B. List:* Catalytic Asymmetric Three-Component Acyl-Strecker Reaction. Org. Lett. **9**, 1149-1151 (2007).

493. *Pan, S.C., J. Zhou and B. List:* Katalytisch-asymmetrische Acylcyanierung von Iminen. Angew. Chem. **119**, 618-620 (2007); Angew. Chem. Int. Ed. **46**, 612-614 (2007).

494. *Panda, S.K., J.T. Andersson and W. Schrader:* Mass-spectrometric analysis of complex volatile and non-volatile crude oil components: a challenge. Anal. Bioanal. Chem. **389**, 1329-1339 (2007).

495. *Panda, S.K., W. Schrader, A. al-Hajji and J. T. Andersson:* Distribution of Polycyclic Aromatic Sulfur Heterocycles in Three Saudi Arabian Crude Oils as Determined by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy Fuels **21**, 1071-1077 (2007).

496. *Pavel, C.C., B. Zibrowius, E. Löffler and W. Schmidt:* On the influence of ion exchange on the local structure of the titanosilicate ETS-10. Phys. Chem. Chem. Phys. **9**, 3440-3446 (2007).

497. *Pelster, S.A., R. Kalamajka, W. Schrader and F. Schüth:* Monitoring the Nucleation of Zeolites by Mass Spectrometry. Angew. Chem. **119**, 2349-2352 (2007); Angew. Chem. Int. Ed. **46**, 2299-2302 (2007).

498. *Pelster, S., F. Schüth and W. Schrader:* A detailed study on the use of Electrospray Mass Spectrometry to investigate speciation in concentrated silicate solutions. Anal. Chem. **79**, 6005-6012 (2007).

499. *Pelster, S.A., B. Weimann, B.B. Schaack, W. Schrader and F. Schüth:* Dynamics of Silicate Species in Solution Studied by Mass Spectrometry with Isotopically Labeled Compounds. Angew. Chem. **119**, 6794-6797 (2007); Angew. Chem. Int. Ed. **46**, 6674-6677 (2007).

500. *Peters, M.V., R. Goddard and S. Hecht:* Synthesis and Characterization of Azobenzene-Confined Porphyrins. J. Org. Chem. **71**, 7846-7849 (2007).

501. *Polarz, S., A. Orlov, F. Schüth and A.-H. Lu:* About the preparation of high-surface area zinc oxide with ordered porosity, different pore-sizes and nanocrystalline walls. Chem.-Eur. J. **13**, 592-597 (2007).

502. *Prechtl, M.H.G., M. Hölscher, Y. Ben-David, N. Theyssen, R. Loschen, D. Milstein and W. Leitner:* H/D Exchange at Aromatic and Heteroaromatic Hydrocarbons Using D_2O as the Deuterium Source and Ruthenium Dihydrogen

Complexes as the Catalyst. Angew. Chem. **119**, 2319-2322 (2007); Angew. Chem. Int. Ed. **46**, 2269-2272 (2007).

503. *Prechtl, M.H.G., B.-D. Yehoshoa, D. Giunta, S. Busch, Y. Taniguchi, W. Wisniewski, H. Görls, R.J. Mynott, N. Theyssen, D. Milstein and W. Leitner:* Synthesis and Characterisation of Nonclassical Ruthenium Hydride Complexes Containing Chelating Bidentate and Tridentate Phosphine Ligands. Chem.-Eur. J. **13**, 1539-1546 (2007).

504. *Procelewska, J., J. Llamas Galilea, F. Clerc, D. Farrusseng and F. Schüth:* Computational Methods in the Development of a Knowledge-Based System for the Prediction of Solid Catalyst Performance. Combinat. Chem. High Throughput Screening **10**, 37-50 (2007).

505. *Reetz, M.T.:* Directed Evolution of Enzymes for Asymmetric Syntheses. In: Asymmetric Synthesis – The Essentials. (Eds.) M. Christmann, S. Bräse. Wiley-VCH, Weinheim 2007, 207-211.

506. *Reetz, M.T.:* Evolution im Reagenzglas: Ein Beitrag zur Weißen Biotechnologie. In: Schriften der Gesellschaft zur Förderung der Westfälischen Wilhelms-Universität zu Münster e.V. (Hrsg.) O. Schober. Verlag Aschendorff, Münster 2007, Heft 81.

507. *Reetz, M.T.:* Evolution in the Test-Tube as a means to Create Selective Biocatalysts. Chimia **6**, 100-103 (2007).

508. *Reetz, M.T. and O. Bondarev:* Mixtures of Chiral Phosphorous Acid Diesters and Achiral P Ligands in the Enantio- and Diastereoselective Hydrogenation of Ketimines. Angew. Chem. **119**, 4607-4610 (2007); Angew. Chem. Int. Ed. **45**, 4523-4526 (2007). Korrektur: Angew. Chem. **119**, 8253 (2007).

509. *Reetz, M.T. and J.D. Carballeira:* Iterative Saturation Mutagenesis (ISM) for Rapid Directed Evolution of Functional Enzymes. Nat. Protoc. **2**, 891-903 (2007).

510. *Reetz, M.T. and B. Hauer:* Biocatalysis and Biotransformation. Frontiers of Biocatalysis: Theory and Applications. Curr. Opin. Chem. Biol. **11**, 172-173 (2007).

511. *Reetz, M.T., R. Mondière and J.D. Carballeira:* Enzyme Promiscuity: First Protein-Catalyzed Morita–Baylis–Hillman Reaction. Tetrahedron Lett. **48**, 1679-1681 (2007).

512. *Reetz, M.T., M. Puls, J.D. Carballeira, A. Vogel, K.-E. Jaeger, T. Eggert, W. Thiel, M. Bocola and N. Otte:* Learning from Directed Evolution: Further Lessons from Theoretical Investigations into Cooperative Mutations in Lipase Enantioselectivity. ChemBioChem **8**, 106-112 (2007).

513. *Reetz, M.T., M. Rentzsch, A. Pletsch, M. Maywald, P. Maiwald, J.J.-P. Peyralans, A. Maichele, Y. Fu, N. Jiao, F. Hollmann, R. Mondière and A. Taglieber:* Directed Evolution of Enantioselective Hybrid Catalysts: A Novel Concept in Asymmetric Catalysis. Tetrahedron **63**, 6404-6414 (2007).

514. *Reetz, M. T.:* Controlling the Selectivity and Stability of Proteins by New Strategies in Directed Evolution: The Case of Organocatalytic Enzymes. In: Ernst Schering Foundation Symposium Proceedings. Springer Verlag, Berlin 2007.

515. *Rehder, D., T. Polenova and M. Bühl:* Vanadium-51 NMR. Ann. Rep. NMR Spectrosc. **62**, 49-114 (2007).

516. *Ritterskamp, P., A. Kuklya, M.-A.. Wüstkamp, K. Kerpen, C. Weidenthaler and M. Demuth:* Ein auf Titandisilicid basierender, halbleitender Katalysator zur Wasserspaltung mit Sonnenlicht – reversible Speicherung von Sauerstoff und Wasserstoff. Angew. Chem. **119**, 7917-7921 (2007); Angew. Chem. Int. Ed. **46**, 7770-7774 (2007).

517. *Rodrigues, A.-S., E. Kirillov, C.W. Lehmann, T. Roisnel, B. Vuillemin, A. Razavi and J.-F. Carpentier:* Allyl *ansa*-Lanthanidocenes: Single-Component, Single-Site Catalysts for Controlled Syndiospecific Styrene and Styrene-Ethylene (Co)Polymerization. Chem.-Eur. J. **13**, 5548-5565 (2007).

518. *Rohe, B., R. Weiss, S. Vukojević, C. Baltes, M. Muhler, M. Tausch and M. Epple:* CuO/ZnO Nanoparticles in a Matrix of Amorphous Silica as High-Surface Precursors for Methanol Synthesis. Eur. J. Inorg. Chem. **2007**, 1723-1727.

519. *Rumplecker, A., F. Kleitz, E.-L. Salabaş and F. Schüth:* Hard Templating Pathways for the Synthesis of Nanostructured Porous Co_3O_4. Chem. Mater. **19**, 485-496 (2007).

520. *Rumplecker, A., B. Zibrowius, W. Schmidt, C.-M. Yang and F. Schüth:* Evolution of mesoporosity and microporosity of SBA-15 during a treatment with sulfuric acid. In: Recent Progress in Mesostructured Materials. (Eds.) D. Zhao, S. Qiu, Y. Tang, C. Yu. Stud. Surf. Sci. Catal. **165**, 195-199 (2007).

521. *Schmidt, W., U. Wilczok, C. Weidenthaler, O. Medenbach, R. Goddard, G. Buth and A. Cepak:* Preparation and Morphology of Pyramidal MFI Single-Crystal Segments. J. Phys. Chem. B **111**, 13538-13543 (2007).

522. *Schmitkamp, M., D. Chen, W. Leitner, J. Klankermayer and G. Franciò:* Enantioselective catalysis with *tropos* ligands in chiral ionic liquids. Chem. Commun. (Cambridge, U. K.) **2007**, 4012-4014.

523. *Schrader, W., P.P. Handayani, C. Burstein and F. Glorius:* Investigating organocatalytic reactions: mass spectrometric studies of a conjugate *umpolung* reaction. Chem. Commun. (Cambridge, U. K.) **2007**, 716-718.

524. *Schüth, F. and F. Marlow:* Colloidal Crystals Find New Order (News and Views). Nature (London) **449**, 550-551 (2007).

525. *Scurto, M., E. Newton, R.R. Weikel, L. Draucker, J. Hallett, C.L. Liotta, W. Leitner and C.A. Eckert:* Melting Point Depression of Ionic Liquids with CO_2: Phase Equilibria. Ind. Eng. Chem. Res. (2007), DOI: 10.1021/ie070889t.

526. *Senn H.M. and W. Thiel:* QM/MM Studies of Enzymes. Curr. Opin. Chem. Biol. **11**, 182-187 (2007).

527. *Senn, H.M. and W. Thiel:* QM/MM Methods for Biological Systems. Top. Curr. Chem. **268**, 173-290 (2007).

528. *Stempniewicz, M., A.S.G. Khalil, M. Rohwerder and F. Marlow:* Diffusion in Coiled Pores – Learning from Microrelease and Microsurgery. J. Am. Chem. Soc. **129**, 10561-10566 (2007).

529. *Stempniewicz, M., M. Rohwerder and F. Marlow:* Release from Silica SBA-3-like Mesoporous Fibers: Cross-Wall Transport and External Diffusion Barrier. ChemPhysChem **8**, 188-194 (2007).

530. *Stempniewicz, M., M. Rohwerder and F. Marlow:* Release of Guest Molecules from Modified Mesoporous Silica. In: Recent Progress in Mesostructured Materials. (Ed.) D. Zhao. Stud. Surf. Sci. Catal. **165**, 825-828 (2007).

531. *Taglieber, A., H. Höbenreich, J.D. Carballeira, R.J.G. Mondière and M.T. Reetz:* Alternate-Site Enzyme Promiscuity. Angew. Chem. **119**, 8751-8754 (2007); Angew. Chem. Int. Ed. **46**, 8597-8600 (2007).

532. *Tegeder, P., S. Hagen, F. Leyßner, M.V. Peters, S. Hecht, T. Klamroth, P. Saalfrank and M. Wolf:* Electronic structure of the molecular switch tetra-*tert*-butyl-azobenzene adsorbed on Ag(111). Appl. Phys. A **88**, 465-472 (2007).

533. *Tesche, B., F.C. Jentoft, R. Schlögl, S.R. Bare, L.T. Nemeth, S. Valencia and A. Corma:* Electronmicroscopical Characterization of Zeolite Structures. Microsc. Microanal. **13**, Suppl. 3, 264-265 (2007).

534. *Thiel, W.:* Fast Semiempirical Calculations. In: Molecular Quantum Mechanics: Analytic Gradients and Beyond. (Eds.) A. G. Csaszar, G. Fogarasi, H. F. Schaefer and P. G. Szalay, ELTE Institute of Chemistry, Budapest 2007, 119-121.

535. *Trapp, O.*: A dynamic molecular probe to investigate catalytic effects and Joule heating in enantioselective MEKC. Electrophoresis **28**, 691-696 (2007).

536. *Trapp, O.:* Durchsatzsteigerung von Trenntechniken durch “Multiplexing”. Angew. Chem. **119**, 5706-5710 (2007); Angew. Chem. Int. Ed. **46**, 5609-5613 (2007).

537. *Trapp, O., S.K. Weber, S. Bauch and W. Hofstadt:* High-throughput screening of catalysts by combining reaction and analysis. Angew. Chem. **119**, 7447-7451 (2007); Angew. Chem. Int. Ed. **46**, 7307-7310 (2007).

538. *Tuttle, T., E. Kraka, W. Thiel and D. Cremer:* A QM/MM Study of the Bergman Reaction of Dynemicin A in the Minor Groove of DNA. J. Phys. Chem. B **111**, 8321-8328 (2007).

539. *Tuttle, T. and W. Thiel:* Substrate Orientation in 4-Oxalocrotonate Tautomerase and its Effect on QM/MM Energy Profiles. J. Phys. Chem. B **111**, 7665-7674 (2007).

540. *Tuttle, T., D. Wang, W. Thiel, J. Köhler, M. Hofmann and J. Weis:* Mechanism of Olefin Hydrosilylation Catalyzed by $[RuCl(NCCH_3)_5]^+$: A DFT Study. J. Organomet. Chem. **692**, 2282-2290 (2007).

541. *van Esch, J., E.H. Valkenier, S. Hartwig and S. Hecht:* Foldamers at Interfaces. In: Foldamers: Structure, Propereties, and Application". (Eds.) S. Hecht, I. Huc. Wiley-VCH, Weinheim 2007, 403-425.

542. *Vidaković, T., M. Christov, K. Sundmacher, K.S. Nagabhushana, W. Fei, S. Kinge and H. Bönnemann:* PtRu colloidal catalysts: Characterisation and determination of kinetics for methanol oxidation. Electrochim. Acta **52**, 2277-2284 (2007).

543. *Vinković Vrček, I., M. Biruš and M. Bühl:* Structure and Bonding of Vanadium(V) Complexes with Hydroxyurea in Aqueous Solution: Density Functional Theory Investigations of Isomers and Intramolecular Rearrangements. Inorg. Chem. **46**, 1488-1501 (2007).

544. *Voss, T., G. T. Svacha, E. Mazur, S. Müller, C. Ronning, D. Konjhodzic and F. Marlow:* High Order Waveguide Modes in ZnO Nanowires. Nano Lett. **7**, 3675-3680 (2007).

545. *Waller, M. P., H. Braun, N. Hojdis and M. Bühl:* Geometries of Second-Row Transition-Metal Complexes from Density-Functional Theory. J. Chem. Theor. Comput. **3**, 2234-2242 (2007).

546. *Waller, M.P. and M. Bühl:* Vibrational Corrections to Geometries of Transition Metal Complexes from Density Functional Theory. J. Comput. Chem. **28**, 1531-1537(2007).

547. *Waller, M.P., M. Bühl, K. R. Geethalakshmi, D. Wang and W. Thiel:* ^{51}V NMR Chemical Shifts Calculated from QM/MM Models of Vanadium Chloroperoxidase. Chem.-Eur. J. **13**, 4723-4732 (2007).

548. *Yang, C.-M., H.-A. Lin, B. Zibrowius, B. Spliethoff, F. Schüth, S.-C. Liou, M.-W. Chu and C.-H. Chen:* Selective Surface Functionalization and Metal Deposition

in the Micropores of Mesoporous Silica SBA-15. Chem. Mater. **19**, 3205-3211 (2007).

549. *Yang, J.W., M. Stadler and B. List:* Prolin-katalysierte Mannich-Reaktion von Aldehyden mit *N*-Boc-Iminen. Angew. Chem. **119**, 615-617 (2007); Angew. Chem. Int. Ed. **46,** 609-611 (2007).

550. *Yang, J.W., M. Stadler and B. List:* Practical Proline-Catalyzed Asymmetric Mannich Reaction of Aldehydes with *N*-Boc-imines. Nat. Protoc. **2**, 1937-1942 (2007).

551. *Yurchenko, S.N., W. Thiel and P. Jensen:* Theoretical ROVibrational Energies (TROVE): A Robust Numerical Approach to the Calculation of Rovibrational Energies for Polyatomic Molecules. J. Mol. Spectrosc. **245**, 126-140 (2007).

552. *Zhang, J., M. Comotti, F. Schüth, R. Schlögl and D. Su:* Commercial Fe- or Co-containing Carbon Nanotubes as Catalysts for NH_3 Decomposition. Chem. Commun. (Cambridge, U. K.) **2007**, 1916-1918.

553. *Zheng, J., A. Altun and W. Thiel:* Common System Setup for the Entire Catalytic Cycle of Cytochrome $P450_{cam}$ in Quantum Mechanical/Molecular Mechanical Studies. J. Comput. Chem. **28**, 2147-2158 (2007).

554. *Zhou, J. and B. List:* Organocatalytic Asymmetric Reaction Cascade to Substituted Cyclohexylamines. J. Am. Chem. Soc. **129**, 7498-7499 (2007).

555. *Zhou, J. and B. List:* Synthesis of *trans*-3-Substituted Cyclohexylamines via Brønsted Acid Catalyzed and Substrate-Mediated Triple Organocatalytic Cascade Reaction. Synlett **2007**, 2037-2040.

6.2 List of Invited Talks Given by Members of the Institute (2005-2007)

2005

Aïssa, C., Semaine d'Etude de Chimie Organique 42*,* Urrugne, FR, 24 May 2005

Belder, D., Universität Ulm, DE, 23 February 2005

Belder, D., University of Twente, Enschede, NL, 30 April 2005

Belder, D., Universität Regensburg, DE, 29 June 2005

Belder, D., Technische Universität München, DE, 2 November 2005

Belder, D., Mini-Symposium Lab on Microchip, Siegen, DE, 17-18 November 2005

Bühl, *M.,* GDCh-Diskussionstagung, Bochum, DE, 17-18 January 2005

Bühl, *M.,* Universität Stuttgart, DE, 1 February 2005.

Bühl, *M.,* Universität Bonn, DE, 19 April 2005.

Bühl, *M.,* 12th International Conference on Biological Inorganic Chemistry, Ann Arbor, Michigan, USA, 31 July-5 August 2005.

Bühl, *M.,* 41st Symposium on Theoretical Chemistry, Innsbruck, AT, 5-7 September 2005.

Bühl, *M.,* Université de Strasbourg, FR, 21 September 2005.

Felderhoff, M., Fuel Cell 2005, Stuttgart, DE, 24-25 September 2005

Felderhoff, M., 361st Heraeus-Seminar, Bad Honnef, DE, 28 October 2005

Fink, G., Makromolekulares Kolloquium, Freiburg, DE, 24-26 February 2005

Fink, G., GDCh, Universität Paderborn, DE, 18 April 2005

Fink, G., 2nd Blue Sky Conference on Catalytic Olefin Polymerization and 4th JAIST/JLPO Workshop on Heterogeneous Ziegler-Natta Catalysis, Sorrento, IT, 26 June-1 July 2005

Fink, G., Technische Universität Berlin, DE, 12 June 2005

Fink, G., Eindhoven University of Technology, NL, 8 September 2005

Fink, G., Makromolekulares Symposium, Hamburg, DE, 10-12 October 2005

Fink, G., TICONA GmbH, Industriepark Höchst, DE, 5 December 2005

Fürstner, A., GDCh, Leibniz-Institut für Organische Katalyse an der Universität Rostock, DE, 20 January 2005

Fürstner, A., GDCh, Universität Bielefeld, DE, 27 January 2005

Fürstner, A., GDCh, Universität Leipzig, DE, 03 February 2005

Fürstner, A., Johnson and Johnson Pharmaceutical Research and Development, Raritan, NJ, USA, 23 February 2005

Fürstner, A., GlaxoSmithKline, King of Prussia, PA, USA, 24 February 2005

Fürstner, A., Princeton University, NJ, USA, 25 February 2005

Fürstner, A., FLOHET 6, University of Florida, FL, USA, 28 February 2005

Fürstner, A., Bristol-Mayer-Squibb-Lecture, Philadelphia, PA, USA, 2 March 2005

Fürstner, A., Abbott Process Chemistry Lecture, Madison, WI, USA, 3 March 2005

Fürstner, A., 1st Austrian-German-Italian Meeting "Organic Chemistry", Vienna, AT, 2 April 2005

Fürstner, A., GDCh, Ludwig-Maximilian-Universität München, DE, 10 March 2005

Fürstner, A., Universität Leiden, NL, 23 May 2005

Fürstner, A., UCB Corporate Communication, Braine-l'Alleud, BE, 3 June 2005

Fürstner, A., Merck Lecture 2005, Imperial College, London, UK, 7 June 2005

Fürstner, A., Chemistry Course 2005, Boehringer Ingelheim, Vienna, AT, 16-17 June 2005

Fürstner, A., Université Claude Bernard Lyon I, Villeurbanne, FR, 28 June 2005

Fürstner, A., GDCh, Universität Göttingen, DE, 30 June 2005

Fürstner, A., International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis, OMCOS 13, Geneva, CH, 18 July 2005

Fürstner, A., The International Society of Heterocyclic Chemistry (ISHC) Junior Award Lecture, Palermo, IT, 4 July 2005

Fürstner, A., 1st German-French Congress, Goslar, DE, 8 September 2005

Fürstner, A., Merck, Rome, IT, 19 September 2005

Fürstner, A., DIP-Symposium, Haifa, IL, 29 September 2005

Fürstner, A., GDCh, Bayer CropScience, Monheim, DE, 12 October 2005

Fürstner, A., National Taiwan University, Taipei, TW, 28 October 2005

Fürstner, A., 10th Taiwan International Chemical Conference, Tsing Hua University, Hsinchu, TW, 29 October 2005

Fürstner, A., Shanghai Institute of Organic Chemistry, CN, 1 November 2005

Fürstner, A., Eisai Co. Ltd., Tsukuba, JP, 4 November 2005

Fürstner, A., 1st Asian-European Symposium on Metal-Mediated Efficient Organic Synthesis, Nagasaki, JP, 7 November 2005

Fürstner, A., Mukaiyama Award Lecture, Waseda University Tokyo, JP, 9 November 2005

Fürstner, A., BASF, Ludwigshafen, DE, 25 November 2005

Fürstner, A., Seminar Bayer HealthCare, Wuppertal, DE, 6 December 2005

Fürstner, A., GDCh, Otto-von-Guericke-Universität Magdeburg, DE, 8 December 2005

Haenel, *M.W.*, International Conference on Coal Science and Technology, Okinawa, JP, 11 October 2005

Haenel, *M.W.*, 63. Sitzung des DGMK-Arbeitskreises Kohlenveredlung, Institut für Thermische Energietechnik, Universität Kassel, DE, 18 November 2005

Hecht, S., MPI für Polymerforschung, Mainz, DE, 18 January 2005

Hecht, S., OC-Kolloquium, Universität Dortmund, DE, 1 February 2005

Hecht, S., ERA-Chemistry Workshop, Mainz, DE, 14 February 2005

Hecht, S., CERC-3 Workshop on Functional Molecular Nanostructures, Baden-Baden, DE, 4 May 2005

Hecht, S., Hochschullehrernachwuchs-Workshop der Fachgruppe Makromolekulare Chemie, BASF Ludwigshafen, DE, 4 July 2005

Hecht, S., 8th SPSJ International Polymer Conference, Fukuoka, JP, 28 July 2005

Hecht, S., University of Tokyo, JP, 1 August 2005

Hecht, S., ETH Zürich, CH, 11 October 2005

Hecht, S., Humboldt-Universität zu Berlin, DE, 8 December 2005

Kästner, J., 41st Symposium for Theoretical Chemistry, Innsbruck, AT, 5 September 2005

Kästner, J., PsiK 2005 Conference, Schwäbisch Gmünd, DE, 17 September 2005

Kästner, J., Daresbury Laboratory, Warrington, GB, 29 September 2005

Keal, T. W., Symposium on Retinal Proteins, Heidelberg, DE, 2 Dezember 2005

Khan, A., JCF Symposium, Berlin, DE, 8 April 2005

Konjhodzic, D., DPG-Tagung, Berlin, DE, 6 March 2005

Konjhodzic, D., E-MRS Spring Meeting, Strasbourg, FR, 9 March 2005

Konjhodzic, D., Institut für Festkörperphysik, Universität Duisburg-Essen, DE, 6 December 2005

Lehmann, C.W., Pharmaceutical Powder X-ray Diffraction Symposium, Barcelona, ES, 19-25 February 2005

Lehmann, C.W., Institut für Werkstoffforschung, Dresden, DE, 10-13 May 2005

Lehmann, C.W., Universität Bonn, DE, 12 October 2005

Lehmann, C.W., Institut für Angewandte Photonik, PRORA, Berlin, DE, 23-25 November 2005

Leitner, W., Tag der Chemie, RWTH Aachen, DE, 28 January 2005

Leitner, W., Graduiertenkolleg, TU Berlin, DE, 11 February 2005

Leitner, W., 229th ACS Meeting, San Diego, USA, 12 March 2005

Leitner, W., ConNeCat Vollversammlung, Weimar, DE, 16 March 2005

Leitner, W., Green Chemistry, IFOK Rostock, DE, 30 March 2005

Leitner, W., GDCh, TU Darmstadt, DE, 12 April 2005

Leitner, W., GDCh, Paderborn, DE, 18 April 2005

Leitner, W., 7th International Symposium on Supercritical Fluids, Orlando, USA, 2 May 2005

Leitner, W., Conference on Knowledge-based Materials and Technologies, Tallin, EE, 2 June 2005

Leitner, W., 1st International Congress on Ionic Liquids (COIL), Salzburg, AT, 21 June 2005

Leitner, W., 2nd International Conference on Green and Sustainable Chemistry, Washington DC, USA, 23 June 2005

Leitner, W., GCV/DECHEMA-Jahrestagung, Wiesbaden, DE, 5-8 September 2005

Leitner, W., XVIth FECHEM Conference on Organometallic Chemistry, Budapest, HU, 6 September 2005

Leitner, W., UMSICHT: Zur Sache, Oberhausen, DE, 22 September 2005

Leitner, W., Université de Bourgogne, Dijon, FR, 17 October 2005

Leitner, W., STE/gste-Tagung, Jülich, DE, 10-11 November 2005

Leitner, W., GDCh, Merseburg, DE, 22 November 2005

Leitner, W., Institut für Biotechnologie, FZ Jülich, DE, 7 December 2005

Leitner, W., Institut für Anorganische Chemie, Universität Bonn, DE, 8 December 2005

Leitner, W., GDCh, TU München, DE, 20 December 2005

List, B., Gakushuin University, Tokyo, JP, 1 March 2005

List, B., Tokyo University of Science, JP, 3 March 2005

List, B., Kyoto University, JP, 9 March 2005

List, B., University of Tokyo, JP, 11 March 2005

List, B., VIII Spring Meeting of Synthetic Chemistry, Abo/Turku, FI, 17 March 2005

List, B., Lanxess, Catalysis Symposium, Leverkusen, DE, 29 April 2005

List, B., Institute for Research in Organic Catalysis, Rostock, DE, 23 May 2005

List, B., Xth ICN Symposium, Paris, FR, 2 June 2005

List, B., University of Seville, ES, 14 June 2005

List, B., Tetrahedron Symposium, Bordeaux, FR, 27 June 2005

List, B., GDCh, J. W. Goethe Universität, Frankfurt am Main, DE, 5 July 2005

List, B., 22nd Summer Seminar on Organic Synthesis, Takayama, JP, 6 September 2005

List, B., Tokyo Institute of Technology, JP, 7 September 2005

List, B., Boehringer-Ingelheim, Biberach, DE, 27 September 2005

List, B., Nottingham University, UK, 24 October 2005

List, B., AstraZeneca, Charnwood, UK, 25 October 2005

List, B., Durham University, UK, 26 October 2005

List, B., AstraZeneca, Alderley Park, UK, 27 October 2005

List, B., Roche, Basel, CH, 7 November 2005

List, B., Industry meets University Lecture, Wermelskirchen, DE, 11 November 2005

List, B., Graduiertenkolleg, TU Berlin, DE, 18 November 2005

List, B., DSM, Geleen, NL, 24 November 2005

Marlow, F., 14. DECHEMA Dissussionstagung: Angewandte Technische Chemie, Frankfurt, DE, 23 February 2005

Marlow, F., DPG-Tagung Berlin, DE, 5 March 2005

Marlow, F., Universität Kiel, DE, 9 May 2005

Marlow, F., TU Berlin, DE, 5 June 2005

Marlow, F., Merck AG, Darmstadt, DE, 27 June 2005

Marlow, F., Universität Gießen, DE, 11 July 2005

Marlow, F., UCSB Department of Material Science, Santa Barbara, USA, 15 August 2005

Marlow, F., UCSB Department of Chemistry, Santa Barbara, USA, 17 August 2005

Marlow, F., Universität Kaiserslautern, DE, 14 November 2005

Marlow, F., TU Chemnitz, DE, 26 November 2005

Pörschke, K.-R., 229th ACS National Meeting, San Diego, USA, 13–17 March 2005

Pörschke, K.-R., Festveranstaltung zum 80. Geburtstag von G. Wilke, Mülheim/Ruhr, DE, 9 June 2005

Pörschke, K.-R., Universitat de Girona, Girona, ES, 13 September 2005

Pörschke, K.-R., STEREOCAT-2005, Barcelona, ES, 15-18 September 2005

Reetz, M. T., NIOK Bioconference, Noordwijkerhout, NL, 7 January 2005

Reetz, M. T., Novozymes A/S, Bagsvaerd, DK, 3 February 2005

Reetz, M. T., GDCh, Universität Konstanz, DE, 10 February 2005

Reetz, M. T., Green Chemistry, IfOK Universität Rostock, DE, 1 April 2005

Reetz, M. T., 7th Symposium Lilly Foundation: New Frontiers in Organic Synthesis, Euroforum Infantes, Madrid, ES, 15 April 2005

Reetz, M. T., GDCh, Universität Karlsruhe, DE, 28 April 2005

Reetz, M. T., John Osborn Lecture, Strasbourg, FR, 29 April 2005

Reetz, M. T., Bayer Cropscience Lecture, University of East Anglia, Norwich, UK, 11 May 2005

Reetz, M. T., Otto-Warburg Vorlesung, Bayreuth, DE, 19 May 2005

Reetz, M. T., Technologieforum Weiße Biotechnologie, DECHEMA, Frankfurt am Main, DE, 2 June 2005

Reetz, M. T., Steinheimer Gespräche des Fonds für den Hochschullehrernachwuchs, Hanau/Steinheim, DE, 4 June 2005

Reetz, M. T., Gordon Research Conference, Oxford, UK, 14 August 2005

Reetz, M. T., XVIth FECHEM, Budapest, HU, 7 September 2005

Reetz, M. T., GDCh-Jahrestagung, Karl-Ziegler-Preis, Düsseldorf, DE, 13 September 2005

Reetz, M. T., Süd-Chemie AG, Bruckmühl, DE, 21 September 2005

Reetz, M. T., DIP Symposium, Technion-Israel Institute of Technology, Haifa, IL, 29 September 2005

Reetz, M. T., SFB 380 Symposium, RWTH Aachen, DE, 10 October 2005

Reetz, M. T., Schering AG, Berlin, DE, 25 October 2005

Reetz, M. T., GDCh, Technische Universität Darmstadt, DE, 1 November 2005

Reetz, M. T., Hamilton Award Lectureship, University of Nebraska, Lincoln, USA, 10-11 November 2005

Reetz, M. T., Universität Leipzig, DE, 24 November 2005

Reetz, M. T., Koninklijke Nederlandse Akademie van Wetenschappen, Amsterdam, NL, 19 December 2005

Schmidt, W., CNRS MADIREL, Marseille, FR, 1 June, 7 June 2005

Schrader W., Kolloquium Analytische Chemie, FZ Jülich, DE, 1 February 2005

Schrader W., Bruker Daltonics, Bremen, DE, 5 April 2005

Schrader W., Drexel University, Philadelphia, USA, 12 September 2005

Schrader W., Villanova University, Villanova, PA, USA, 13 September 2005

Schrader W., Juniata College, Huntingdon, PA, USA, 15 September 2005

Schrader W., Penn State University, State College, PA, USA, 19 September 2005

Schrader W., Juniata College, Huntingdon, PA, USA, 22 September 2005

Schrader W., Kolloquium für anorganische und analytische Chemie, Universität Marburg, DE, 21 November 2005

Schrader W., Chemical Engineering, Universidad Central de Venezuela, Caracas, VE, 14 Dezember 2005

Schüth, F., GDCh, Institut für Polymerforschung Dresden, DE, 13 January 2005

Schüth, F., 14. Diskussionstagung Anorganisch-Technische Chemie, Dechema-Haus, Frankfurt, DE, 23-24 February 2005

Schüth, F., GDCh, Universität Darmstadt, DE, 10 May 2005

Schüth, F., WOG Workshop, Brüssel, BE, 19 May 2005

Schüth, F., EMRS 2005 Spring Meeting, Strasbourg, FR, 31 May-3 June 2005

Schüth, F., 89th International Bunsen Discussion Meeting, Hennesse, DE, 16-17 June 2005

Schüth, F., IPHE International Hydrogen Storage Technology Conference, Lucca, IT, 19-22 June 2005

Schüth, F., XIIth Polish Zeolite Conference, Ciazen, PL, 23 June 2005

Schüth, F., SECAT 05, Madrid, ES, 27-29 June 2005

Schüth, F., FEZA School on Zeolites, Masarykova College, Prag, CZ, 21-22 August 2005

Schüth, F., New Advances in Crystal Growth & Nucleation, Il Ciocco Conference Center, Barga, IT, 1-3 September 2005

Schüth, F., Summer School on Catalysis, Liverpool Center for Materials and Catalysis, University of Liverpool, UK, 12 September 2005

Schüth, F., GDCh-Jahrestagung 2005, Düsseldorf, DE, 14 September 2005

Schüth, F., 5th World Congress on Oxidation Catalysis, Sapporo, JP, 24-28 September 2005

Schüth, F., 4. Materialwissenschaftler-Tag, TU Darmstadt, DE, 7 October 2005

Schüth, F., SFB Kolloquium, Universität Duisburg-Essen, DE, 25 October 2005

Schüth, F., SFB Kolloquium, Universität Heidelberg, DE, 28 October 2005

Schüth, F., Three Keynote Lectures, Deutschland in Japan 2005/2006, "Chemistry. Elements of Life. Innovations of the German Chemical Industry", Tokyo University, Nagoya and Osaka University, JP, 5-12 November 2005

Schulz, F., Biotrans, Delft, NL, 7 July 2005

Senn, H. M., Theoretical Chemistry Seminar, Universität Bonn, DE, 9 June 2005

Theyssen, N., DGMK/SCI-Conference, Milano, IT, 13 October 2005

Thiel, W., WATOC2005, Cape Town, ZA, 16 January 2005

Thiel, W., International Conference: Computational Tools for Molecules, Clusters and Nanostructures, Karlsruhe, DE, 24 January 2005

Thiel, W., SFB Kolloquium, Universität Heidelberg, DE, 18 February 2005

Thiel, W., Sanibel Conference, St. Simon's Island, Georgia, USA, 6 March 2005

Thiel, W., GDCh, Universität Tübingen, DE, 2 June 2005

Thiel, W., IUPAC2005 Congress, Peking, CN, 16 August 2005

Thiel, W., 230th ACS National Meeting, Washington, USA, 31 August 2005

Thiel, W., Scienomics Seminar, Paris, FR, 8 September 2005

Thiel, W., ISQBP Loew Memorial Meeting, New York, USA, 6 October 2005

Thiel, W., Graduiertenkolleg 352: Symposium on Catalysis, Technische Universität Berlin, DE, 17 November 2005

Thiel, W., University of Science and Technology, Hong Kong, HK, 22 November 2005

Thiel, W., International Symposium: Theoretical Methods and Computational Modeling of Complex Systems, Xiamen University, CN, 25 November 2005

Trapp, O., Ruhr-Universität Bochum, DE, 24 June 2005

Trapp, O., Chirality-2005 (ISCD 17), Parma, IT, 13 September 2005

Trapp, O., Bergische Universität Wuppertal, DE, 8 November 2005

Tuttle, T., Wacker Consortium, München, DE, 24 May 2005

Tuttle, T., DIP-Symposium, Technion, Haifa, IL, 29 September 2005

Tuttle, T., Rijksuniversiteit Groningen, NL, 18 November 2005

Tuttle, T., Wacker Consortium, München, DE, 8 December 2005

Weidenthaler, C., Workshop on Non-Ambient Diffraction, Tirrenia, IT, 16-18 March 2005

Weidenthaler, C., Graduiertenkolleg, Universität Köln, DE, 20 June 2005

2006

Belder, D., Universität Leipzig, DE, 10 April 2006

Bocola, M., BIOCAT 2006, Hamburg, DE, 4 September 2006

Bouchez, L., 232nd ACS National Meeting, San Francisco, CA, USA, 13 September 2006

Bühl, *M.,* Universität Jena, DE, 16 February 2006

Bühl, *M.,* Symposium Computational Chemistry, Rauischholzhausen, DE, 11 April 2006

Bühl, *M.,* 37th International Conference on Coordination Chemistry, Cape Town, ZA, 13-18 August 2006

Bühl, *M.;* 5th International Symposium on the Chemistry and Biological Chemistry of Vanadium, San Francisco, USA, 10-14 September 2006

Bühl, *M.,* Université de Strasbourg, FR, 5 October 2006

Felderhoff, M., FuncHy 2006, Geesthacht, DE, 20-22 September 2006

Felderhoff, M., Metal Hydrides 2006, Hawaii, USA, 2 October 2006

Fink, G., Boreskov Institute of Catalysis, Novosibirsk, RU, 22-24 August 2006

Fürstner, A., Université Louis Pasteur Strasbourg, FR, 9 January 2006

Fürstner, A., Otto-Bayer-Prize Lecture, Leverkusen, DE, 18 January 2006

Fürstner, A., Merck, Darmstadt, DE, 19 January 2006

Fürstner, A., GDCh, Universität des Saarlandes, Saarbrücken, DE, 23 January 2006

Fürstner, A., Seminar Sanofi-Aventis, Bad Brückenau, DE, 27-28 January 2006

Fürstner, A., Ecole Polytechnique Fédérale de Lausanne, CH, 14 February 2006

Fürstner, A., Rencontres de Chimie Organique, Ecole Nationale Superieure de Chimie de Paris, FR, 24 February 2006

Fürstner, A., 231st ACS National Meeting, Atlanta, GA, USA, 27 March 2006

Fürstner, A., Abbott, Lake Forest, IL, USA, 29 March 2006

Fürstner, A., Chemical Genomics Center-Meeting, Dortmund, DE, 22-23 May 2006

Fürstner, A., TU Graz, AT, 8 June 2006

Fürstner, A., TU Darmstadt, DE, 20 June 2006

Fürstner, A., Pre-Symposium "Natural Product Chemistry", Tokushima, JP, 21 July 2006

Fürstner, A., 25th IUPAC Conference on Biodiversity and Natural Products Chemistry, Kyoto, JP, 27 July 2006

Fürstner, A., Eli Lilly UK, Erl Wood Manor, Windlesham, Surrey, UK, 19 September 2006

Fürstner, A., Syngenta, Basel, CH, 21 September 2006

Fürstner, A., Seminar Bayer HealthCare, New Haven, CT, USA, 27 October 2006

Fürstner, A., Columbia University, New York, USA, 30 October 2006

Fürstner, A., Boehringer Ingelheim, Ridgefield, CT, USA, 31 October 2006

Fürstner, A., Heinrich Wieland Prize Lecture, Munich, DE, 3 November 2006

Fürstner, A., Boehringer Ingelheim, Vienna, AT, 17 November 2006

Fürstner, A., University of Leeds, UK, 22 November 2006

Fürstner, A., Eli Lilly Symposium, Harvard University, Cambridge, MA, USA, 4 December 2006

Fürstner, A., GDCh, Universität Frankfurt am Main, DE, 12 December 2006

Goddard, R., ANKA User Meeting, Karlsruhe, DE, 9-10 October 2006

Haenel, *M.W.*, 232nd American Chemical Society National Meeting, Division of Fuel Chemistry, San Francisco, USA, 13 September 2006

Haenel, *M.W.*, 65. Sitzung des DGMK-Arbeitskreises Kohlenveredlung, Bundesforschungsanstalt für Forst- und Holzwirtschaft, Hamburg, DE, 10 November 2006

Hecht, S., Université de Genève, CH, 19 January 2006

Hecht, S., Friedrich-Schiller-Universität Jena, DE, 24 January 2006

Hecht, S., Chemiedozententagung, Hamburg, DE, 20 March 2006

Hecht, S., CHEXTAN Meeting, Radboud University Nijmegen, NL, 7 April 2006

Hecht, S., BASF Ludwigshafen, DE, 11 April 2006

Hecht, S., BAYER Materials Science, Leverkusen, DE, 11 May 2006

Hecht, S., Habilitationsvortrag, Freie Universität Berlin, DE, 21 June 2006

Hecht, S., 1st Sino-German Frontiers of Chemistry Symposium, Kloster Seeon, DE, 22 July 2006

Hecht, S., ACS Meeting, San Francisco, USA, 10-12 September 2006

Hecht, S., IBM Research Center, Almaden, USA, 15 September 2006

Hecht, S., Materials Research Laboratory, University of California, Santa Barbara, USA, 18 September 2006

Hecht, S., MPI für Festkörperforschung, Stuttgart, DE, 22 November 2006

Hecht, S., Fachbereich Physik, Freie Universität Berlin, DE, 11 December 2006

Kästner, J., Institut für Theoretische Physik, TU Clausthal, DE, 11 Januar 2006

Kästner, J., SFB Kolloquium, Universität Düsseldorf, DE, 9 February 2006

Kästner, J., Workshop on Molecular Simulation, Heidelberg, DE, 21 September 2006

Kennedy, J.W.J., 89th Canadian Chemistry Conference, Halifax, CA, 31 May 2006

Khalil, A. S. G., 1st Workshop "InsidePores", Montpellier, FR, 3 March 2006

Khan, A., ICI Student Award Symposium, ACS Fall Meeting, San Francisco, USA, 10 September 2006

Konjhodzic, D., Institut für physikalische Chemie, FU Berlin, DE, 22 May 2006

Kumar, D., Workshop on Molecular Simulation, Heidelberg, DE, 21 September 2006

Lehmann, C.W., Tianjin Normal University, Tianjin, CN, 10-14 January 2006

Lehmann, C.W., Elektronendichtetagung ECDM IV, Bollmannsruh/Brandenburg, DE, 26-29 January 2006

Lehmann, C.W., Sagamore XV Conference, The University of Warwick, Warwick, GB, 13-18 August 2006

Lehmann, C.W., Kristallographiesommerschule, Hardehausen, DE, 4-8 September 2006

Leitner, W., Anorganisch-analytisches Kolloquium, Marburg, DE, 30 January 2006

Leitner, W., Université-Industrie de la Société Française de Chimie Bourgogne, Dijon, FR, 3 March 2006

Leitner, W., GDCh, Universität Konstanz, DE, 11 May 2006

Leitner, W., Achema, Frankfurt, DE, 17 May 2006

Leitner, W., GDCh, Universität Köln, DE, 23 June 2006

Leitner, W., JMC Chiral Technologies, Cambridge, UK, 29 June 2006

Leitner, W., 15th International Symposium on Homogeneous Catalysis, Sun City, ZA, 20-25 August 2006

Leitner, W., EuCheMS, Budapest, HU, 27-31 August 2006

Leitner, W., EPFL Lausanne, CH, 25 September 2006

Leitner, W., Université Paris Sud, Orsay, FR, 14 November 2006

Leitner, W., BASF, Ludwigshafen, DE, 25 November 2006

List, B., Dechema, Frankfurt, DE, 9 Januar 2006

List, B., DFG-SPP Organocatalysis, Mülheim, DE, 9 February 2006

List, B., Novartis Young Investigator Award Lecture, Boston, USA, 13 February 2006

List, B., Glaxo-Smith-Kline, USA, 15 February 2006

List, B., BASF, Ludwigshafen, DE, 21 February 2006

List, B., Novartis Young Investigator Award Lecture, Basel, CH, 24 March 2006

List, B., Nankai University, Tianjin, CN, 6 April 2006

List, B., Peking University, Beijing, CN, 7 April 2006

List, B., Novartis Young Investigator Award Lecture, Tsukuba, JP, 10 April 2006

List, B., Mitsubishi Chemical Co., Yokohama, JP, 11 April 2006

List, B., Astellas Co., Osaka, JP, 13 April 2006

List, B., Graduate School of Engineering, Kyoto University, JP, 14 April 2006

List, B., Graduate School of Science, Kyoto University, JP, 17 April 2006

List, B., Hokkaido University, Sapporo, JP, 19 April 2006

List, B., Tohoku University, Sendai, JP, 21 April 2006

List, B., German-Chinese Conference on Organocatalysis, Hangzhou, CN, 22 April 2006

List, B., Meeting on Organic Chemistry, Marseille, FR, 5 May 2006

List, B., Chiral Europe 2006, Bürgenstock, CH, 7 June 2006

List, B., GDCh, Universität Kiel, DE, 15 June 2006

List, B., Solvias, Basel, CH, 23 June 2006

List, B., Balticum Organicum Syntheticum (BOS 2006), Tallin, EE, 27 June 2006

List, B., First International Organocatalysis Meeting, Glasgow, UK, 7 July 2006

List, B., GDCh, Universität Wuppertal, DE, 21 August 2006

List, B., First European Chemistry Conference, Budapest, HU, 29 August 2006

List, B., Orchem, Bad Nauheim, DE, 8 September 2006

List, B., IASOC Conference, Ischia, IT, 17 September 2006

List, B., Novartis Young Investigator Award Lecture, Horsham, UK, 19 September 2006

List, B., Novartis Young Investigator Award Lecture, Vienna, AT, 2 October 2006

List, B., Organocatalysis Meeting, Tutzingen, DE, 8 October 2006

List, B., Bayer Health Care, Wuppertal, DE, 23 October

List, B., Pfizer, Sandwich, UK, 3 November 2006

List, B., Wiechert Lecture, FU Berlin, DE, 6 December 2006

List, B., DFG Antragskolloquium, Berlin, DE, 7 December 2006

Lu, A.-H., Carbon Conference 2006, Aberdeen, UK, July 2006

Marlow, F., MPG-FhG Strategietreffen, Düsseldorf, DE, 24 April 2006

Marlow, F., ISC Würzburg, DE, 20 July 2006

Marlow, F., Bunsentagung, Erlangen, DE, 23 May 2006

Marlow, F., Universität Gießen, DE, 22 June 2006

Marlow, F., Kolloquium Optische Technologien, Universität Münster, DE, 9 November 2006

Nevado, C., 232nd ACS National Meeting, San Francisco, CA, USA, 13 September 2006

Nevado, C., III Symposium of Young Researchers RSEQ-Sigma-Aldrich, Institut Catalán d'Investigació Química (ICIQ), Tarragona, ES, 16 October 2006

Parac, M., Theoretical Chemistry Seminar, Universität Bonn, DE, 30 November 2006

Parac, M., Theoretical Chemistry Seminar, Universität Düsseldorf, DE, 14 December 2006

Pörschke, K.-R., 231st ACS National Meeting, Atlanta, USA, 26-30 March 2006

Prechtl, M., International Conference on Organometallic Chemistry, Zaragoza, ES, 27 July 2006

Reetz, M. T., The Institute of Physical and Chemical Research RIKEN, Saitama, JP, 17 January 2006

Reetz, M. T., Start-up Symposium, University of Kyoto, JP, 18 January 2006

Reetz, M. T., Universität Hamburg, DE, 24 January 2006

Reetz, M. T., Joint Inorganic/Organic Colloquia, University of Cambridge, UK, 26 January 2006

Reetz, M. T., Universität Stuttgart, DE, 3 February 2006

Reetz, M. T., Hogeschool Rotterdam, NL, 13 February 2006

Reetz, M. T., Universidad de Alicante, ES, 21 February 2006

Reetz, M. T., Universidad de Tarragona, ES, 22 February 2006

Reetz, M. T., IRBM-MRL, Rom, IT, 28 February 2006

Reetz, M. T., University of Puerto Rico, Rio Petras, PR, 10 March 2006

Reetz, M. T., University of Florida, Gainesville, USA, 14 March 2006

Reetz, M. T., UCI Organic Synthesis Lecture, University of California, Irvine, USA, 15-16 March 2006

Reetz, M. T., Industrial Biotransformations Conference, Barcelona, ES, 4 May 2006

Reetz, M. T., International Symposium on Organocatalysis in Organic Synthesis, University of Glasgow, UK, 7 July 2006

Reetz, M. T., Gordon Conference Biocatalysis, Bryant University, Smithfield, Rhode Island, USA, 9 July 2006

Reetz, M. T., Goldschmidt, Essen, DE, 9 August 2006

Reetz, M. T., First European Chemistry Congress, Budapest, HU, 28 August 2006

Reetz, M. T., Symposium "Trends in Organic Chemistry – Enzymatic Synthesis", AlbaNova, Stockholm, SE, 4 September 2006

Reetz, M. T., DECHEMA, Wiesbaden, DE, 27 September 2006

Reetz, M. T., BASF Research Seminar, Albersweiler/Pfalz, DE, 10 October 2006

Reetz, M. T., Symposium "Enzyme Catalysis", Uppsala, SE, 19 October 2006

Reetz, M. T., Prelog-Lecture, ETH Zürich, CH, 6 November 2006

Reetz, M. T., Workshop "ChemBionics: Prospects of Biohybrid Molecules", Rauischholzhausen, Marburg/Lahn, DE, 27 November 2006

Reetz, M. T., Ernst Hellmut Vits-Preis, Universität Münster, DE, 28 November 2006

Reetz, M. T., Stereochemistry Lecturer, Universität Groningen, NL, 14 December 2006

Sauer, S. P. A., Institut für Physikalische Chemie, Universität Jena, DE, 17 Februar 2006

Sauer, S. P. A., Institut für Theoretische Chemie, Universität Bielefeld, DE, 5 May 2006

Sauer, S. P. A., Institut für Physikalische Chemie, Universität Heidelberg, DE, 15 May 2006

Sauer, S. P. A., Institut für Physikalische und Theoretische Chemie, Universität Kaiserslautern, DE, 18 May 2006

Schmidt, W., Netzsch Kopplungsseminar "Gasanalyse gekoppelt mit thermischer Analyse", Bonn, DE, 12 April 2006

Schmidt, W., Institut für Technische Chemie, Universität Stuttgart, Stuttgart, DE, 24 October 2006

Schrader W., Kolloquium der Fa. Thermo, Frankfurt/Main, DE, 2 May 2006

Schüth, F., Dechema-Arbeitsausschuss Katalyse, Dechema-Haus Frankfurt, DE, 19 Januar 2006

Schüth, F., GDCh, Universität Köln, DE, 28 April 2006

Schüth, F., 3rd International Symposium on Advanced Materials, Ulsan, COR, 11-13 May 2006

Schüth, F., Lehrerfortbildungsveranstaltung der ACHEMA 2006, Frankfurt, DE, 15 May 2006

Schüth, F., 5th DPI Workshop on Combinatorial and High-Throughput Approaches in Polymer Science, TU Eindhoven, NL, 26 June 2006

Schüth, F., 2nd Workshop on Combinatorial Materials Research, FLAMAC, Zwijnaarde, BE, 30 June 2006

Schüth, F., British Zeolite Association, XXIXth Chiselhurst Style Annual Meeting, St. Martin's College, Ambleside, UK, 31 July-4 August 2006

Schüth, F., 5th International Mesostructured Materials Symposium (IMMS 2006), Fudan University, Shanghai, CN, 5-7 August 2006

Schüth, F., Toyota R & D Laboratories, Nagoya, JP, 9-11 August 2006

Schüth, F., 1st Interdisciplinary Max-Planck-PhDnet Workshop, Köln, DE, 17 August 2006

Schüth, F., 232nd ACS National Meeting, San Francisco, CA, USA, 9-14 September 2006

Schüth, F., 5th International Conference on Inorganic Materials, Ljubljana, SK, 25-26 September 2006

Schüth, F., "Chemische Verfahren zur Wasserstoffspeicherung", Gemeinsame Veranstaltung der Max-Planck-Gesellschaft und des SZ-Forums Wissen der Süddeutschen Zeitung, München, DE, 23 October 2006

Schüth, F., GDCh, Philipps-Universität Marburg, DE, 13 December 2006

Senn, H. M., Laboratoire de physique quantique, Université Paul Sabatier, Toulouse, FR, 10 January 2006

Senn, H. M., BASF Scientific Computing, Ludwigshafen, DE, 21 February 2006

Senn, H. M., PAW Workshop, CECAM, Lyon, FR, 13 June 2006

Senn, H. M., Gordon Research Conference on Computational Chemistry, Les Diablerets, CH, 9 October 2006

Stempniewicz, M., International Zeolite Conference, Shanghai, CN, 6 August 2006

Theyssen, N., Mettler Toledo International Real Time Analytics Users' Conference, Barcelona, ES, 28 February 2006

Theyssen, N., Green Solvents for Processes, Friedrichshafen, DE, 9 October 2006

Thiel, W., GDCh, Universität Frankfurt, DE, 10 January 2006

Thiel, W., GDCh, Universität Oldenburg, DE, 12 January 2006

Thiel, W., MSC+ Colloquium, Universität Groningen, NL, 2 February 2006

Thiel, W., SFB Symposium, Universität Würzburg, DE, 13 February 2006

Thiel, W., Cardiff Easter Conference, Cardiff University, UK, 3 April 2006

Thiel, W., KNAW Conference: Multi-Scale Modelling, Amsterdam, NL, 5 April 2006

Thiel, W., Symposium Computational Chemistry, Rauischholzhausen, DE, 12 April 2006

Thiel, W., Physikalisch-chemisches Seminar, Universität Basel, CH, 3 May 2006

Thiel, W., ICQC Satellite Meeting: Large Molecular Systems, Okazaki, JP, 18 May 2006

Thiel, W., Symposium: Trends in Enzymology, Como, IT, 8 June 2006

Thiel, W., 11th International Conference on Theoretical Aspects in Catalysis, Berlin-Schmöckwitz, DE, 14 June 2006

Thiel, W., Fritz-Haber-Institut, Berlin, DE, 6 July 2006

Thiel, W., Festkolloquium Physikalische Chemie, RWTH Aachen, DE, 11 July 2006

Thiel, W., ESPA 2006 Conference, Santiago de Compostela, ES, 20 July 2006

Thiel, W., International Mass Spectrometry Conference, Prag, CZ, 1 September 2006

Thiel, W., 232nd ACS National Meeting, Symposium: Modern Semiempirical MO Theory, San Francisco, USA, 10 September 2006

Thiel, W., 232nd ACS National Meeting, Symposium: DFTB, An Approximate DFT Method, San Francisco, USA, 11 September 2006

Thiel, W., 232nd ACS National Meeting, Symposium: Theory of Rare Events and Accelerated Dynamics, San Francisco, USA, 11 September 2006

Thiel, W., 232nd ACS National Meeting, Symposium: Theoretical Inorganic Chemistry, San Francisco, USA, 12 September 2006

Thiel, W., Workshop SFB 633, Bad Honnef, DE, 2 October 2006

Thiel, W., Gordon Research Conference on Computational Chemistry, Les Diablerets, CH, 9 October 2006

Thiel, W., Institut Francais du Pétrol, Scienomics Seminar, Paris, FR, 6 November 2006

Trapp, O., Chemie-Dozententagung, Hamburg, DE, 20 March 2006

Trapp, O., MPI für Eisenforschung, Düsseldorf, DE 24 April 2006

Trapp, O., Eberhard Karls Universität Tübingen, DE, 23 May 2006

Trapp, O., FhI für Silikatforschung, Würzburg, DE, 20 July 2006

Trapp, O., Eberhard Karls Universität Tübingen, DE, 5 December 2006

Weidenthaler, C., Fakultät für Geowissenschaften, LMU München, DE, 13 July 2006

Yurchenko, S.N., QUASAAR Winter School, Grenoble, FR, 29 January 2006

Yurchenko, S.N., PRAHA 2006, Prag, CS, 30 August 2006

Ziegler, E., Annual Meeting of the Israeli Humboldt Club, Jerusalem, IL, 23 March 2006

2007

Alcarazo, M., IV Symposium of Young Researchers from the Spanish Royal Society of Chemistry, University of Burgos, E, 21 November 2007

Altarsha, M., International Symposium on Selective Oxidation Catalysis, Stuttgart, DE, 29 October 2007

Bühl, *M.,* Universität Erlangen, DE, 5 February 2007

Bühl, *M.,* Workshop on Computational Chemistry, Istanbul, TR, 7-9 March 2007

Bühl, *M.,* Université de Strasbourg, FR, 27 September 2007

Bühl, *M.,* Universität Bonn, DE, 15 November 2007

Bühl, *M.,* Universität Zagreb, HR, 7 December 2007

Felderhoff, M., Hdt Seminar, Essen, DE, 28 March 2007

Felderhoff, M., Purdue University, USA, 12-14 April 2007

Fink, G., International Symposium, MPI für Polymerforschung, Mainz, DE, 1-2 March 2007

Fink, G., Helsinki University of Technology, Helsinki, FI, 7-8 June 2007

Fink, G., Basell Polyolefine GmbH, Industriepark Höchst, DE, 22 June 2007

Fürstner, A., GDCh, Humboldt-Universität zu Berlin, DE, 22 January 2007

Fürstner, A., Schering AG, Berlin, DE, 23 January 2007

Fürstner, A., GDCh, Universität Potsdam, DE, 24 January 2007

Fürstner, A., Graduiertenkolleg "Catalyst and Catalytic Reactions in Organic Synthesis" (GRK 1038), Albert-Ludwigs-Universität Freiburg, DE, 5 February 2007

Fürstner, A., Nordrhein-Westfälische Akademie der Wissenschaften, Düsseldorf, DE, 14 March 2007

Fürstner, A., Deutsche Akademie der Naturforscher Leopoldina, Halle (Saale), DE, 27 March 2007

Fürstner, A., University of Toledo, Toledo, OH, USA, 22 April 2007

Fürstner, A., Pfizer, Ann Arbor, MI, USA, 23 April 2007

Fürstner, A., Wayne State University, Detroit, MI, USA, 24 April 2007

Fürstner, A., Michigan State University, East Lansing, MI, USA, 25 April 2007

Fürstner, A., University of Michigan, Ann Arbor, MI, USA, 26 April 2007

Fürstner, A., Laval University, Québec, CA, 30 April 2007

Fürstner, A., GDCh, Leibniz Universität Hannover, DE, 10 May 2007

Fürstner, A., 10th International Conference on the Chemistry of Antibiotics and other Bioactive Compounds, ICCA-10, Vanderbilt University, Nashville, TN, USA, 13 August 2007

Fürstner, A., Roessler Lecture (I), Cornell University, Ithaca, NY, USA, 25 October 2007

Fürstner, A., Roessler Lecture (II), Cornell University, Ithaca, NY, USA, 26 October 2007

Fürstner, A., Eli Lilly Lecture (I), University of Pittsburgh, PA, USA, 29 October 2007

Fürstner, A., Eli Lilly Lecture (II), University of Pittsburgh, PA, USA, 30 October 2007

Fürstner, A., Merck Inc., Medicinal Chemistry Group, Rahway, NJ, USA, 31 October 2007

Fürstner, A., Merck Inc., Process Chemistry Group, Rahway, NJ, USA, 1 November 2007

Fürstner, A., GlaxoSmithKline, Harlow, UK, 21 November 2007

Haenel, *M.W.*, 66. Sitzung des DGMK-Arbeitskreises Kohlenveredlung, Choren Industries GmbH, Freiberg, DE, 30 March 2007

Haenel, *M.W.*, International Conference on Coal Science and Technology, Nottingham, UK, 29 August 2007

Hecht, S., Johannes Gutenberg Universität, Mainz, DE, 13 February 2007

Hecht, S., Makromolekulares Kolloquium, Universität Freiburg, DE, 22 February 2007

Hecht, S., Schülergesellschaft, Humboldt-Universität zu Berlin, DE, 8 March 2007

Hecht, S., Universität Stuttgart, DE, 5 June 2007

Hecht, S., GDCh, TU München, DE, 10 July 2007

Hecht, S., ADUC-Award Symposium, GDCh-Jahrestagung, Ulm, DE, 18 September 2007

Hecht, S., SFB613 Workshop, Bielefeld, DE, 8 October 2007

Hecht, S., GDCh-Kolloquium, Universität Kassel, DE, 6 November 2007.

Jensen, V.R., EuCheMS Conference on Organometallic Chemistry, Sofia, BG, 2 September 2007

Khalil, A., Conference of the RSC, London, UK, 2 July 2007

Klußmann, M., Universität Basel, CH, 15 March 2007

Lehmann, C.W., ESCA Workshop Applications of X-ray Diffraction and Fluorescence, Kairo, EG, 14-18 January 2007

Lehmann, C.W., IQPC 3rd Annual Forum on Polymorphism, Düsseldorf, DE, 27-28 February 2007

Lehmann, C.W., Jahrestagung Deutsche Gesellschaft für Kristallographie, Bremen, DE, 5-9 March 2007

Lehmann, C.W., ECM24 – Satellite Workshop, Marrakesch, MA, 20-23 August 2007

Lehmann, C.W., Universität Stockholm, SE, 13-15 September 2007

Lehmann, C.W., Bruker Nutzertreffen, Göttingen, DE, 9-11 October 2007

Lehmann, C.W., Particle Design for Solid Oral Dosage Forms, Amsterdam, NL, 16-17 October 2007

Leitner,W., BioNoCo Workshop, Aachen, DE, 9 January 2007

Leitner,W., Fa. COGNIS, Düsseldorf, DE, 15 January 2007

Leitner,W., DECHEMA-Arbeitsauschuss Katalyse, Frankfurt, DE, 22 January 2007

Leitner,W., 615. Dechema Kolloquium, Frankfurt, DE, 1 February 2007

Leitner,W., Inorganic and Materials Colloquium, University of Bristol, UK, 5 February 2007

Leitner,W., Inorganic Seminar, University of St. Andrews, UK, 6 February 2007

Leitner,W., GDCh Arbeitsgruppe Nachhaltige Chemie, Frankfurt, DE, 20 March 2007

Leitner,W., GDCh, Universität Saarbrücken, DE, 23 April 2007

Leitner,W., Keynote Lecture, 8th International Symposium on Green Chemistry, Beijing, CN, 22 May 2007

Leitner,W., Chemistry Seminar, Dalian University of Technology, CN, 25 May 2007

Leitner,W., SFB 623 Kolloquium, Heidelberg, DE, 1 June 2007

Leitner,W., Woche der Umwelt, Berlin, DE, 6 June 2007

Leitner,W., Keynote Lecture, Advances in Organic Chemistry, Bratislava, SK, 19 September 2007

Leitner,W., Organic Chemistry Seminar, Université de Genève, CH, 1 November 2007

Leitner,W., Symposium on Green and Sustainable Chemistry, Osaka, JP, 15-17 November 2007

Leitner,W., Graduiertenkolleg, Universität Potsdam, DE, 9 November 2007

Leitner,W., Chemical Engineering Seminar, University of Lissabon, PT, 26 November 2007

Leitner,W., Weizmann Institute, Rehovot, IL, 2-3 December 2007

Leitner,W., DFG Kolloquium SPP 1179, Berlin, DE, 6 December 2007

Leitner,W., DFG Kolloquium SPP 1191, Bamberg, DE, 12-14 December 2007

List, B., Life Science Tagung, Hannover, DE, 9 February 2007

List, B., Eli Lilly, Windlesham, UK, 23 March 2007

List, B., Schering Organocatalysis Meeting, Berlin, DE, 18 April 2007

List, B., Symposium on Organocatalysis, Toronto, CA, 24 April 2007

List, B., Henkel, Düsseldorf, DE, 8 May 2007

List, B., Kyoto Organocatalysis Meeting, Kyoto, JP, 30 May 2007

List, B., International Symposium on Carbanion Chemistry, Madison, WI, USA, 7 June 2007

List, B., GDCh, TU Braunschweig, DE, 25 June 2007

List, B., OBC-Lecture Award, Cambridge, UK, 17 July 2007

List, B., IBCN Meeting, Singapore, 13 August 2007

List, B., BMOS Conference, Sao Paulo, Brazil, 28 August 2007

List, B., Université de Strasbourg, FR, 1 October 2007

List, B., Universität Bern, CH, 10 October 2007

List, B., Institute of Organic Chemistry and Biochemistry, Prague, CZ, 22 October 2007

List, B., AstraZeneca, Charwood, UK, 15 November 2007

List, B., DFG Berichtskolloquium, Berlin, DE, 7 December 2007

Marlow, F., Abschlusskolloquium DFG SPP 1113, Bad Honnef, DE, 24 March 2007

Marlow, F., Universität Würzburg, DE, 17 July 2007

Meudtner, R.M. KOPO '07, Blaubeuren, DE, 26 September 2007

Peters, M.V., JCF Symposium, Chemnitz, DE, 22 March 2007

Prechtl, M., 40. Jahrestreffen Deutscher Katalytiker, Weimar, DE, 15 March 2007

Ramos da Silva, M., Universidade Federal de Minas Gerais**,** Belo Horizonte, BR, 16 November 2007

Ramos da Silva, M., Universidade Federal de Pernambuco, Recife, BR, 29 November 2007

Reetz, M. T., Lecture Series-Prague, Prag, CZ, 21 February 2007

Reetz, M. T., Irseer Naturstofftage, DECHEMA, Frankfurt am Main, DE, 22 February 2007

Reetz, M. T., Universität Gießen, DE, 2 March 2007

Reetz, M. T., Universität Greifswald, DE, 3 March 2007

Reetz, M. T., Universidad de Oviedo, ES, 13 March 2007

Reetz, M. T., Pfizer Distinguished Lectureship, Kingston, CA, 30 March 2007

Reetz, M. T., Organic Syntheses Lectureship, Illinois, USA, 2 April 2007

Reetz, M. T., Bristol Synthesis Meeting, The AstraZeneca and UCB Lecture, Bristol, UK, 17 April 2007

Reetz, M. T., Ernst Schering Research Foundation Workshop, Berlin, DE, 20 April 2007

Reetz, M. T., European BioPerspectives, Köln, DE, 1 June 2007

Reetz, M. T., Lilly Research Lecturer, Warwick, UK, 5 June 2007

Reetz, M. T., Biotrans, Oviedo, ES, 8 July 2007

Reetz, M. T., European BioPerspectives, Dortmund, DE, 3 September 2007

Reetz, M. T., International Symposium "Templates in Chemistry and Beyond", Bonn, DE, 14 September 2007

Reetz, M. T., DFG Symposium "Enzyme Design-Substrate and Ligand Recognition, Rational and Combinatorial Strategies", Bad Herrenalb, DE, 30 September 2007

Reetz, M. T., Shanghai Institute of Organic Chemistry, CN, 28 October 2007

Reetz, M. T., Tianjin University, CN, 30 October 2007

Reetz, M. T., Chinese Academy of Science, Beijing, CN, 31 October 2007

Reetz, M. T., Peking University, Beijing, CN, 1 November 2007

Reetz, M. T., Symposium IRTG, Münster, DE, 16 November 2007

Reetz, M. T., Symposium Weizmann-Institute, Rehovot, IL, 2 December 2007

Reetz, M. T., Symposium "A Journey in Green Chemistry and Catalysis", Delft, NL, 6-7 December 2007

Schmidt, W., Sino-German Workshop, Dalian University of Technology and Max-Planck-Institute for Coal Research, Dalian, CN, 20 August 2007

Schmidt, W., Institute of Chemical Engineering, Dalian University of Technology, Dalian, CN, 22 August 2007

Schmidt, W., Lecture Series, Modern Methods in Heterogeneous Catalysis Research, Fritz-Haber-Institut, Berlin, DE, 2 November 2007

Schmidt, W., CNRS, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Lyon, FR, 30 November 2007

Schrader, W., Analytische Chemie, Universität Essen, DE, 5 February 2007

Schrader, W., Kolloquium der Fa. Thermo im Rahmen der DGMS Tagung, Bremen, DE, 12 March 2007

Schrader, W., Kolloquium FZ Jülich, DE, 12 October 2007

Schüth, F., Zentrum für Brennstoffzellen GmbH, Duisburg, DE, 24 January 2007

Schüth, F., Anorganisches Kolloquium, Universität Bayreuth, DE, 30 January 2007

Schüth, F., 4th BMBF Forum for Sustainability: Sustainable Neighbourhood – from Lisbon to Leipzig through Research, Leipzig, DE, 8 May 2007

Schüth, F., GDCh, Universität Magdeburg, DE, 31 May 2007

Schüth, F., Berzelii Centre EXSELENT on Porous Materials, Stockholm University, SE, 18 June 2007

Schüth, F., III International Conference on Catalysis: Fundamentals and Applications, Boreskov Institute of Catalysis SB RAS, Novosibirsk, RU, 6-8 July 2007

Schüth, F., 15th International Zeolite Conference, Jilin University, Changchun, CN, 18 August 2007

Schüth, F., Sino-German Research Center, Dalian University of Technology and Max-Planck-Institute for Coal Research, Dalian, CN, 20 August 2007

Schüth, F., Chinese Academy of Science, Institute of Chemical Physics, Dalian, CN, 21 August 2007

Schüth, F., EuropaCat VIII, Turku/Åbo, FI, 27-31 August 2007

Schüth, F., Liverpool Centre for Materials and Catalysis, Summerschool on Catalysis, Liverpool, UK, 5 September 2007

Schüth, F., GDCh-Wissenschaftsforum Chemie "Energie, Materialien, Synthese", Ulm, DE, 17-18 September 2007

Schüth, F., GVC/Dechema-Jahrestagung 2007, Aachen, DE, 18 October 2007

Theyssen, N., ProcessNet Fachtagung Unkonventionelle Reaktionssysteme, Frankfurt/Main, DE, 19 April 2007

Theyssen, N., OXEA, Oberhausen, DE, 28 June 2007

Theyssen, N., Universität Jena, DE, 9 July 2007

Thiel, W., Computational Chemistry Workshop, Istanbul, TR, 7-8 March 2007

Thiel, W., Bogazici University, Department of Chemistry, Istanbul, TR, 9 March 2007

Thiel, W., BIOQUANT Workshop, Universität Heidelberg, DE, 15 March 2007

Thiel, W., SFB 663 Kolloquium, Bad Münstereifel, DE, 14 April 2007

Thiel, W., IMM Symposium, University of Nijmegen, NL, 8 May 2007

Thiel, W., Department of Theoretical Chemistry, Lund University, SE, 8 June 2007

Thiel, W., SFB 424 Symposium, Universität Münster, DE, 15 June 2007

Thiel, W., 23rd Theoretical Chemistry Meeting of Catalonia, Tarragona, ES, 5 June 2007

Thiel, W., IMA Workshop: Classical and Quantum Approaches in Molecular Modeling, Minneapolis, USA, 3 August 2007

Thiel, W., 12th International Conference on the Applications of Density Functional Theory, Amsterdam, NL, 30 August 2007

Thiel, W., 2nd International Meeting on Computational Solutions in the Life Sciences, Opatija, HR, 8 September 2007

Thiel, W., Symposium on Biomolecular Simulation, ETH Zürich, CH, 24 September 2007

Thiel, W., Indo-German Conference on Modeling Chemical and Biological Reactivity, Hyderabad, IN, 26 September 2007

Thiel, W., CECAM Workshop, Lyon, FR, 2 October 2007

Thiel, W., GDCh, Universität Bonn, DE, 23 October 2007

Thiel, W., MMM Workshop, Sant Feliu de Guixols, ES, 29 October 2007

Thiel, W., University of Girona, ES, 30 October 2007

Trapp, O., Sino-German-Workshop, LMU München, DE, 8 March 2007

Trapp, O., Chemie-Dozententagung, Halle, DE, 13 March 2007

Trapp, O., ANAKON 2007, Jena, DE, 28 March 2007

Trapp, O., Universität zu Köln, DE, 7 May 2007

Trapp, O., Universität Münster, DE, 15 May 2007

Trapp, O., Universität Marburg, DE, 11 June 2007

Trapp, O., Chirality-2007 (ISCD 19), San Diego, USA, 9 July 2007

Trapp, O., MPI für Dynamik komplexer technischer Systeme, Magdeburg, DE, 19 July 2007

Trapp, O., GDCh, Universität des Saarlandes, Saarbrücken, DE, 5 November 2007

Weidenthaler, C., GÖCh-Vortrag, Universität Graz, AT, 30 May 2007

Weidenthaler, C., German-Sino Workshop, Dalian University of Technology, CN, 20 August 2007

Weidenthaler, C., Seminar on X-ray Photoelectron Spectroscopy, Dalian University of Technology, CN, 22 August 2007

Weidenthaler, C., MinPet 2007, Meran, IT, 20 September 2007

6.3 Scientific Honors, Lectureships, Awards

Bogdanovic, B.,
- Outstanding Achievement Award MH 2006
- H. C. Brown Award 2006
- Foreign Member of the Serbian Academy of Sciences 2006

Bühl, M.
- Visiting Professor at the Université de Strasbourg, 2005

Fürstner, A.
- Bristol-Myers-Squibb Lecture, Philadelphia, PA, USA, 2 March 2005
- Abbott Process Chemistry Lecture, Madison, WI, USA, 3 March 2005
- Merck Lecture 2005, Imperial College, London, UK, 7 June 2005
- Junior Award of the International Society of Heterocyclic Chemistry 2005
- Mukaiyama Award of the Society of Synthetic Organic Chemistry 2005
- Otto-Bayer-Prize 2006
- Heinrich Wieland Prize 2006
- Eli Lilly Symposium, Harvard University, Cambridge, MA, USA, 4 December 2006
- Pfizer Michigan-Tour, USA, 22-28 April 2007
- Roessler Lecture Series, Cornell University, Ithaca, NY, USA, 25-26 October 2007
- Eli Lilly Lectureship, University of Pittsburgh, Pittsburgh, PA, USA, 29-30 October 2007

Hecht, S.
- ADUC Young Investigator Award of the German Chemical Society 2005
- Thieme Journal Award 2007

List, B.
- Novartis Young Investigator Award 2005
- AstraZeneca European Lecturer 2005
- Visiting Professor at Gakushuin University, Tokyo, Japan 2005
- The Society of Synthetic Chemistry, Japan: Lectureship Award 2005
- Degussa Lecture, Durham, UK, 26 November 2005
- JSPS Fellowship Award, Japan 2006
- Wiechert Lecture, Berlin, DE, 6 December 2006
- OBC-Lecture Award 2007
- AstraZeneca Award in Organic Chemistry 2007

Palkovits, R.
- Hendrik Casimir-Karl Ziegler Forschungspreis, June 2006

Reetz, M. T.
- John Osborn Lecture, Strasbourg, FR, 29 April 2005
- Bayer Cropscience Lecture, University of East Anglia, Norwich, UK, 11 May 2005
- Otto-Warburg Vorlesung, Bayreuth, DE, 19 May 2005
- Karl-Ziegler-Preis 2005

- Hamilton Award Lectureship, University of Nebraska, Lincoln, USA,10-11 November 2005
- UCI Organic Synthesis Lecture, University of California, Irvine, USA,15-16 March 2006
- Prelog-Medal-Lecture, ETH Zürich, CH, 6 November 2006
- Ernst Hellmut Vits-Preis 2006
- Stereochemistry Lecturer, Groningen, NL, 14 December 2006
- Senator of the Chemistry Section, Deutsche Akademie der Naturforscher Leopoldina, since 2007
- Honorary Professor of Shanghai Institute of Organic Chemistry, 2007

Schrader W.,
- Visiting Professor at Juniata College, Huntingdon USA, 2005

Schüth, F.
- Honorary Professor of Dalian University of Technology, 2007

Thiel, W.
- Member of Deutsche Akademie der Naturforscher Leopoldina, 2007
- Member of International Academy of Quantum Molecular Sciences, 2007

Trapp, O.
- Emmy Noether Research Grant 2005-2009 (DFG)
- Transatlantic Frontiers of Chemistry Symposium 2006
- Thieme Journal Award 2007
- Research Grant Award of the Merck Research Laboratories 2007

6.4 Contacts with Universities

All of the 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 outlining official co-operation between the two institutions. During the period 2005 – 2007 the following lectures/workshops were held:

Bühl, M., Dichtefunktionaltheorie- Grundlagen und Anwendungen, Universität-GH Wuppertal, WS 2004/2005

Bühl, M., Computer-gestützte Berechnung von Molekülstrukturen, Universität-GH Wuppertal, WS 2005/2006, WS 2006/2007, WS 2007/2008

Fink, G., Spezielle Makromolekulare Chemie: Stereospezifische Polymerisation und Stereochemie von Polymeren, Heinrich-Heine-Universität Düsseldorf, SS 2005

Fink, G., Spezielle Makromolekulare Chemie: Polymertechnik und Polymerisationsverfahren, Heinrich-Heine-Universität Düsseldorf, WS 2005/2006

Fink, G., Spezielle Organische Chemie: Polymerisationskinetik und Polymerisationstechnik, Heinrich-Heine-Universität Düsseldorf, SS 2006

Fink, G., Spezielle Organische Chemie: Reaktions- und Polymertechnik, Heinrich-Heine-Universität Düsseldorf, WS 2006/2007

Fink, G., Makromolekulare Chemie II, Heinrich-Heine-Universität Düsseldorf, SS 2007

Fink, G., Spezielle Organische Chemie: Reaktionskinetik und Polymertechnik (mit industriellen Anlagen), Heinrich-Heine-Universität Düsseldorf, WS 2007/2008

Fürstner, A., Moderne Synthesemethoden, Technische Universität Graz, A, WS 2004/2005, SS 2006

Fürstner, A., Stereoselektive Synthesen I, Universität Dortmund, DE, WS 2004/2005, WS 2006/2007

Fürstner, A., Stereoselektive Synthesen II, Universität Dortmund, DE, SS 2005, SS 2007

Fürstner, A., Naturstoffsynthese I, Universität Dortmund, DE, WS 2005/2006, WS 2006/2007

Fürstner, A., Naturstoffsynthese II, Universität Dortmund, DE, SS 2006

Haenel, *M.W*., Übergangsmetalle in der Organischen Synthese, Heinrich-Heine-Universität Düsseldorf, DE, WS 2004/2005, WS 2005/2006, WS 2006/2007, WS 2007/2008

Haenel, *M.W*., Organische Chemie II: Chemie der Aromaten und Heterocyclen, Heinrich-Heine-Universität Düsseldorf, DE, SS 2005, SS 2006

Haenel, *M.W*., Spezielle Aromatenchemie: Cyclophane – polycyclische Aromaten – Fullerene – Nanotubes, Heinrich-Heine-Universität Düsseldorf, DE, SS 2007

Hecht, S., Pericyclic Reactions, Universität Dortmund, DE, WS 2005/2006

Hecht, S., Organic Chemistry II (Tutorial), Universität Dortmund, DE, WS 2005/2006

Lehmann, C.W., Methoden der Strukturaufklärung, Bergische Universität Wuppertal, SS 2005, SS 2006, SS 2007

Lehmann, C.W., Praktikum Methoden der Strukturaufklärung, Mülheim/Ruhr, WS 2005/2006, WS 2006/2007

Leitner, W., Guest Professorship at the Université de Bourgogne, Dijon, FR, 2005

Leitner, W., Allgemeine Technische Chemie und Makromolekulare Chemie, Universität Aachen, SS 2005, WS 2005/2006, SS 2006, WS 2006/2007, SS 2007, WS 2007/2008

Leitner, W., Einführung in die Technische Chemie und Makromolekulare Chemie, Universität Aachen, SS 2005, WS 2005/2006, SS 2006, WS 2006/2007, SS 2007, WS 2007/2008

Leitner, W., Technische Chemie II, Universität Aachen, SS 2005, SS 2006, SS 2007

Leitner, W., Technische Chemie IVa, Universität Aachen, SS 2005, WS 2005/2006, SS 2006, WS 2006/2007, SS 2007, WS 2007/2008

Leitner, W., Technische und Makromolekulare Chemie I (Bachelor Studiengang), Universität Aachen, WS 2007/2008

List, B., Organokatalyse, Universität zu Köln, WS 2004/2005, SS 2005, WS2005/2006, SS 2006, WS 2006/2007, SS 2007

Pörschke, K.-R., Metallorganische Komplexchemie, Heinrich-Heine-Universität Düsseldorf, D, SS 2005, WS 2005/06, SS 2006, WS 2006/07, SS 2007, WS 2007/08

Marlow, F., Physical Chemistry in Nanostructured Systems III (Photonic Crystals), Freie Universität Berlin SS 2005, SS 2006, SS 2007

Marlow, F., „Molekulare Materialien“ im Bachelor-Studiengang Chemie/Molekulare Materialien an der Universität Duisburg, WS 2004/2005, WS 2005/2006, WS 2006/2007

Marlow, F., Vorlesung „Electronic and Optical Properties of Thin Films” Blockvorlesung (10 h) für Doktoranden im Ausbildungsprogamm der IMPRS SurMat (Universität Bochum, MPI Mülheim und MPI Düsseldorf), 2006

Marlow, F., Physikalische Chemie Nanostrukturierter Systeme IV (Molekulare Materialien), Freie Universität Berlin, WS 2007/08

Reetz, M. T., Advanced Course “Biocatalysis”, University of Technology, Delft, NL, 2005, 2006, 2007

Reetz, M. T, Basic Biocatalysis, Ruhr-Universität Bochum, SS 2007

Schrader, W., Experimentalvorlesung Analytische Chemie II – Quantitative Analyse, SS 2005

Schrader, W., Introduction into Modern Mass Spectrometry, Universität Münster, SS 2006, SS 2007

Schüth, F., Präparation fester Katalysatoren, Teil I und II, Ruhr-Universität Bochum, SS 2005, SS 2006, SS 2007

Schüth, F., Anorganische Chemie moderner Funktionsmaterialien im Master-Studiengang Chemie, Ruhr-Universität Bochum, SS 2006, SS 2007

Schüth, F. and Trapp, *O.*, Grundzüge der Chemie für Studierende des Maschinenbaus und des Studiengangs Umwelttechnik und Ressourcenmanagement, Ruhr-Universität Bochum, WS 2005/2006, WS 2006/2007, WS 2007/2008

Schüth, F., Moderne Aspekte der Chemie und Biochemie: Seminar des Sonderforschungsbereiches (SFB) 558: Metall-Substrat-Wechselwirkungen in der heterogenen Katalyse, Ruhr-Universität Bochum, WS 2005/2006, WS 2006/2007,WS 2007/2008

Thiel, W., Molekülmodellierung, Universität Düsseldorf, SS 2006

Thiel, W., SFB-Graduiertenkurs, Universität Düsseldorf, SS 2007

Trapp, O., Seminar zur Vorlesung Metallorganische Chemie II, Ruhr-Universität Bochum, SS 2005

Trapp, O., Fortgeschrittenenpraktikum Synthesechemie, Ruhr-Universität Bochum, WS 2005/2006, WS 2006/2007, WS 2007/2008

Trapp, O., Massenspektrometrie im Rahmen des Synthesechemieseminars, Ruhr-Universität Bochum, WS 2005/2006, WS 2006/2007, WS 2007/2008

6.5 Special Events and Activities

Colloquium on the Occasion of the 80th Birthday of
Prof. Dr. Dr. h.c. mult. Günther Wilke
Heterocyclencarbene: Effiziente und vielseitige Steuerliganden in der metallorganischen Homogenkatalyse
June 9, 2005
Prof. Dr. Dr. h.c. mult. Wolfgang A. Herrmann
TU München, DE

Karl-Ziegler-Lectureship 2005
Workshop on mechanisms and dynamics in thermal reactions of hydrocarbons
November 30 to December 2, 2005
Main Lecture November 30, 2005
Professor Kendall N. Houk
UCLA, USA

80 Years Fischer-Tropsch-Synthesis
Zur Entdeckung der Fischer-Tropsch-Synthese und den Folgen für das Kaiser-Wilhelm-Institut für Kohlenforschung
December 15, 2005
Professor Manfred Rasch
Corporate Archives, ThyssenKrupp AG and
Gas to liquids: Fischer Tropsch at work for a New Industry
Dr. Matthijs Senden
Shell Global Solutions International BV, Amsterdam, NL

Karl-Ziegler-Lectureship 2006
Workshop on Acid catalysis in organic synthesis
November 7–9, 2006
Main Lecture November 8, 2006
Professor Hisashi Yamamoto
University of Chicago, USA

Liebig Lectureship 2006

Workshop on the mechanistic puzzle of platinum and gold-catalyzed reactions of enynes and beyond

November 29, 2006

Professor Antonio Echavarren

Institute of Chemical Research of Catalonia, Tarragona, ES

Karl-Ziegler-Lectureship 2007

Workshop on catalysis by design: single and multisite catalysts

November 13-15, 2007

Main Lecture November 14, 2007

Professor Avelino Corma

Universidad Politécnica de Valencia, ES

Visiting Scientist Professor Dr. Jan-Erling Bäckvall

Department of Organic Chemistry, Stockholm University, Stockholm, SE

September 2004 - February 2005

Host: M. T. Reetz

Visiting Scientist Professor Dr. Margaret M. Kayser

Department of Chemistry, University of New Brunswick, Saint John, CA

22 April - 1 May 2005

Host: M. T. Reetz

Visiting Scientist Professor Dr. Zexing Cao

State Key Laboratory of Physical Chemistry of Solid Surfaces,

Department of Chemistry, Xiamen University, Xiamen, CN

1 January - 31 March 2006

Host: W. Thiel

Visiting Scientist Professor Dr. Stephan P. A. Sauer

Department of Chemistry, University of Copenhagen, Copenhagen, DK

1 August 2005 - 31 July 2006

Host: W. Thiel

Lecture course on catalysis, a four-semester programm, 2006-2007

F. Schüth *Basic Heterogeneous Catalysis (16 weeks)*
A. Fürstner *Basic Homogeneous Catalysis (8 weeks)*
B. List *Basic Organocatalysis (8 weeks)*
W. Thiel *Theoretical Approaches in Catalysis (6 weeks)*
M. T. Reetz *Basic Biocatalysis (6 weeks)*

School Contact Program (M.W. Haenel)**:**
During the period 2005-2007 about 15 classes of secondary schools from Mülheim and surroundings were invited to information visits. In addition, 49 students from chemistry classes in secondary schools performed chemical experiments in the laboratories of the Institute.

GIRLS' DAY at the MPI
28 April 2005, 27 April 2006, 26 April 2007
Organizer: C. Weidenthaler

Introduction into X-ray powder diffraction methods
MPI in-house Seminar: 24-28 January 2005, 20-24 March 2006, 22-26 October 2007
Organizer: C. Weidenthaler

International Workshop "Watching the Action II: Non-ambient X-ray Powder Diffraction Methods for In-House Instruments", 26-28 September 2007
Organizer: C. Weidenthaler

Organocatalysis in Germany
Meeting of nation-wide DFG Priority Program (SPP 1179) "Organocatalysis", sponsored by the German Research Foundation
9 February 2006
Conference Organization: B. List

Organic Synthesis
Regular check of procedures submitted
A. Fürstner

6.6 List of Talks Given by Guests (2005 - 2007)

2005

1 February 2005	Dr. Maase (BASF AG, Ludwigshafen, DE) *Ionic liquids on the large scale – how they can help to improve chemical processes*
25 February 2005	Professor John A. Robinson (University Zürich, CH) *Protein epitope mimetics in ligand and vaccine design*
12 April 2005	Professor Atanasios Giannis, Universität Leipzig, DE) *Natural products and their analogues as tools for chemical biology*
25 April 2005	Professor Margaret Kayser (Univ. of Brunswick, St. John, CN) *Fundamentals of medicinal chemistry*
30 May 2005	Professor Dalibor Sames (Columbia University, New York, USA) *C-H bond functionalization in complex organic synthesis*
1 June 2005	Dr. Daniel Boese (Universität Karlsruhe, DE) *The development of a novel density functional for thermochemical kinetics and the computation of molecular anharmonic force fields*
20 June 2005	Professor Tim Jamison (MIT, Cambridge, USA) *Catalytic, stereoselective fragment coupling reactions in total synthesis*
21 June 2005	Dr. Ivan Huc (Europ. Inst. of Chem. and Biology, Bordeaux, FR) *Structure, dynamics and assembly of folded biomimetic helical nanoarchitectures*
22 June 2005	Dr. Andrew Griffiths (Université Louis Pasteur, Strasbourg, FR) *Direct evolution in microdroplets*
28 June 2005	Dr. Muhannad Altarsha (Universität Nancy, FR) *Molecular modeling of the catalytic mechanism of urate oxidase*
1 July 2005	Professor Ronald Griessen (Freie Universität Amsterdam, NL) *How to use switchable mirrors in the search for new hydrogen storage materials and catalysts*
13 July 2005	Professor F. Dean Toste (UC Berkeley, USA) *Development and applications of "open flask" transition metal catalysts for organic synthesis*

14 July 2005	Professor Masaharu Nakamura (University of Tokyo, JP) *Development of catalytic C-C bond formations toward exploitation of chemical resources*
19 July 2005	Professor Choong Eui Song (Corean Chemical Society and Sungkyunkwan University, COR) *Significant improvement of catalytic efficiencies in ionic liquids*
20 July 2005	Professor Qi-Lin Zhou (Nankai University, Tianjin, CN) *The synthesis and applications of chiral spira phosphorous ligands*
22 July 2005	Professor Kuiling Ding (Shanghai Inst. of Organic Chem., CN) *Development of homogeneous and heterogeneous chiral catalysts for practical enantioselective reactions*
27 July 2005	Professor Yoshiaki Nakao (Kyoto University, JP) *Pd- and Ni-catalyzed new reactions with high atom economy*
29 August 2005	Dr. Petri Pihko (Helsinki University of Technology, FI) *Organocatalytic tools for asymmetric synthesis*
9. September 2005	Professor Andrei K. Yudin (University of Toronto, CA) *New catalytic processes for the selective construction of carbon-nitrogen bonds in organic synthesis*
10 October 2005	Professor Tamejiro Hiyama (Kyoto University, JP) *From carbenoid to gem-dimetallic reagents for organic synthesis*

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13 January 2005	Professor William Tolman (University of Minnesota, USA) *Using synthetic chemistry to understand dioxygen activation by copper protein active sites*
7 April 2005	Dr. H. Hugl (Bayer Chemicals AG, DE) *Custom manufacturing of fine chemicals – A challenging exercice for chemists*
31 May 2005	Professor Eric Meggers (University of Pennsylvania, USA) *Bridging bioorganic and bioinorganic chemistry*
8 June 2005	Professor Dirk Trauner (UC Berkeley, USA) *Chemical synthesis and synthetic biology*
28 July 2005	Dr. Philip Kraft (Givaudan, CH) *Musks & More: Design and synthesis of new odorants*

2 August 2005 — Professor Yian Shi (Colorado State University, USA)
Developing chiral ketone catalysts for asymmetric epoxidation of olefins with broad substrate scope

16. September 2005 — Professor Kenso Soai (Tokyo University of Science, JP)
Role of asymmetric autocatalysis in chiral discrimination and origin of chirality

13 October 2005 — Professor Franc Meyer (Universität Göttingen, DE)
Cooperating metal centers: metalloenzyme active sites, synthetic models and beyond

3 November 2005 — Professor Scott Miller (Boston College, USA)
Diverse peptide-based catalysts for various organic reactions

5 December 2005 — Professor Michael Harmata (University of Missouri, USA)
From the 4+3 cycloaddition to the retro-Nazarov reaction

2006

13 January 2006 — Dr. Wilhelm Schwieger (Universität Erlangen-Nürnberg, DE)
Zeolithhaltige Kompositionsmaterialien mit hierarchischer Porenstruktur: Präparation – Eigenschaften – Anwendungs-potential

24 January 2006 — Dr. Günther Rupprechter (Fritz-Haber-Institut, Berlin, DE)
Monitoring adsorbed molecules during catalytic reactions at mbar pressure

6 February 2006 — Professor Ram Mohan (Illinois Wesleyan University, USA)
Environmentally friendly organic synthesis using bismuth compounds

7 February 2006 — Dr. Viveka Alfredsson (University of Lund, SE)
Pluronic-assisted mesoporous silica synthesis – mechanism of formation

7 February 2006 — Dr. Kazuki Nakanishi (Kyoto University, JP)
Hierarchically porous monolithic materials via sol-gel accompanied by phase separation

22 March 2006 — Professor David B. Berkowitz (University of Nebraska, USA)
Recent developments at the synthetic organic/enzymatic interface

29 March 2006 — Dr. Eduardo Fabiano (University of Lecce, IT)
Validation of density functional theory for the study of ground- and excited-state properties of oligothiophenes and derivatives

31 March 2006	Professor Elena Sheka (Humboldt-Universität, Berlin, DE) *Electron unpairing in fullerenes and nanotubes*
4 April 2006	Professor Richard F. W. Jackson (University of Sheffield, UK) *Non-natural amino acids: synthesis and applications in asymmetric sulphur oxidation catalysis*
5 April 2006	Dr. Ulrich Eberle (GM Fuel Cell Activities, Mainz-Kastel, DE) *The science and technology of hydrogen storage*
12 April 2006	Professor John Eisch (State Univ. of N. Y. at Binghamton, USA) *Novel metallocene derivatives of the titanium group of transition metals: their syntheses and mode of action in Ziegler olefin polymerisation*
25 April 2006	Professor Jeremy K. M. Sanders (University of Cambridge, UK) *Dynamic combinatorial chemisty: new opportunities for molecular recognition and catalysis*
26 April 2006	Dr. Angelos Michaelides (Fritz-Haber-Institut, Berlin, DE) *Electronic structure simulations of everyday materials: water, ice and salt*
9 May 2006	Professor Liu-Zhu Gong (University of Science and Technology of China, CN) *Organocatalyzed asymmetric direct aldol reactions with proline amides*
10 May 2006	Professor Min Shi (Shanghai Inst. of Organic Chemistry, CN) *Reusable chiral thiophosphoramide ligands in asymmetric catalysis*
12 May 2006	Professor Huw M. L. Davies (University of Buffalo, USA) *C-H activation as a strategic reaction in organic synthesis*
31 May 2006	Dr. Klaus Halbritter (BASF, AG Ludwigshafen, DE) *Highlights of innovative industrial chemistry*
21 June 2006	Dr. Marko Schreiber (FU Berlin, DE) *CASPT2 calculations of excited states in biomolecules*
3 July 2006	Professor Takahiko Akiyama (Gakushuin University, Tokyo, JP) *Chiral Broensted acid catalyzed aza Diels-alder reactions*
3 July 2006	Professor Geoffrey Ozin (University of Toronto, CA) *Intelligent colors*

12 July 2006	Professor Jieshan Qiu (Dalian University of Technology, CN) *Selective preparation of nano- and micro-sized carbon materials*
25 July 2006	Professor Zhanglin Lin (Tsinghua University, Beijing, CN) *Directed evolution: methods and applications*
27 July 2006	Dr. Michael T. Janicke (Los Alamos National Laboratory, USA) *Modern catalysis research at the Los Alamos National Laboratory*
10 August 2006	Dr. Rajkumar Halder (Univ. Del País Vasco, San Sebastian, ES) *Catalytic enantioselective conjugate addition of carbamates and aza-Henry reaction with N-Boc protected imines*
16 August 2006	Dr. Jörn Bolle (B.A.D., Mülheim, DE) *Arbeitsmedizinisch – toxikologische Mitarbeiterberatung nach § 14 Gefahrstoffverordnung*
5 September 2006	Dr. Florian Ausfelder (Universidad Complutense, Madrid, ES) *Untersuchung von Reaktionsdynamiken mit physikalischen Methoden*
6 September 2006	Professor Phil Baran (Scripps Research Institute, La Jolla, USA) *The catalytic cycle of discovery in total synthesis*
12 September 2006	Professor Dennis Hall (University of Alberta, Edmonton, CA) *New catalytic processes, natural product synthesis, and chemical biology using boronic acids*
22 September 2006	Dr. Alexis Bouet (National Inst. of Applied Sciences, Rouen, FR) *Synthesis of 7,5-fused lactames and their evaluation as new chiral ligands*
25 September 2006	Professor Robert Glaser (Ben-Gurion Univ. of the Negev, IL) *Polysectioning of achiral objects – Helical stereochemistry and chiral apple halves*
6 October 2006	Professor Li Deng (Brandeis University, Boston, USA) *Asymmetric catalysis with cinchona alkaloids*
17 October 2006	Professor John M. Brown (Oxford University, UK) *Recognition, ligand resolutions and asymmetric catalysis*
18 October 2006	Dr. Patricia Garcia Garcia (Universidad de Oviedo, ES) *Reactivity of Fischer alkynyl(alkoxy)carbene complexes towards unsaturated systems*
2 November 2006	Dr. Stephan Kujawa (FEI Company, Eindhoven, NL) *Aberration corrected (S)TEM in nano-research entering a new era*

27 November 2006 Professor Christophe Copéret (ESCPE-CNRS, Villeurbanne, FR)
Activating metal centers by grafting on silica : a molecular understanding of silica supported well-defined olefin metathesis catalysts

8 December 2006 Professor Sason Shaik (The Lise Meitner-Minerva Center for Computational Quantum Chemistry, Jerusalem, IL)
Selectivity of Cytochrome P450 Enzymes: What really counts?

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26 January 2006 Professor Reinhart Ahlrichs (Institut für Physikalische Chemie, Universität Karlsruhe, DE)
Eigenschaften von Clustern: Messung und Berechnung

2 February 2006 Professor Donald Hilvert (ETH Zürich, CH)
Conformational diversity and catalysis

16 March 2006 Professor Michael J. Krische (University of Austin, Texas, USA)
Hydrogen-mediated C-C bond formation: discover, development, and diversions

27 April 2006 Professor Hansjörg Grützmacher (ETH Zürich, CH)
Chemistry with paramagnetic late transition metal complexes

1 June 2006 Professor Rainer Herges (Universität Kiel, DE)
Aromatics do the twist, die Synthese der ersten Moebius-Annulene

12 October 2006 Professor Shu Kobayashi (Tokyo University, JP)
Truly efficient and powerful catalyst systems in organic synthesis

26 October 2006 Professor Krijn P. de Jong (Utrecht University, NL)
Electron tomography for fundamental studies on the preparation of supported catalysts

2007

18 January 2007 Professor Adriaan Minnaard (Groningen University, NL)
Asymmetric conjugate addition reactions and their application in natural product synthesis

13 February 2007 Professor Yasuhiro Uozumi (Inst. of Molec. Science, Okazaki, JP)
Heterogeneous aquacatalytic organic reactions with amphiphilic polymer-supported palladium complexes and nanoparticles

27 February 2007	Professor Zhibin Guan (University of California at Irvine, USA) *Novel cyclophene-based late transition metal catalysts for olefin polymerization and copolymerization with polar monomers*
28 February 2007	Professor Ilan Marek (Technion-Israel Institute of Technology, Haifa, IL) *New methods for the preparation of enantiomerically pure quarternary stereocenters*
2 March 2007	Professor Chia-Min Yang (National Tsing Hua University, TW) *Structural modulation and selective functionalization of ordered large-pore silica mesophases*
7 March 2007	Dr. Wayne M. Coco (Direvo Biotech AG, Köln, DE) *Protein engineering by directed evolution using high-throughput confocal fluorimetry screens*
30 April 2007	Professor Max Lu (University of Queensland, AU) *Functional nanomaterials for clean coal technologies and fuel-cell applications*
4 May 2007	Dr. Mika Linden (Abo Akademi University, Turku, FI) *Quantifying the extent of surface functionalization of mesoscopically ordered inorganic materials*
7 May 2007	Professor Vijay Nair (Cochin University of Science & Technology, Trivandrum, IN) *Novel carbon-carbon and carbon-heteroatom bond-forming reactions mediated by NHCs and other nucleophiles*
14 May 2007	Professor Jacek Mlynarski (Polish Acad. of Sci., Warsaw, PL) *Direct asymmetric aldol reactions promoted by lanthanide complexes (Aldol-Tishchenko Reaction) and zinc complexes in aqueous media*
22 May 2007	Professor Thomas Schrader (Universität Essen, DE) *Interfering with biological processes via artificial receptors*
22 May 2007	Professor Janine Cossy (National Center for Research and Sciences, Paris, FR) *Synthesis of heterocyclic compounds*
11 June 2007	Professor Gérard Cahiez (University de Cergy-Pontoise, FR) *New iron- and cobalt-catalyzed cross-coupling reactions*
15 June 2007	Professor Roy Periana (University of Southern California, USA) *Design and study of new coordination complexes for the selective,*

	low temperature, oxidation of hydrocarbons based on the CH activation reaction
25 June 2007	Professor Ken B. Wagener (Univ. of Florida, Gainsville, USA) *Precise polyolefins*
9 August 2007	Professor Gregory Yablonsky (Washington Univ, St. Louis, USA) *Pulse-response studies in heterogeneous catalysis*
10 August 2007	Professor Matthias Tamm (Technische Univ. Braunschweig, DE) *Efficient room-temperature alkyne metathesis with well-defind imidazolin-2-iminato Tungsten alkylidyne complexes*
5 September 2007	Professor Robert Glaser (Ben-Gurion Univ. of the Negev, IL) *Chiral recognition via helical sense and phase in a crystalline supramolecular array of intermeshed triple-helices*
19 September 2007	Professor Valerii Bukhtiyarov (Boreskov Inst., Novosibirsk, RU) *The size effects in catalysis by supported Au and Pt nanoparticles*
19 September 2007	Professor Varinder K. Aggarwal (University of Bristol, UK) *Chiral corbenoids for asymmetric synthesis*
21 September 2007	Dr. Peter Gregory (Advanced Materials, Weinheim, DE) *Publishing science and how to maximise your chances*
9 October 2007	Professor Andreas Bommarius (Georgia Tech, USA) *Biocatalyst improvement with data-driven protein engineering*
11 October 2007	Professor Feng-Shou Xiao (State Key Lab., Jilin Univ., CN) *Organic template-free and environmentally benign template synthesis of zeolites and mesoporous zeolites*
26 October 2007	Professor Scott E. Denmark (Univ. of Illinois, Urbana, USA) *Asymmetric catalysis in main-group chemistry: a new frontier?*
8 November 2007	Professor Dirk Guldi (Univ. Erlangen-Nürnberg, DE) *Carbon nanostructure materials: from charge transfer to photovoltaics*
21 November 2007	Professor Sean C. Smith (Univ. of Queensland, Brisbane, AU) *Fluorescent protein modeling: quantum chemistry, mechanism and dynamics*
22 November 2007	Professor Sean C. Smith (Univ. of Queensland, Brisbane, AU) *Computational simulation of catalysis in nanocomposite materials for hydrogen storage applications*

29 November 2007 Professor Frank Würthner (Universität Würzburg, DE)
Self-assembled functional dye architectures for supramolecular electronics and photovoltaics

30 November 2007 Professor Stefan Matile (University of Geneva, CH)
Synthetic functional architecture at interfaces: ion channels, sensors and photosystems

10 December 2007 Professor Yi Lu (Univ. of Illinois at Urbana-Champaign, USA)
Biosynthetic inorganic chemistry

12 December 2007 Professor Eric Meggers (Universität Marburg, DE)
Morphing natural architectures into metal complexes with novel properties: from metallo-nucleic acids to metals in enzyme inhibitors

13 December 2007 Dipl.-Chem. Heiner Friedrich (University of Utrecht, NL)
Electron tomography of catalysts

14 December 2007 Professor Kay Severin (EPFL, Lausanne, CH)
In and out of control: functional nanostructures and sensors by self-assembly

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8 February 2007 Professor Harald Gröger (Universität Erlangen, DE)
Designer-Zellen für die Organische Synthese

21 June 2007 Professor Peter Kündig (Universität Genf, CH)
Advances in transition metal Lewis acid-mediated and -catalyzed reactions

23 August 2007 Professor Johann Mulzer (Wien University, AT)
Total synthesis and drug development

13 September 2007 Professor K. Peter C. Vollhardt (UC Berkeley, USA)
Apparent progress in the total synthesis of carbon

25 October 2007 Professor Wolfgang Domcke (TU München, DE)
Conical intersections and photostability of the building blocks of life

6.7 Alexander von Humboldt Senior Awardees Hosted by the Institute

Professor Dr. Peter G. Schultz
The Scripps Research Institute
Department of Chemistry
10550 North Torrey Pines Road
La Jolla, CA 92037
USA

Professor Richard R. Schrock
Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139
USA

Professor Dr. Maurice Brookhart
University of North Carolina
Department of Chemistry
Chapel Hill, NC 27599
USA

Professor Dr. Galen Stucky
University of California at Santa Barbara
Department of Chemistry and Biochemistry
Biomolecular Science and Engineering Program
Materials Department
Santa Barbara, CA 93106
USA

Professor Dr. Osamu Terasaki
Stockholm University
Department of Structural Chemistry
Arrhenius Laboratory
Stockholm, SE 10692
Sweden

6.8 Local Activities of the Young Chemists Forum (JCF) of the German Chemical Society (GDCh)

List of Talks Given by Guests

8 December 2005	Professor Heinrich Wamhoff (Rheinische Friedrich-Wilhelms-Universität Bonn, DE) *Wein und Gesundheit – neue Inhaltsstoffe und neue Einsichten*
7 March 2006	Dr. Andreas Pletsch (BASF, Ludwigshafen, DE) *From MPI to GCI – a switch from coal to fine chemistry*
3 August 2006	Dr. Ariel Fenster (McGill University, Montreal, CA) *Science and art – facts and fakes*
24 October 2007	Professor T. Vilgis (MPI für Polymerforschung, Mainz, DE) *Proteins, polymers, polyelectrolytes: molecular kitchen aids*
5 December 2007	Udo Pollmer (Europäisches Institut für Lebensmittel- und Ernährungswissenschaften, Gemmingen, DE) *Wer nicht genießt, wird ungenießbar!*

6.9 How to Reach the Institute

Travel Directions

By Road:

If approaching from the south on the A3 autobahn, exit at Breitscheid and join the A52 heading for Essen. After about 100 m turn off onto the B1 in the direction of Mülheim an der Ruhr. After about 8 km, follow the signs marked Max-Planck-Institute.

If travelling from the north (A3 autobahn) or west (A40 autobahn), exit at Duisburg-Kaiserberg in the direction of Mülheim an der Ruhr, continue to the town center (Friedrichstraße) and follow the signs marked Max-Planck-Institute.

If arriving from the east (A40 from Essen), join the B1 heading for Mülheim an der Ruhr. After about 5 km, follow the signs marked Max-Planck-Institute.

By Rail:

Take the train to Duisburg or Essen, and then the local railway (S-Bahn) 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