MAX-PLANCK-GESELLSCHAFT

Max-Planck-Institut für Kohlenforschung

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MAX-PLANCK-GESELLSCHAFT

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Dr. Wolfgang Schmidt (since August 2003)

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Professor Dr. Günther Wilke
Professor Dr. Roland Köster

Table of Contents

1 The Max-Planck-Institut für Kohlenforschung 9
1.1 History 11
1.2 Current Research Areas 14
1.3 Organigram 2003 16
1.4 Members of the Scientific Advisory Board 17
1.5 Members of the Board of Governors 18

2 Research Programs 19
2.1 Department of Synthetic Organic Chemistry 21
2.1.1 Transition Metal Catalyzed Reactions (M. T. REETZ) 27
2.1.2 Directed Evolution as a Means to Create Enantioselective Enzymes (M. T. REETZ) 31
2.1.3 Directed Evolution as a Means to Create Selective Hybrid Catalysts (M. T. REETZ) 36
2.1.4 Nanosized Metal and Metal Oxide Colloids (M. T. REETZ) 39
2.1.5 Olefin Polymerization with Silica Supported Metallocene/MAO Catalysts (G. FINK) 41
2.1.6 Metallocene-Catalyzed C7-Linkage in the Hydrooligomerization of Norbornene by σ-Bond Metathesis: Insight into the Microstructure of Polynorbornene (G. FINK) 44
2.1.7 Homo-, Co- and Terpolymerization of Different α-Olefins and Functionalized Monomers with Metallocenes and New Catalysts (G. FINK) 47
2.1.8 New Transition Metal-Catalyzed Reactions for Organic Synthesis (L. J. GOOSSEN) 48
2.1.9 Hydrogenation/Hydrogenolysis of Bituminous Coals with Homogeneous Borane Catalysts (M. W. HAENEL) 52
2.1.10 Development of Thermostable Homogeneous Catalysts Based on Polycyclic Arenes and Heteroarenes (M. W. HAENEL) 54
2.1.11 Supercritical Carbon Dioxide as Reaction Medium for Catalysis (W. LEITNER / N. THEYSSEN) 58

2.2 *Department of Homogeneous Catalysis* 63
2.2.1 Mononuclear and Polynuclear Transition Metal Complexes with Pentalene and Related Polycycles as Ligands (K. JONAS) 65
2.2.2 Organocatalytic Asymmetric α-Alkylation of Aldehydes (B. LIST) 73
2.2.3 Organocatalytic Asymmetric Intramolecular Michael Reaction of Aldehydes (B. LIST) 75
2.2.4 Metal-Free Catalytic Hydrogenation (B. LIST) 77
2.2.5 Allyl Complexes of the d^{10}-Metals Nickel and Palladium (K.-R. PÖRSCHKE) 80
2.2.6 Stereochemical Nonrigidity of Ni- and Pd-allyl Complexes (K.-R. PÖRSCHKE) 82

2.3 *Department of Heterogeneous Catalysis* 85
2.3.1 Understanding the Synthesis of Solid Catalysts (F. SCHÜTH) 91
2.3.2 Combinatorial Catalysis and Novel Reactor Concepts (F. SCHÜTH) 94
2.3.3 High Surface Area Catalyst Materials (F. SCHÜTH) 97
2.3.4 Light Metal Hydrides for Hydrogen and Energy Storage (F. SCHÜTH / B. BOGDANOVIĆ) 101
2.3.5 Nanostructured Metal Colloids (H. BÖNNEMANN) 104
2.3.6 Porous and Nanostructured Materials (S. KASKEL) 107
2.3.7 Nanostructured Optical Materials (F. MARLOW) 109
2.3.8 Novel Mesostructures (F. MARLOW) 111

2.4 *Department of Organometallic Chemistry* 113
2.4.1 Methathesis of Alkenes and Alkynes (A. FÜRSTNER) 118
2.4.2 Iron Catalyzed Cross Coupling Reactions (A. FÜRSTNER) 123
2.4.3 Novel Concepts for Catalysis (A. FÜRSTNER) 127
2.4.4 Catalysis Based Syntheses and Evaluation of Bioactive Natural Products (A. FÜRSTNER) 131
2.4.5 New Concepts for Catalysis (F. GLORIUS) 135

2.5 *Department of Theory* 139
2.5.1 Ab Initio Methods (W. THIEL) 143
2.5.2 Density Functional Methods (W. THIEL) 147
2.5.3 Semiempirical Methods (W. THIEL) 150

2.5.4 Combined Quantum Mechanical/Molecular Mechanical Methods (W. THIEL) 153
2.5.5 Molecular Modeling (K. ANGERMUND) 157
2.5.6 Computational Chemistry of Transition-Metal Compounds (M. BÜHL) 159

3 Scientific Service Units 163
3.1 Technical Laboratories (N. THEYSSEN) 166
3.2 Chromatography and Separation Science (D. BELDER) 167
3.3 Mass Spectrometry (W. SCHRADER) 169
3.4 Nuclear Magnetic Resonance (R. MYNOTT) 171
3.5 Chemical Crystallography (C. W. LEHMANN) 173
3.6 Electron Microscopy (B. TESCHE) 175
3.7 Library and Information Management (W. RICHTER) 177
3.8 Computer Group (A. KOSLOWSKI) 178

4 The Training of Young Scientists 181

5 Technology Transfer 191

6 Special Events and Activities 195
6.1 Open House 197
6.2 60th Birthday of Manfred T. Reetz 198
6.3 Visit of the Cabinet of the State Government 199
6.4 Other Events and Activities 200

7 Appendices 203
7.1 List of Publications 205
7.2 List of Invited Talks Given by Members of the Institute 231
7.3 Scientific Honors, Lectureships, Awards 246
7.4 Contacts with Universities 248
7.5 List of Talks Given by Guests 250
7.6 Alexander von Humboldt Senior Awardees Hosted by the Institute 257
7.7 Local Activities of the Young Chemists Forum (JCF) of the German Chemical Society (GDCh) 258
7.8 How to Reach the Institute 260

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 aluminum alkyls to ethylene 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 stereochemistry of polypropylene). Ziegler subsequently created the Ziegler-Fund (in 1968) and the Ziegler-Foundation (in 1970) which still play an important role in financing the Institute.

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

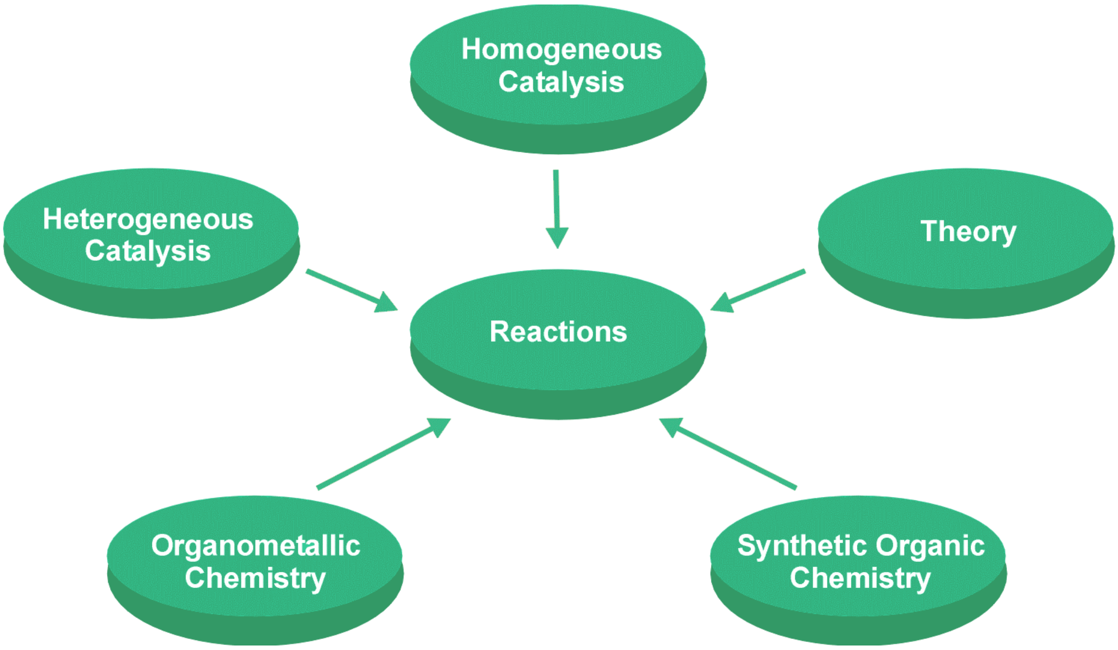
Department of Homogeneous Catalysis, while Manfred T. Reetz headed the Department of Synthetic Organic Chemistry. Thereafter the appointments of Ferdi Schüth (Heterogeneous Catalysis), Alois Fürstner (Organometallic Chemistry) and Walter Thiel (Theory) followed. Thus, the scientific activities of the 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 became vacant. The Institute had subsequently engaged in an intensive process of head-hunting, and several possible successors for Andreas Pfaltz had been invited to present their research. Initially, it was intended to fill the position with a scientist active in the field of homogeneous metal complex catalysis, in direct succession of the work of Andreas Pfaltz. However, around 2000 a new direction in catalysis emerged, the field of organocatalysis. Professor Benjamin List from the Scripps Institute, La Jolla, was identified as a prominent pioneer in this field, and he was hired on a C3-position (associate professor) in 2003, with the intention of promoting him to a director position within a few years. This process has now been initiated, a commission of the Max Planck Society is working, and it is expected that Benjamin List will be appointed director around the middle of the year.

During the last 10 years far-reaching organizational changes were carried out, including a strong reduction in the number of permanent positions, change in the salary system, re-organization of the Scientific Service Units and workshops as well as changes in the statutes of the Institute. The Directors of the Departments now form the newly created Board of Directors which is responsible for all decisions. The bylaws of the Institute had to be adapted to accommodate these changes. The new bylaws also stipulate that the affairs of the Institute are managed by a Managing Director elected from the Board of Directors, who serves for a term of three years. Starting from January 1st 2003, this change went into effect, and Ferdi Schüth succeeded Manfred Reetz as Managing Director for the term ending on December 31st 2005. This change went smoothly and without any problems.

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.

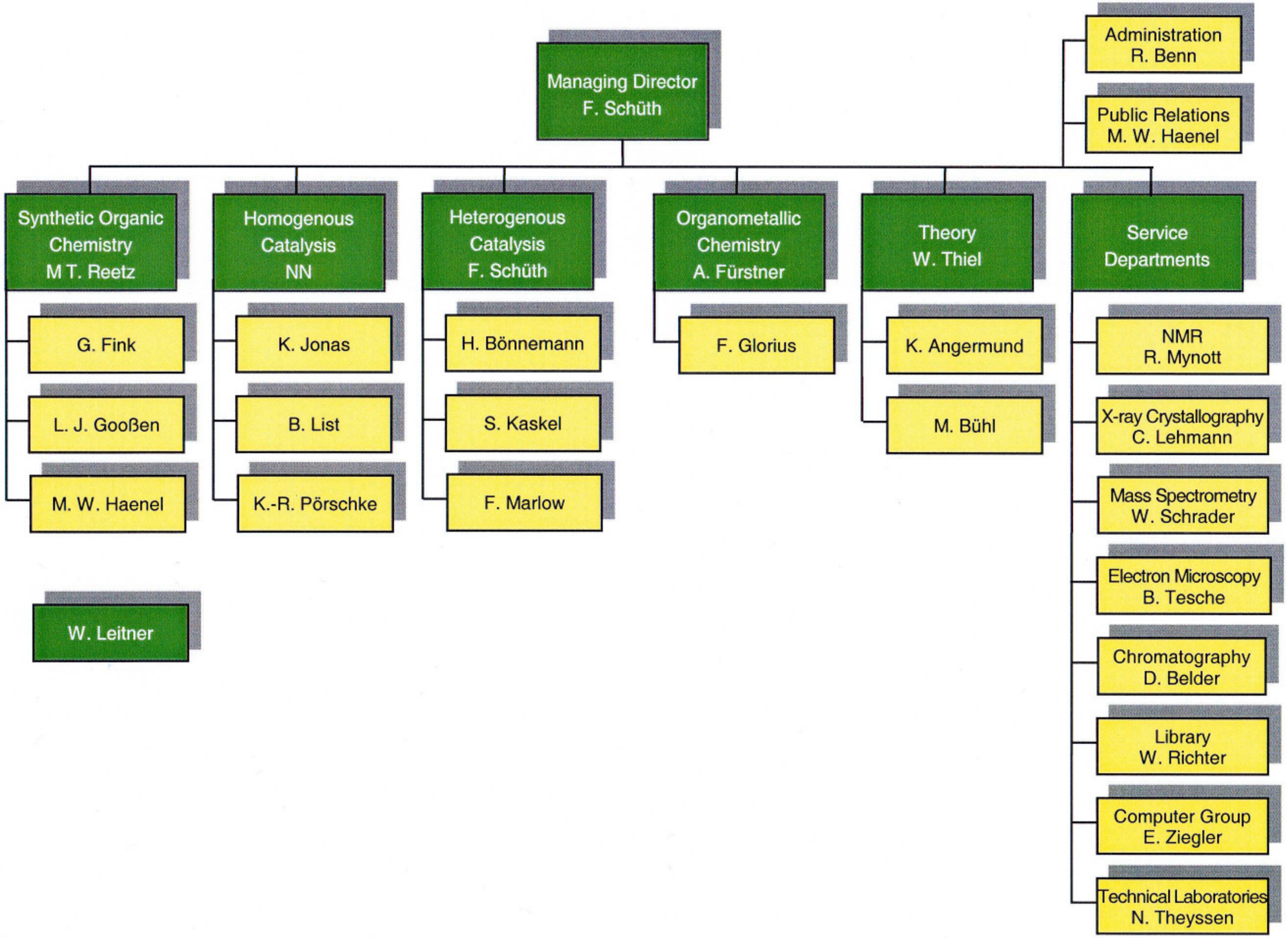


Catalysis is viewed world-wide as the key technology in the establishment of economically and ecologically sound chemical processes of the future. However, the efficiency of numerous catalytic systems is far from ideal, and for many important chemical transformations appropriate catalysts have not even 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, 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, 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 in the Middle of the Reporting Period (July 2003)



1.4 Members of the Scientific Advisory Board

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

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

Members of the Board of Governors 2002

Ministerium für Schule und Weiterbildung, Wissenschaft und Forschung des Landes Nordrhein-Westfalen
Dr. Jens Baganz, Oberbürgermeister der Stadt Mülheim an der Ruhr
Dr. Barbara Bludau
Dr. Jürgen Engelhard
Prof. Dr. Fred Robert Heiker
Dr. Ulrich Knips
Dr. Jörn Rüter
Dr. Werner Schwilling

Prof. Dr. Günther Wilke, Honorary Member

Members of the Board of Governors 2003 and 2004

Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen
Dr. Barbara Bludau
Dr. Jürgen Engelhard
Prof. Dr. Fred Robert Heiker
Dr. Ulrich Knips
Dagmar Mühlenfeld, Oberbürgermeisterin der Stadt Mülheim an der Ruhr
Dr. Jörn Rüter
Dr. Werner Schwilling

Prof. Dr. Günther Wilke, Honorary Member

CHAPTER 2

Research Programs

2.1 Department of Synthetic Organic Chemistry

Director:

Manfred T. Reetz (born 1943)
Publications: 51, 63, 94, 97, 99-114, 121, 176, 193, 210, 258-271, 284, 290, 304, 311, 338, 397-412

Further group leaders:

Gerhard Fink (born 1939)
retired from the Institute in June 2004
Publications: 5, 76, 144, 145, 152, 195, 218, 235, 236, 280, 287, 296, 298, 307, 340, 341, 364, 384, 432

Lukas J. Gooßen (born 1969)
left the Institute in August 2004
Publications: 52-57, 214, 215, 263, 352-356

Matthias W. Haenel (born 1944)
Publication: 211

Walter Leitner (born 1963)
left the Institute in February 2002, now associated as external scientific member of the Institute
Publications: 17, 34, 62, 79, 82, 83, 92, 95, 114, 132, 135, 154, 212, 239, 240, 281, 288, 426

Other publication: 77, 187

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 of 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
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

1980-2004	>120 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-	Member of Advisory Board, Catalysis NRSC (The Netherlands)
1999-	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-	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

since 1985	Member of Advisory Committee of numerous scientific conferences

Research in the Department of Synthetic Organic Chemistry

The primary current objective of the Department of Synthetic Organic Chemistry is the development of new catalytic systems for use in synthetic organic chemistry (M. T. Reetz, M. W. Haenel, L. J. Gooßen), with additional activities in polymer chemistry (G. Fink) and coal transformation (M. W. Haenel). Generally, model reactions are involved, although in other cases specific transformations of real practical interest are chosen. We attempt to offer new solutions to solving some of the challenging problems well known in the catalysis community: Maximizing efficiency and ecological viability. This also includes the exploration of totally new approaches which may not be efficient in the first instance, but which may lay down the foundation for future development into practical (and perhaps) industrial processes. All of the results are derived from basic research, which means that interest in understanding any significant advancements on a molecular basis constitutes an integral part of the various projects.

The development of new methods in the area of enantioselective catalysis is of great academic and practical interest worldwide. Since success in this truly difficult endeavor is based on experience, intuition, knowledge of reaction mechanisms, and the ability to utilize molecular modeling and other theoretical methods (and of course trial and error!), many different approaches and ideas need to be discussed and tested. The Institute is an ideal forum for this type of research. In addition to efforts from this Department, several groups in the other Departments are likewise involved, leading to a lively exchange of ideas and in some cases to collaborations. An obvious approach concerns the development of novel types of chiral ligands for asymmetric transition metal catalysis, the guiding lines being kinetics and theoretical analyses based on MM/QM (in collaboration with the Theory Department). Although in the past the number of steps involved in the synthesis of a given ligand played no role, the focus is now on cheap chiral starting materials. The maximum number of synthetic steps which follow should not exceed two or three. Moreover, novel combinatorial approaches are being developed and applied (M. T. Reetz).

A completely different strategy in asymmetric catalysis concerns directed evolution as a means to create enantioselective enzymes for use in synthetic organic chemistry (M. T. Reetz). This way of approaching enantioselectivity is totally independent of any structural knowledge of the enzyme or of its mode of catalytic action. Instead, it relies on Darwinistic principles. This approach was pioneered by the Reetz group in the late

1990s, using lipases. The results were so promising that the group has extended the basic idea to include other enzymes such as epoxide hydrolases and oxidases. Selective partial oxidation of organic substrates is of great interest for the future, especially in those cases in which synthetic catalysts fail. The theoretical analysis (in collaboration with the Department of Theory) of highly enantioselective enzyme mutants is a crucial component of these projects. Indeed, the collaborative efforts with W. Thiel have shown that it is possible to learn from directed evolution.

Another novel project has been initiated which goes far beyond the natural limitations inherent in enzyme catalysis, namely the directed evolution of hybrid catalysts composed of a protein and a ligand/metal center. Thus, the methods of molecular biology are being used as a means to perform ligand tuning in transition metal catalysis. Crucial to success in both areas is, inter alia, the development of high-throughput screening systems for determining the *ee*-values of thousands of reactions catalyzed by randomly mutated enzymes. Such assay systems can also be used in combinatorial transition metal catalysis if so desired. Indeed, the Institute is a leader in the development of high-throughput screening systems for enantioselectivity.

A different area of interest is catalyst use and recovery in environmentally benign media. Two rather different approaches are being taken, namely catalytic and biocatalytic reactions in unusual solvents such as supercritical CO_2 or ionic liquids on the one hand (W. Leitner, M. T. Reetz), and reactions catalyzed by thermally stable metal complexes on the other (M. W. Haenel). In both cases new ligands need to be designed and synthesized, the development of novel concepts in reaction engineering also being an integral part of the research (W. Leitner). The development of transition metal complexes characterized by unusually high thermal stability allow for special types of applications such as CH-activation or dehydrogenation as well as catalyst separation by simple distillation of the organic product at elevated temperatures without catalyst decomposition (M. W. Haenel). This is the easiest solution to the problem of catalyst recovery!

Efficiency based on environmentally benign reagents and/or catalysts in an atom economical manner under mild conditions is the primary goal of Pd-catalyzed ketone syntheses, salt-free Heck reactions and other synthetic organic reactions (L. J. Gooßen). The Au-catalyzed hydroarylation of alkynes is another example of atom-economical reactions (M. T. Reetz).

The Department of Synthetic Organic Chemistry has conceptional ties to other groups, especially to the Department of Theory. Several important collaborative efforts have emerged in addition to the one described above. The development of novel methods for the fabrication of transition metal colloids as well as colloids composed of transition metal *oxides*, their immobilization on solid supports and the possible use of such heterogeneous catalysts in electrocatalysis is another important research area (M. T. Reetz). This particular long-term effort bears some relationship to the research in the group of H. Bönnemann (Department of Heterogeneous Catalysis), although the respective approaches are different.

Linking homogeneous and heterogeneous catalysis is being pursued actively in several Departments. Encapsulation of enzymes in hydrophobic sol-gel materials derived from alkylsilanes $RSi(OCH_3)_3$ as precursors is an example (M. T. Reetz). Another case involves the immobilization of structurally well-defined metallocenes on SiO_2 and on other solid supports (G. Fink). Such solid catalysts are known to be useful in the polymerization of ethylene and α-olefins, yet mechanistic details remained obscure for decades, making "design" in the all important immobilization essentially impossible. Fundamental knowledge concerning the details of particle fragmentation and of polymer growth in such systems has been acquired (G. Fink). Other interdisciplinary efforts involving two Departments include the application of theoretical tools such as molecular modeling in illuminating the relationship between the metallocene catalyst structure and the microstructure of the resulting polymer (G. Fink, W. Thiel, K. Angermund), as well as the design and preparation of new olefin polymerization catalysts for functionalized polar monomers (G. Fink). Finally, research concerning the first example of a homogeneously catalyzed hydrogenation reaction of coal is being intensified (M. W. Haenel).

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

Involved: J. Feldthusen Jensen, K. Freitag, Y. Fu, R. Goddard, L. J. Gooßen, X. Li, J.-A. Ma, P. Maiwald, G. Mehler, A. Meiswinkel, H. Oka, T. Sell, K. Sommer, M. Surowiec, P. Wedemann

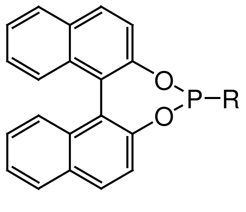
Objective: The two major objectives in this area of research concern 1) the development of economically and ecologically attractive selective catalytic transition metal systems, and 2) the establishment of new concepts in transition metal catalysis. Ideally, objectives 1) and 2) are combined in one system. The specific goals can be summarized as follows:

a) Preparation and application of readily accessible chiral monodentate P-ligands for use in asymmetric catalysis.

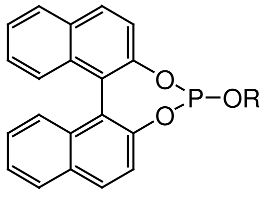
b) Development of new concepts in homogeneous transition metal catalysis, flanked by kinetic studies (in collaboration with D. G. Blackmond, Imperial College, UK), and by theoretical methods (in collaboration with the Theory Department).

c) Use of novel gold-catalysts for C-C-bond forming reactions.

Results: In the last Report (2000-2001) we described the surprising observation that certain monodentate P-ligands are excellent ligands in certain asymmetric reactions. We have since intensified our efforts concerning the use of BINOL-derived phosphonites **1** and phosphites **2** as readily available and highly efficient ligands in asymmetric Rh-catalyzed olefin-hydrogenation reactions (*ee* often > 95%). Since these compounds are considerably cheaper than standard ligands such as BINAP or Duphos, they are attracting industrial interest (two companies have licensed this technology).



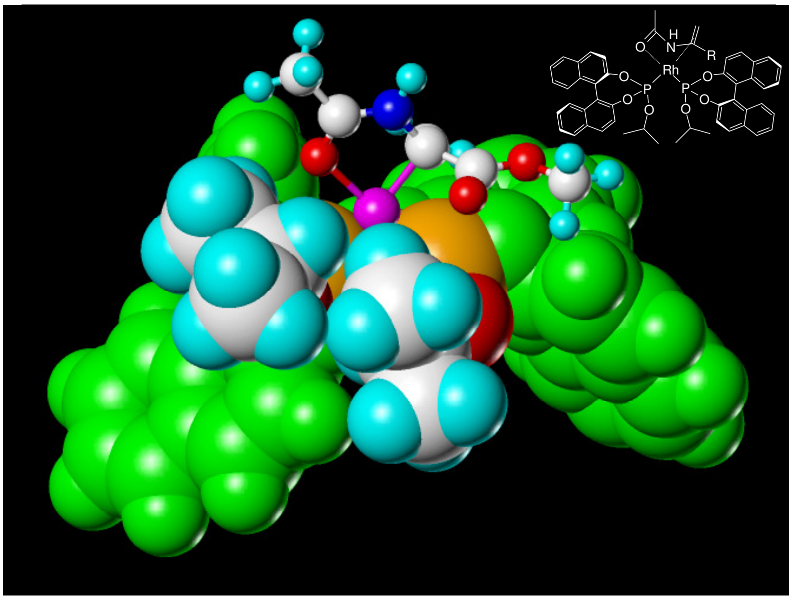
1 (R = alkyl, aryl)



2 (R = alkyl, aryl)

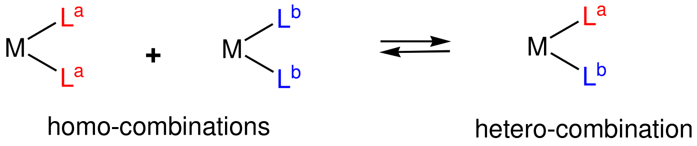
The underlying reason for high enantioselectivity is of considerable theoretical interest, because for decades it was believed that chelating bidentate ligands are necessary for high degrees of asymmetric induction. Therefore, a mechanistic study encompassing

NMR spectroscopy, non-linear effects, kinetics and MM/QM (K. Angermund, W. Thiel, D. G. Blackmond) calculations was initiated and is almost completed. The following picture is emerging: 1) two ligands are attached to Rh; 2) a family of conformationally different catalysts is involved (one important conformer is shown below); 3) an anti-Halpern system is operating!

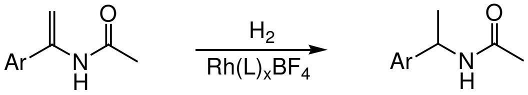


On the practical side, we have prepared more than 60 ligands of the type **1** and **2**. In the preparation of **2** many different achiral and chiral alcohols ROH can be used as building blocks, so that for a given substrate the library of ligands can be screened. For example, upon using a certain carbohydrate-based alcohol, the ligand led to unprecedented enantioselectivity in the Rh-catalyzed hydrogenation of enol carboxylates (90-94% *ee*).

We then went one step further and proposed and implemented a new concept in combinatorial asymmetric transition metal catalysis, namely the use of mixtures of two different monodentate P-ligands:



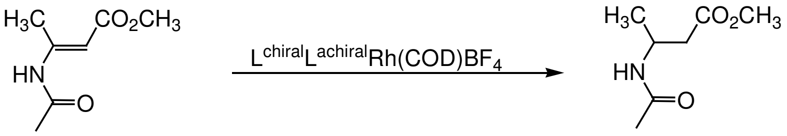
If the hetero-combination is more reactive and more enantioselective than the homo-combinations, then enhanced *ee* will result. *Thus, high catalyst diversity is possible without the need to synthesize more ligands*. We have shown that this new strategy is successful in the hydrogenation of a variety of different types of olefins. Typical examples involving BINOL-derived P-ligands:

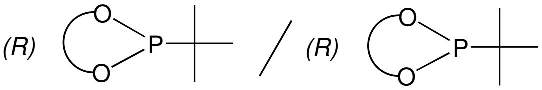
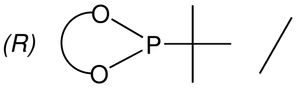
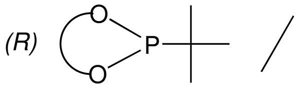
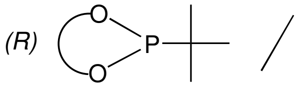
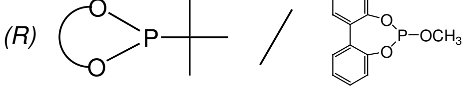
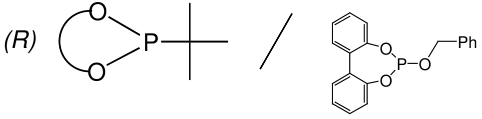


Ar = Ph
Ar = *p*-Cl-Ph
Ar = 2-naphthyl

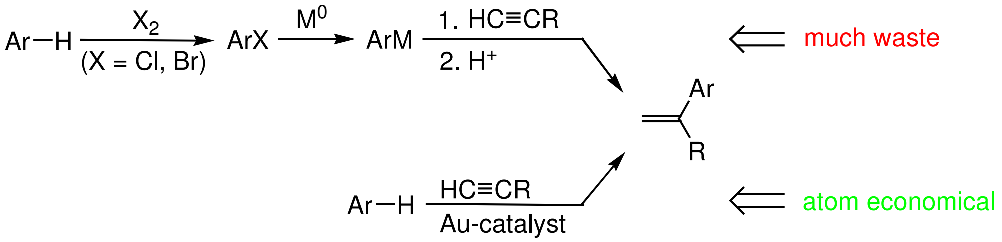
BINOL-derived ligand system	*ee* (%) with Ar = Ph	Ar = *p*-Cl-C$_6$H$_4$	Ar = 2-naphthyl
	75.6	73.0	78.2
	13.2	16.2	3.0
	96.1	95.0	97.0

In further (unpublished) work mixtures of chiral BINOL-derived P-ligands and *achiral* monodentate P-compounds were shown to be highly efficient, which means that half of the ligand system does not need to originate from a chiral source, e.g.:

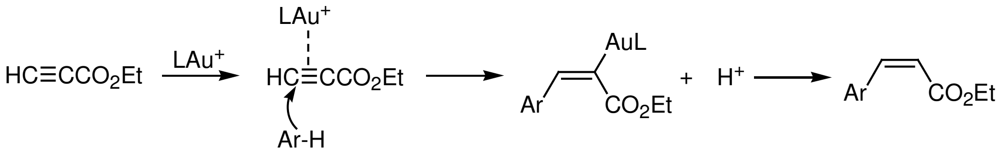


ligand system	*ee* (%)
	44.6 (*S*)
 P(OiPr)$_3$	15.8 (*S*)
 P(OCH$_3$)$_3$	83.6 (*S*)
 P(OPh)$_3$	87.8 (*S*)
	97.6 (*S*)
	97.8 (*S*)

In a different project, gold-catalyzed C-C bond formation was studied, specifically in the hydroarylation of alkynes. This one-step atom-economical reaction is in many cases more efficient than the traditional three-step sequence:



In the case of electron-poor alkynes, opposite regiochemistry was observed. Moreover, *cis*-selectivity turned out to be > 95%. Cationization of the various Au-catalysts that were prepared and tested is generally essential.



This work was "advertised" on the cover of an issue of *Eur. J. Org. Chem.*, and has already occupied a prominent place in the current literature concerning gold-catalysis. Indeed, many groups are now using cationic forms of Au-catalysts.

Publications resulting from this research area: 105, 109, 110, 260, 261, 262, 263, 265, 266, 267, 268, 269, 401, 406, 407, 408

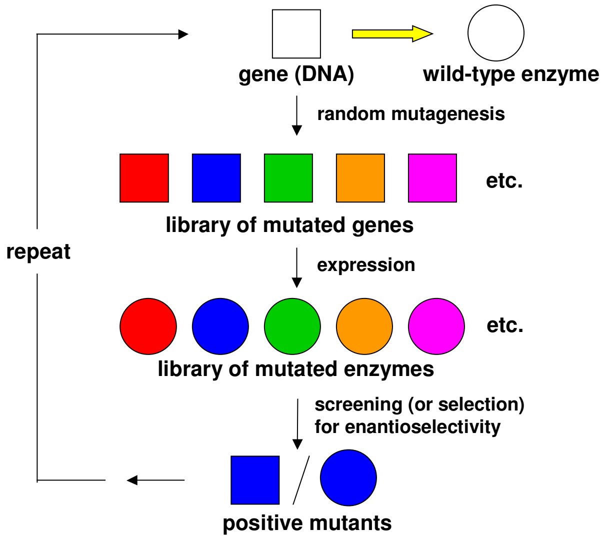
External funding: Fonds der Chemischen Industrie; German-Israeli Project Cooperation (DIP)

Cooperations: D. G. Blackmond (Imperial College, UK); K. Angermund, W. Thiel (Mülheim/Ruhr, DE); J. G. de Vries (DSM, Amsterdam, NL); Z. Gross, I. Marek (Technion - Israel Institute of Technology, IL)

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

Involved: M. Bocola, B. Brunner, C. Clouthier, F. Daligault, A. Eipper, M. Hermes, H. Krumm, R. Lohmer, A. Maichele, T. Schneider, F. Schulz, C. Torre, A. Vogel, L.-W. Wang, W. Wiesenhöfer, D. Zha

Objective: The goal of this long-term project is to generalize the fundamentally new approach to creating enantioselective catalysts for use in synthetic organic chemistry which we proposed several years ago. In contrast to traditional ligand tuning in homogeneous transition metal catalysis or traditional engineering of enzymes using site specific mutagenesis, our concept is independent of catalyst structure or mechanism of reaction. The proper combination of molecular biological methods for random gene mutagenesis and expression with formation of thousands of mutant enzymes coupled with efficient high-throughput assays for enantioselectivity forms the basis of this strategy. Several cycles of mutagenesis/screening create an evolutionary pressure with respect to the property of interest, namely enantioselectivity. Thus, the Darwinistic aspect is crucial and goes far beyond normal combinatorial catalysis.



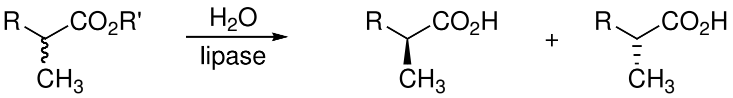
The traditional preoccupation with steric, electronic and/or hydrogen-bonding effects is totally absent, but the immediate problems that confront us in putting this rational concept into *general* practice are just as challenging because we need to continue to:

- develop general high-throughput-screening systems for assaying enantioselectivity of a broad variety of reactions and substrates
- devise efficient ways to explore protein sequence space with respect to enantioselectivity

- study different types of enzymes such as lipases, epoxide hydrolases and oxidases

Another goal of paramount importance is to reveal the crucial reasons for improved enantioselectivity of optimized mutant enzymes, i.e., *to learn from directed evolution.*

Results: In 1997 we reported the first example of an evolutionary process in the creation of an enantioselective enzyme, specifically in the lipase (*Pseudomonas aeruginosa*)-catalyzed kinetic resolution of the chiral ester **1**. Whereas the wild-type enzyme shows a selectivity factor of only *E* = 1.1 in favor of the (*S*)-acid **2**, four rounds of mutagenesis using error-prone PCR provided a mutant lipase displaying improved enantioselectivity (*E* = 11.3). The screening was performed using a crude UV/VIS test on a 96-well microtiter plate which allowed about 400-500 mutants to be assayed per day.

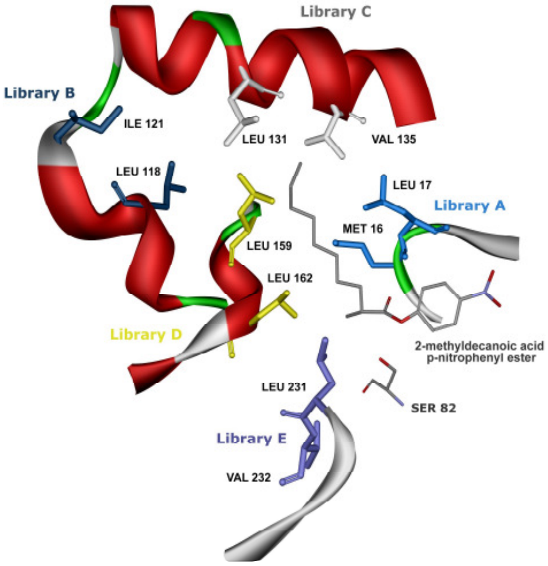


rac-**1** (*S*)-**2** (*R*)-**2**

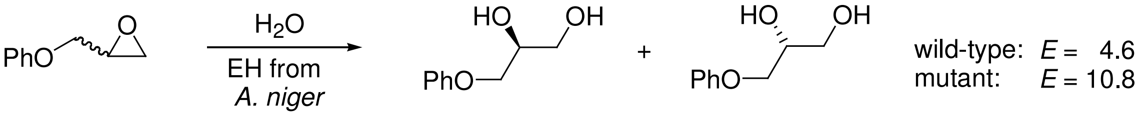
R = C_8H_{17}; R' = *p*-NO_2-C_6H_4

In 2001 enantioselectivity was increased to *E* > 51 by the application of epPCR at higher mutation rate, saturation mutagenesis and DNA shuffling. The best mutant has six amino acid substitutions, five of these mutations occurring at remote sites and one closer to the active site. A major goal of the remaining project was to uncover the reasons for these surprising observations, which was achieved in a collaborative effort with the Theory Department (W. Thiel). The MM/QM study shows that the (*S*)- and (*R*)-substrates are not bound enantioselectively in the Michaelis-Menten complex! Rather, a larger binding pocket has been created which accommodates both enantiomers, but the (*S*)-substrate reacts faster due to a relay mechanism originating from remote positions. The transition state of the reaction of the (*S*)-ester is stabilized by an additional H-bond, which is not possible with the (*R*)-substrate (see report by W. Thiel).

Recently the best lipase mutant was also tested successfully with alkyl esters of **1**, but upon varying the structure of the acid part, problems arose. Sterically demanding substrates such as iboprufen ester or achiral substrates such as benzoic ester are not accepted. The problem of substrate acceptance (not just enantioselectivity) is of fundamental importance and can in principle be solved by the normal forms of directed evolution. However, we decided to develop a faster method *by combining rational design and directed evolution*. In the particular case studied the known crystal structure of the lipase from *Pseudomonas aeruginosa* was used to identify by simple geometrical considerations five positions around the active site (serine 82) which might be crucial for creating a larger binding pocket. In doing so, five libraries A, B, C, D and E of mutants (each 3000 membered) were created by randomizing two geometrically close amino acid positions simultaneously in each case (see below). Libraries A and D turned out to contain a number of mutants which accept a wide range of structurally different chiral and achiral esters, including the above mentioned bulky substrates. We conclude that Combinatorial Active-Site Saturation Test (CAST), as we call this method, is a new approach in directed evolution which holds promise for the future.

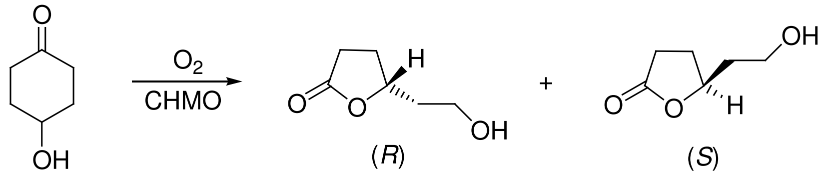


In other work we have developed in collaboration with J. Baratti (Marseilles, F) a practical expression system for the epoxide hydrolase from *Aspergillus niger*. Our MS-based high-throughput *ee*-assay was adapted to epoxides, so that now systematic studies concerning the directed evolution of enantioselective epoxide hydrolases are possible. Preliminary results concerning the kinetic resolution of glycidyl phenyl ether are promising, the selectivity factor *E* increasing from 4.6 to 10.8:

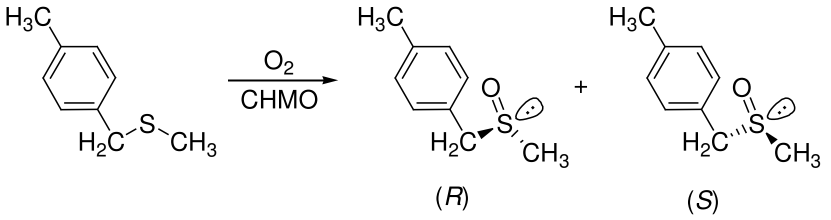


Research in the development of new high-throughput *ee*-screening systems has continued, e.g., second-generation MS-based assay, FTIR-based assay and NMR-based assays including chemical shift imaging (tomography). Throughput in the range of 1000-10000 *ee*-determinations are possible per day. Moreover, lab-on-a-chip, in which an enzyme-catalyzed reactions as well as the *ee*-determination are performed on a glass-chip, is close to reality (see report by D. Belder).

Work has also started in the directed evolution of regio- and enantioselective oxidases. We believe that selective partial oxidation of organic substrates is an important topic for the future, especially whenever synthetic transition metal catalysts fail. In addition to P450-type enzymes for CH-activating regioselective hydroxylations of steroids and other substrates, we are studying cyclohexanone monooxygenases (CHMO) as catalysts in asymmetric Baeyer-Villiger reactions and oxidations of prochiral thio-ethers. The methods of directed evolution in combination with new screening systems led to the discovery of highly enantioselective mutants, e.g.:



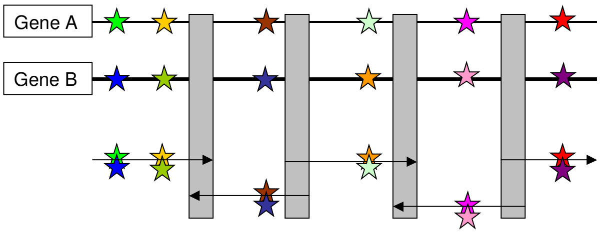
	(*R*)		(*S*)	
wild-type:	55	:	45	(*ee* = 10%)
mutant:	95	:	5	(*ee* = 90%)



	(*R*)		(*S*)	
wild-type:	58	:	42	(*ee* = 16%)
(*R*)-selective mutant:	99.4	:	0.6	(*ee* = 98.8%)
(*S*)-selective mutant:	0.2	:	99.8	(*ee* = 99.6%)

In a purely molecular biological effort we have developed a new and practical method for gene recombination with formation of libraries of mutant genes for directed evolution. It is different from DNA-shuffling. The method is based on the assembly of designed oligonucleotides (ADO) whose design is guided by computer-based sequence alignment. Thus, it is not necessary to have the genes of two (or more) enzymes, which would normally be shuffled. Only the sequence information is required! Low homology can be tolerated, which is not the case in DNA-shuffling. We have applied ADO successfully to the recombination of two lipase family genes from *Bacillus subtilis* (Lip A and Lip B).

1. Alignment of two (or more) genes and computer analysis
2. Design and synthesis of appropriate oligos
3. Assembly with formation of a library of mutant genes



Gray block:	conserved regions of sequence
Stars:	information encoding different amino acids
Double stars:	synthetic oligo fragments with degenerate nucleotides

Other work concerning enzymes as catalysts in organic synthesis focused an sol-gel immobilization of lipases and reactions in environmentally benign solvents such as $scCO_2$ and ionic liquids (see report by W. Leitner), efforts that have come to a successful end. Our biphasic system composed of $scCO_2$ and PEG may even be better.

Publications resulting from this research area: 63, 99, 100, 103, 104, 106, 112, 113, 121, 176, 193, 210, 258, 259, 290, 304, 311, 338, 398, 399, 400, 402, 403, 404, 405, 410, 411; enzyme reactions in unusual media: 101, 114, 270, 271, 412

External funding: EC (two projects); DFG (Schwerpunkt "Gerichtete Evolution"); Fonds der Chemischen Industrie

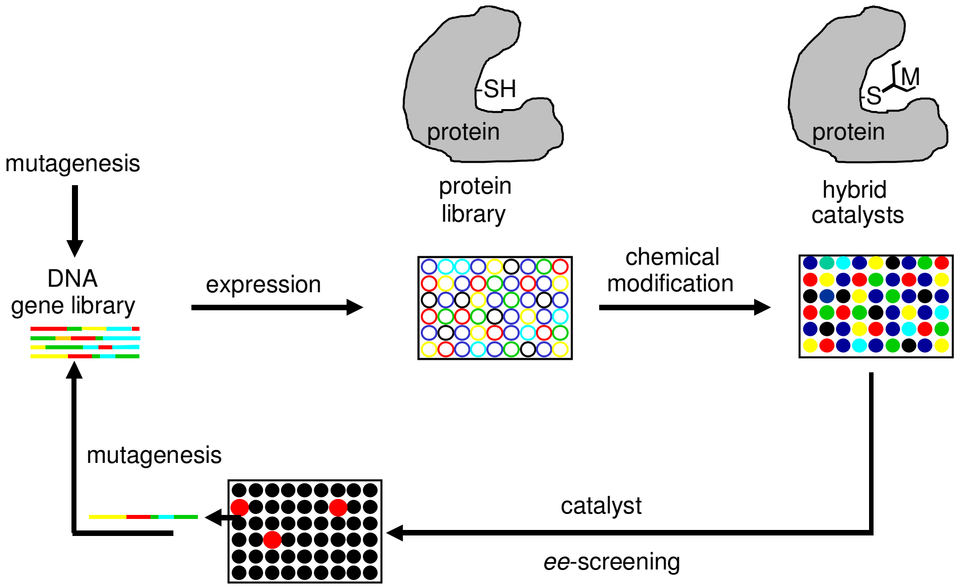
Cooperations: K.-E. Jaeger (Düsseldorf, DE); W. Thiel (Mülheim/Ruhr, DE); M. M. Kayser (Saint John, CA); J. Baratti (Marseilles, FR); R. Bernhardt (Saarbrücken, DE); EC-Project on phage display with B. W. Dijkstra (Groningen, NL), K.-E. Jaeger (Düsseldorf, DE), W. Quax (Groningen, NL), R. Verger (Marseille, FR), Genencor International BV (Rijswijk, NL); EC-Project on directed evolution of epoxide hydolases with D. B. Janssen (Groningen, NL), R. Furstoss (Marseilles, FR), M. Arand (Würzburg, DE), D. J. Leak (London, UK), Fluka (Buchs, CH); W. Leitner (Aachen, DE)

2.1.3 Research Area "Directed Evolution as a Means to Create Selective Hybrid Catalysts" (M. T. Reetz)

Involved: A. Maichele, F. Hollmann, M. Maywald, J. Peyralans, A. Pletsch, M. Rentzsch, A. Taglieber

Objective: The directed evolution of enantioselective enzymes constitutes a novel and powerful approach to asymmetric catalysis, but by nature it is limited to enzyme-catalyzed reactions. The vast number of synthetic opportunities arising from transition metal-mediated processes such as Rh-catalyzed olefin hydrogenation and hydroformylation, Ru-catalyzed olefin metathesis, Pd-catalyzed allylic substitution, etc., are not possible in enzyme catalysis. In 2001 we proposed a concept which has the potential of going beyond this natural limitation.

The concept is based on the idea of implanting a given achiral ligand/metal-center in thousands of mutant enzymes (proteins) previously created by the various methods of random mutagenesis known in the field of directed evolution. The protein does not perform as an enzyme, its sole purpose is to function as a host and therefore as a "second-sphere ligand". By going through several cycles of mutagenesis, chemical modification and screening, an evolutionary pressure is exerted on the system. Theoretically, this means that the methods of molecular biology are used to tune a synthetic transition metal catalyst for any desired property.



Enzymes (wild-type) have already been chemically modified for various purposes (e.g., in the 1980s E. Kaiser attached cofactors covalently to enzymes by an S_N2 reaction at a cysteine residue). Implanting a synthetic metal center in a wild-type enzyme is of limited interest because a single catalyst is formed having an unpredictable catalytic profile. In contrast, en masse implantation in thousands of mutant proteins creates thousands of hybrid catalysts. Each mutant has a different protein environment around the catalytically active metal center and may therefore display a different catalytic profile. High-throughput screening for activity/selectivity then identifies the "best" hybrid catalyst, followed by further cycles of mutagenesis/chemical modification/screening as a means to exert evolutionary pressure and to tune the catalyst.

Results: The above scheme appears simple, but extremely difficult fundamental and technical problems need to solved before real implementation can even be attempted:

1. Finding and using a robust protein-host which has an efficient overexpression system supplying enough material in each well of hundreds of microtiter plates.
2. Separating each mutant protein-host from the rest of the bio-material (other proteins, etc.) present in each well of the microtiter plates by an efficient and fast(!) purification process.
3. Performing (nearly) quantitative en masse chemical modification without the need to perform another purification.
4. Carrying out thousands of transition metal-catalyzed reactions (e.g. hydrogenations) using very high substrate/catalyst ratios.

During the last three years we have invested a great deal of efforts in order to solve these problems. We are now close to completing the construction of two different platforms upon which the concept can be tested, but problems remain.

The first approach concerns covalent introduction of ligand/metal centers in an appropriate protein host. The challenge includes parallelization of protein expression and purification as well as en masse chemical modification.

A second approach concerns chemically modified biotin (diphosphine/Rh as described by Whitesides in 1978) in combination with streptavidin for hydrogenation reactions. Moreover, a system to perform several hundred (not yet thousands!) Rh-catalyzed hydrogenations was set up. In contrast to "normal" combinatorial transition metal catalysis in which relatively large amounts of Rh-catalyst can be used, we are forced to work at Rh/substrate ratios of 1:500 to 1:1000 which requires practically O_2-free reaction conditions. Several cycles of efficient reactor-evacuation and flushing with inert gas are necessary. Currently, no commercial robotic reactor system fulfills these requirements because they do not tolerate high vacuum. Therefore, our in-house workshop had to construct miniature parallel reactors which can be evacuated under relatively high vacuum conditions. Several constructions were designed and built, and finally one version turned out to be successful in combination with a ChemSpeed robot. This allows a vacuum of $2 \cdot 10^{-2}$ millibar, which was tested in Rh-catalyzed hydrogenations at substrate/Rh ratios of > 500. Excellent turnover was observed, which means that the system functions well under these conditions. Unfortunately, the known expression system for streptavidin does not work as reported in the literature, so that more efforts are necessary.

Publications resulting from this research area: 100, 103, 111, 402

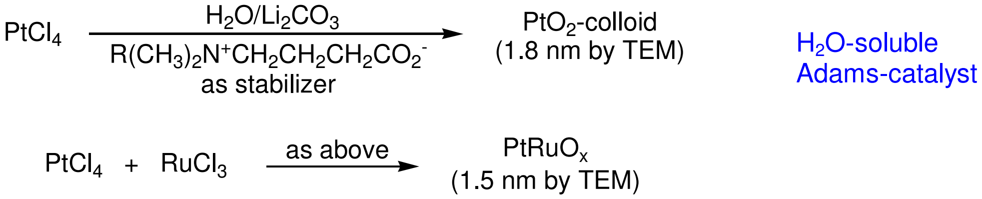
External funding: EC-project (Marie-Curie Network)

Cooperations: R. Sterner (Regensburg, DE)

2.1.4 Research Area "Nanosized Metal and Metal Oxide Colloids" (M. T. Reetz)

Involved: M. Krein, M. Lopez, H. Schulenburg

Objective: Whereas many research groups around the world concentrate on nanostructured transition metal clusters and colloids in which the metal is in the zero-valent form, less activity occurs in the area of metal oxide nanoparticles, especially when water-soluble colloids are involved. Our method for the formation of water-soluble nanosized transition metal oxide colloids is economical and simple to perform: A metal salt is simply treated with water under basic conditions in the presence of a water-soluble stabilizer generating concentrated colloidal solutions, e.g.:



$$PtCl_4 \xrightarrow[\text{as stabilizer}]{H_2O/Li_2CO_3 \quad R(CH_3)_2N^+CH_2CH_2CH_2CO_2^-} PtO_2\text{-colloid (1.8 nm by TEM)}$$

H$_2$O-soluble Adams-catalyst

$$PtCl_4 + RuCl_3 \xrightarrow{\text{as above}} PtRuO_x \text{ (1.5 nm by TEM)}$$

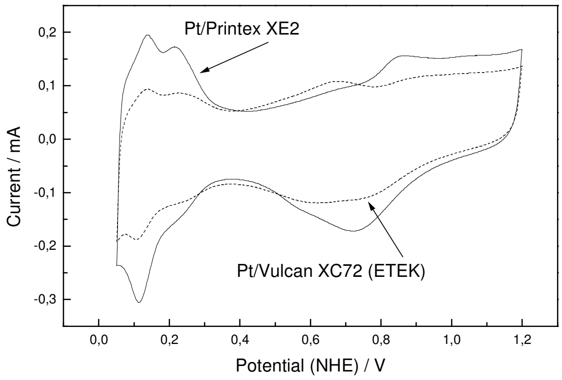
During the last three years we have focused on the following goals:

1. Preparation of mixed bi-, tri- and tetra-metal oxides in the form of water-soluble nanoparticles.
2. Characterization of some representative colloidal mixed metal oxides.
3. Immobilization of such mono- and/or multi-metal oxides on solid supports.
4. Simplification of the method in the absence of stabilizers.
5. Exploratory use of these materials in electrocatalysis (fuel cells).

Results: We have succeeded in applying our method to the preparation of water-soluble colloids such as IrO_2, RuO_x, PdO, $PtOsO_x$, $PtFeO_x$, $PtRuOsO_x$, $PtRuMoO_x$ and even $PtRuOsIrO_x$. The latter exotic colloid was characterized by TEM (1.3-1.6 nm), reduced to PtRuOsIr-colloids without undesired particle growth and immobilized on various solid supports. The PtRuOsIr-combination is the famous Mallouk electrocatalyst (prepared by a different and less straightforward synthesis). In collaboration with F. Mahlendorf (Universität Duisburg-Essen), the electrocatalytic activity of our material turned out to be exceptionally high. We have also optimized our "instant method" of metal oxide formation and in situ immobilization in the absence of organic stabilizers. A suspension of the support (e.g., carbon black) in water is simply treated with metal salts under basic conditions. The metal oxide nanoparticles become attached to the solid support before undesired agglomeration and precipitation of bulk metal oxide can occur, e.g.:

$$PtCl_4 + \text{Vulcan (carbon black)} \xrightarrow[HO^{\ominus}]{H_2O} \underset{\text{(1.8 nm)}}{PtO_x \text{ on Vulcan}} \xrightarrow{\text{reduction}} Pt/C$$

We then made the surprising discovery that the *type of carbon black* has a profound influence on the electrocatalytic activity of the solid catalyst (following electrochemical reduction). Upon substituting the conventional Vulcan XC72 by another carbon black usually used in ink jet technology, Printex XE2, a 34% enhancement of electrocatalytic activity (oxygen reduction) was observed! Moreover, upon performing multiple potential scans between 0.05 and 1.2 V (NHE) in cyclic voltammograms, the electrochemically accessible Pt area was determined from the hydrogen adsorption Q_H. It is much larger in the case of the Printex-based electrocatalyst. The particle size *d* was also determined by CV: 3.9 nm for Printex and 9.5 nm for Vulcan. In agreement with this analysis, HRTEM studies revealed that Pt-particles agglomerate in the case of the traditional Vulcan material, whereas little undesired Pt-particle growth occurs on the Printex support (see report by B. Tesche).



Publications resulting from this research area: 94, 97, 108, 264, 284, 397, 409

External funding: Katalyseverbund Nordrhein-Westfalen; NaKaB (Network of five research groups in NRW and one in Saarland dedicated to research in the area of fuel cells)

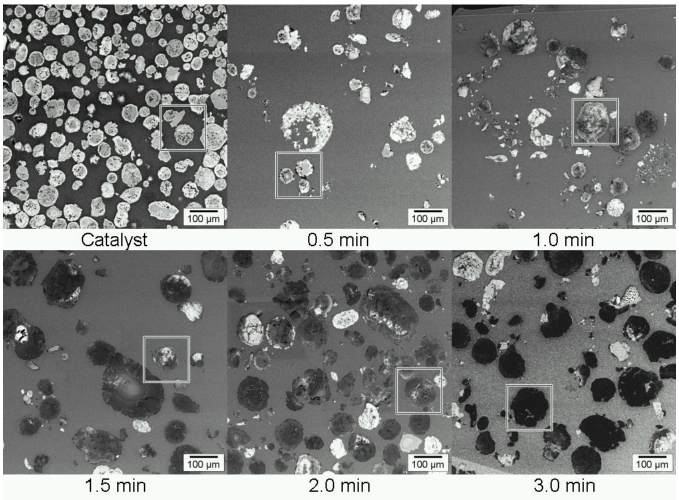
Cooperations: B. Tesche (Mülheim/Ruhr, DE); R. Kirchheim (Göttingen, DE); W. Grünert (Bochum, DE); W. Vogel (Berlin, DE); members of NaKaB: J. W. Schultze (Düsseldorf, DE), F. Mahlendorf (Duisburg, DE), J. Divisek, D. Stolten (FZ Jülich, DE), H. Baltruschat (Bonn, DE), R. Hempelmann (Saarbrücken, DE)

2.1.5 Research Area "Olefin Polymerization with Silica Supported Metallocene / MAO Catalysts" (G. Fink)

Involved: A. Alexiadis, C. Andes, D. Ferrari, K. Hauschild, S. Knoke, F. Korber, B. Weimann

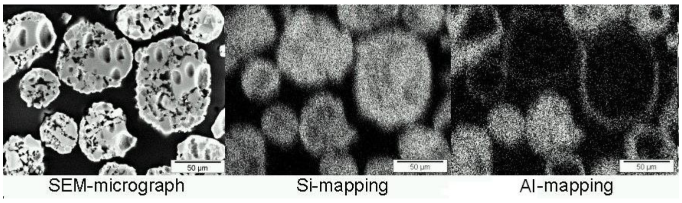
Objective: In industrial practice olefins like ethylene and propylene are polymerized predominantly by slurry, bulk, and gas phase procedures with heterogenized catalysts. The catalyst is typically supported on a porous microsphere on and in which the polymer grows. The objective of this project is to investigate the effect the heterogenization has upon polymerization kinetics, polymer growth and morphology as well as upon particle fragmentation and the subsequent particle expansion. In addition, for polymer reaction engineering reasons it was necessary to mathematically model the complete process including heat and mass transfer.

Results: We focused in the past period on heat flow calorimetry as an innovative method for the investigation of the propylene polymerization in bulk phase. It was in question to what extent the polymerization phenomena in suspension are comparable to the bulk process In order to be able to interpret the process during the initial stages in detail, we investigated the first three minutes of the bulk phase polymerization precisely (see figure). Under the chosen imaging conditions the polypropylene can be assigned to the phase that is darker than the embedding resin.



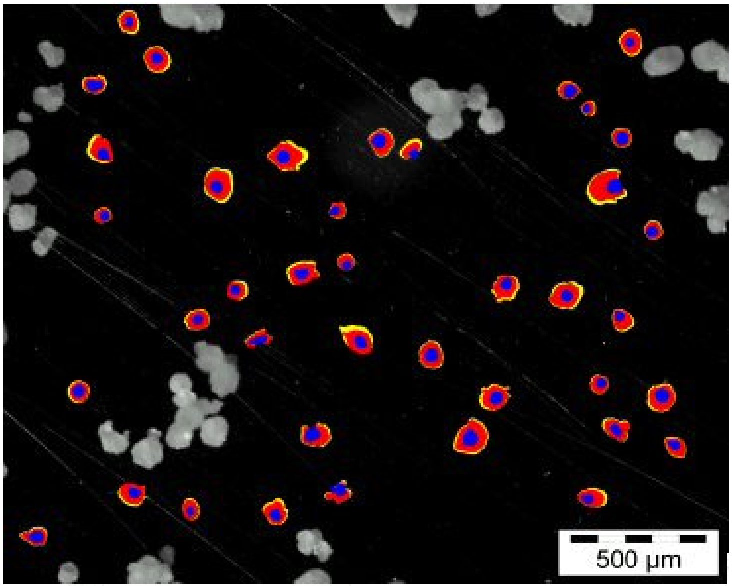
Scanning Electron Microscopy SEM

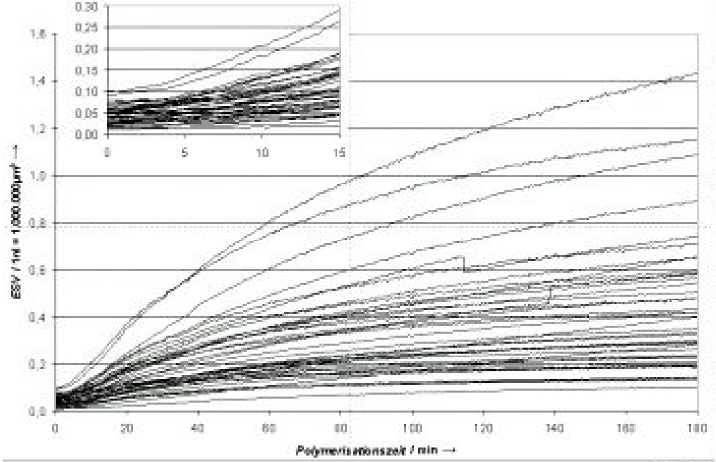
In the bulk phase polymerization particle expansion and carrier fragmentation are much faster due to the more drastic reaction conditions. Nevertheless, it is still possible to observe the shell by shell degradation according to our polymer growth and particle fragmentation model. Varying start up behaviors of single grains

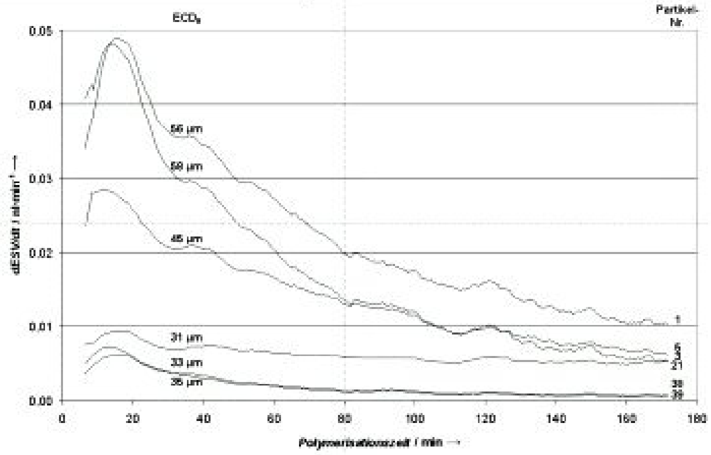


Distribution of the Co-Catalyst MAO

were observed. We were able to correlate this initial polymerization activity of individual grains with the cocatalyst MAO loading and distribution on the catalyst carrier by means of microanalytical techniques (see figure). Only a fraction of all particles reveal an even aluminum distribution throughout the particle, others show up with a shell like aluminum enrichment on the outer particle surface.







As second theme in this research area we focused on videomicroscopy for direct measurement of polymer and particle growth in gas phase polymerization under industrial process conditions. This technique enables the simultaneous detection of the individual growth of a large number of catalyst particles. In addition to visualizing polymer growth and the replication of catalyst morphology, we were able to obtain detailed information about the polymerization kinetics of numerous catalyst particles, which act as discrete microreactors. A detailed description of the experimental setup is given in the report for the period 2000-2001, p.169-170.

As example the figure shows the in situ observation of the ethylene polymerization with a solid Zirconocene / MAO / SiO_2 catalyst.

The figure on the left shows a superposition of the detected particles after 0, after 60 and after 180 minutes of polymerization. It is evident that during the progressive growth of the single grains the shape of the supporting material is replicated through the polymer particle.

The middle part of the figure demonstrates the kinetic evaluation process. It shows the increase of the particle volume ESV as function of time (10 bar ethylene, 60 °C). Here, the slope of the curve, i.e. polymer production, increases constantly over 15 minutes. The irregularities in this stage are evident in the inset. In order to create a model, each single grain can be considered as a discrete microreactor, and the irregularities can be seen as "starting phases" and can be attributed to an inhomogeneous distribution of the cocatalyst through the particle (see above the section bulk polymerization).

The lower part of the figure finally shows the polymerization rate-time profiles generated by smoothing differentiations. This evaluation confirms the fact that particles with a greater diameter tend to grow much faster than those with a smaller diameter. The reason here is insufficient heat transfer that results in a local overheating (hot spots). Higher temperatures lead to a higher polymerization rate causing more rapid fragmentation.

Publications resulting from this research area: 152, 195, 235, 236, 307, 341, 384

External funding: Basell; European Commission (Contract HPRN-CT-2000-00004)

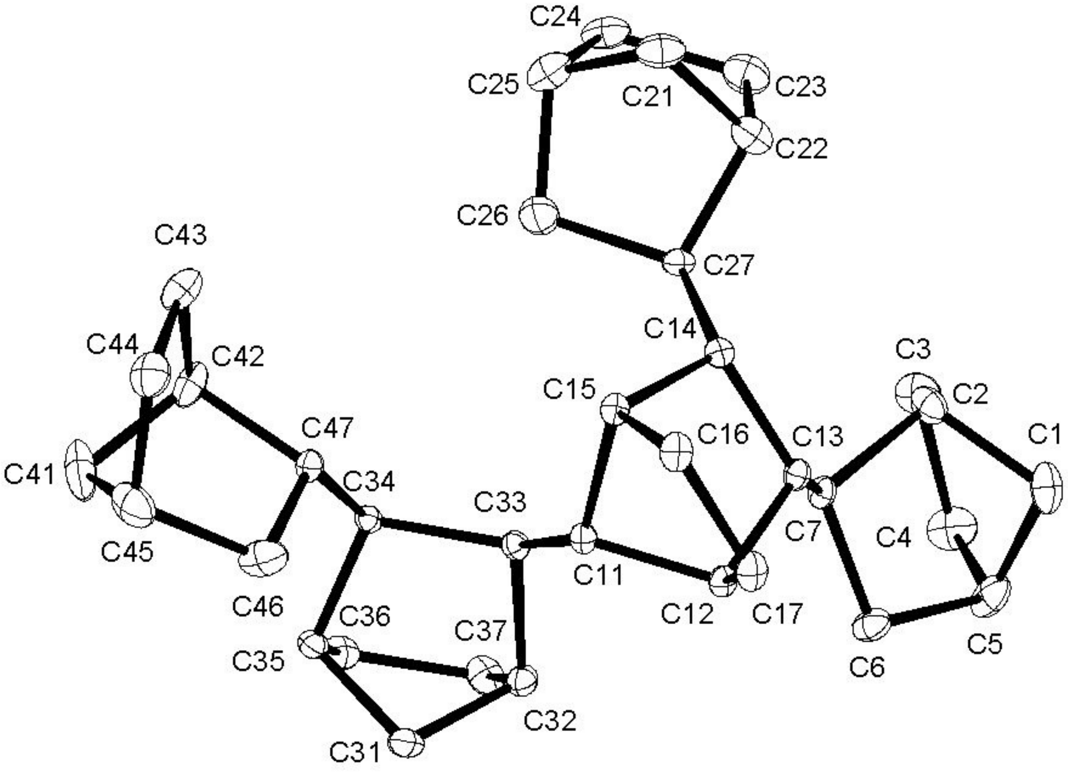
Cooperations: B. Tesche (Mülheim/Ruhr, DE), F. Schüth (Mülheim/Ruhr, DE)

2.1.6 Research Area "Metallocene-Catalyzed C7-Linkage in the Hydrooligomerzation of Norbornene by σ-Bond Metathesis: Insight into the Microstructure of Polynorbornene" (G. Fink)

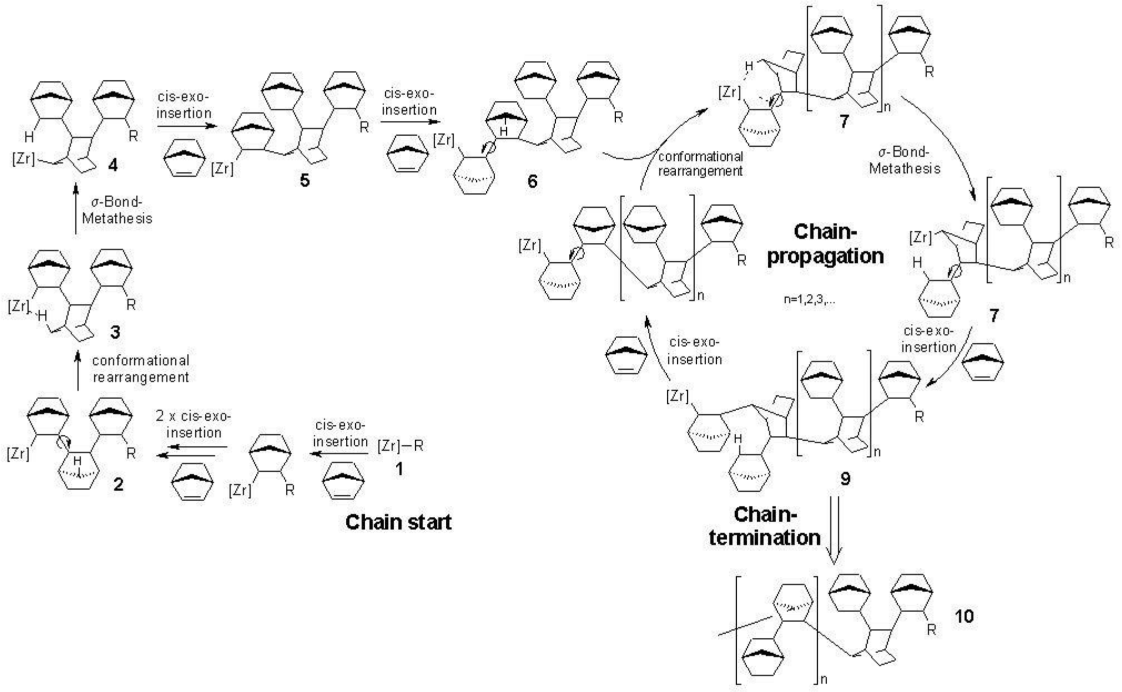
Involved: K. Angermund, G. Breitenbruch, B. Gabor, H. Hermann, W. Joppek, C. Karafilidis, A. Rufinska, J. Rust, C. Weidenthaler, R. Wendt

Objective: The microstructure of metallocene-polymerized polynorbornenes is not well known because many of the homopolymers are insoluble in chlorinated organic solvents even at elevated temperatures. Thus, NMR data are scarce and mostly limited to solid-state spectra. In the ^{13}C solid-state NMR spectra of polynorbornenes generated by the catalyst system rac-[iPr(Ind)ZrCl$_2$] / MAO, some unexpected chemical shifts and unusual narrow lines prompted us to examine the microstructure of these polymers in greater detail. To this end, we synthesized oligomers from the dimers up to the heptamers using the same catalyst and isolated and characterized them.

Results: Surprisingly, we found a new type of linkage in the tetramers, pentamers and higher oligomers. The figure shows the X-ray crystal structure of the pentamer with this novel structure element, formally a 2-exo,7'-syn linkage between C11 and C33.

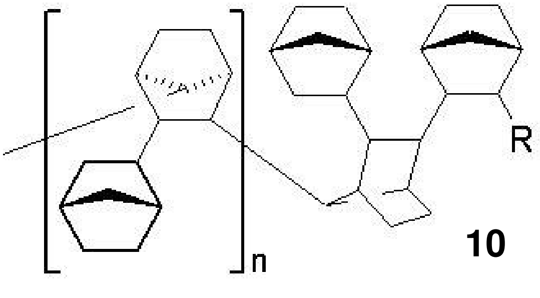


On the basis of all results inclusive D_2-termination experiments we can formulate the final reaction scheme (see figure).



In the case of hydrooligomerization the starting species is a Zr-hydride **1**. As shown by the structure of the dimer and trimer, the first three monomers are inserted in a cis-2,3-exo mode to form a linear chain **2**. However, the chain can change its conformation so that the syn-hydrogen at C7 of the penultimately inserted monomer can interact with the Zr atom in **3**. A σ-bond metathesis follows, with the result that the Zr atom is now bound syn to C7 of the penultimately inserted monomer, forming a 2-exo,2'-exo-bound mono-norbornyl branch in **4**. Further cis-2,3-exo insertions lead to the observed tetramer **5** and pentamer **6**. From here starts the chain propagation cycle.

According to our DFT-calculations, σ-bond metathesis is also feasible both kinetically and thermodynamically.



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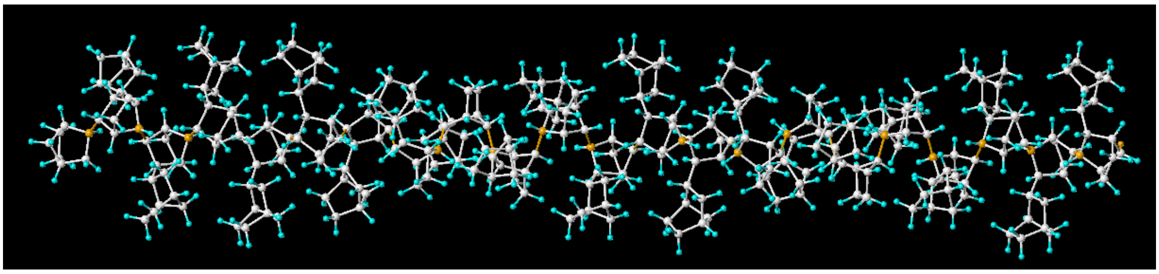
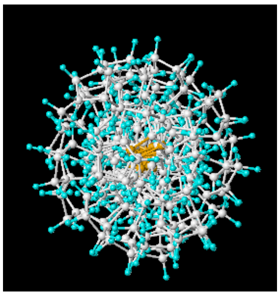
The repeating unit of the polynorbornene microstructure consists of 2-exo,7'-syn linkages in the backbone and 2-exo,2'-exo-linked mononorbonyl branches. Chain beginning consists of a meso, meso-linked trimer.

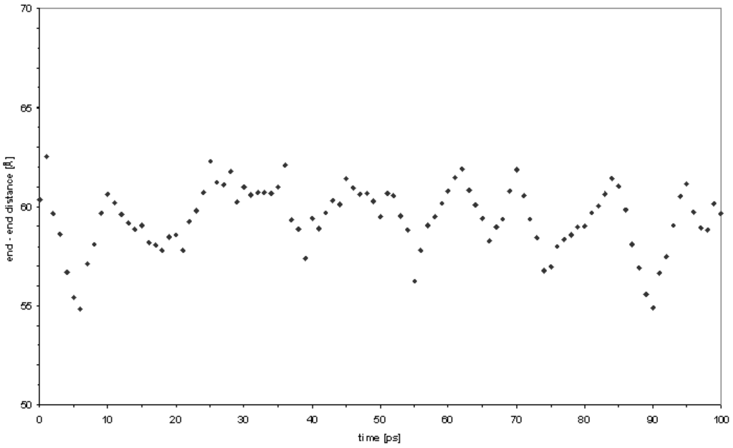
Finally, on the basis of these structure elements theoretical modeling led to the polynorbornene chain shown in the following figures.



This figure is a side view of a helical model of an oligonorbornene built-up by 43 monomers. Starting on the left with the structure elements found in the crystal structure of the pentamer and continued in accordance to the NMR data obtained from the penta- and heptamers the structure was built and optimized using standard force field techniques (*Sybyl version 6.9.1, Tripos Inc., St. Louis, USA*). Bonds between norbornene monomers are colored in brown.



This figure is a view along the helical axis of the oligonorbornene and confirms the compact tight helical superstructure. This means, this tight rigid polynorbornene backbone can not be changed into a statistical coil and this is the reason for the insolubility and infusibility.



The insignificant change in the end-to-end distance of the oligonorbornene of the figure on top in the course of a MD-simulation (Sybyl, NVE, T = 400 K, time step 1 fs, equilibration phase 10 ps, simulation phase 90 ps) confirms these conclusions.

Publications resulting from this research area: 144, 296, 364

External funding: none

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

2.1.7 Research Area "Homo-, Co- and Terpolymerization of Different α-Olefins and Functionalized Monomers with Metallocenes and New Catalysts" (G. Fink)

Involved: K. Angermund, S. Babik, A. Kiefer, R. Wendt, A. Williamson

Objective and results: Under this topic are summarized olefin co- and terpolymerizations with trialkylsilyl- and TIBA-protected polar norbornene derivatives as well as the synthesis of alternating copolymers of ethylene and diolefins containing pendent functional groups using homogeneous metallocene/MAO catalyst systems.
By varying the structure of the protecting group a relationship between the catalyst activity and the steric demand of the protecting group could be established. Kinetic investigations point to a reversible deactivation reaction, during wich a bond between the oxygen atom of the polar norbornene derivative and the center of the active catalyst is formed, competing with the olefin coordination and the subsequent insertion. The degree of polymerization deactivation could be judged based an a correlation between calculated structural parameters of the trialkylsilyl protected norbornene derivatives and the experimentally determined polymerization activity.
Further, new Cr and Mo chelate complexes containing functionalized organoimido and phosphaneiminato ligands were synthesized and found to be very useful for the (co)-polymerization of methyl methacrylate, acrylonitril and vinylacetate. It is remarkable that the polymerizations do occur in the absence of any activator.
Finally, kinetic studies of propylene bulk phase oligomerization and polymerization in a calorimeter with bisiminepyridine iron complexes led to a mechanistic explanation of the question how to control the ratio of the 1,2 versus 2,1 olefine insertion. One method is to alter the sterical demand in the ortho position in the ligand. The more bulky the ligand the more often happens a 2,1 insertion and therefore higher molecular mass of the oligomer, i.e. polymer is formed.

Publications resulting from this research area: 5, 144, 280, 298, 432

External funding: TICONA - Ruhrchemie Oberhausen; TICONA - Frankfurt-Höchst; EC (Contract HPRN-CT-2000-00004)

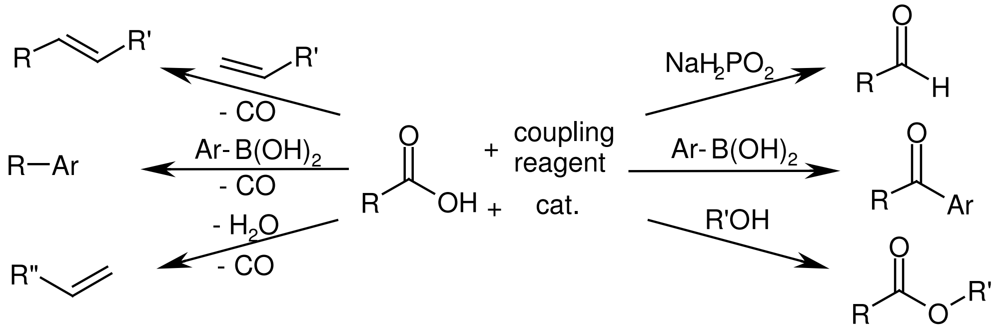
Cooperations: U. Siemeling (Bielefeld, DE); W. Thiel (Mülheim/Ruhr, DE)

2.1.8 Research Area "New Transition Metal-Catalyzed Reactions for Organic Synthesis" (L. J. Gooßen)

Involved: J. Paetzold, D. Koley

Objective: Our research is devoted to the development of transition metal-catalyzed reactions for organic synthesis. New processes were discovered for the preparation of important classes of compounds which had previously been accessible only over numerous steps or with the use of sensitive, aggressive or toxic reagents. Key characteristics of all these new procedures are their excellent practicability and tolerance of functional groups.

Results: Within the last two years, we focused on the development of cross-coupling reactions where the substrates are carboxylic acids instead of the ecologically questionable acyl or aryl halides usually used (Scheme 1). The carboxylic acids were activated *in situ* with coupling reagents, to allow an oxidative addition to transition metal catalysts.



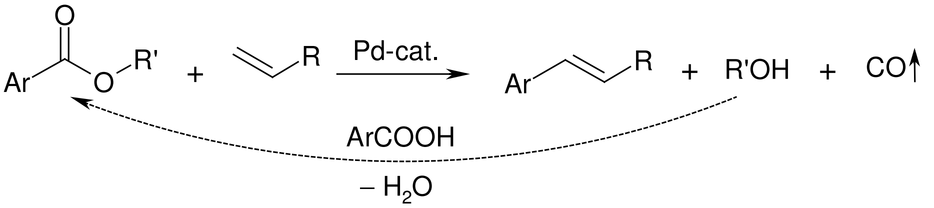
Scheme 1. Reactions of carboxylic acids

This approach led to the discovery of a selective catalytic transfer hydrogenation of carboxylic acids to aldehydes. The acids are converted *in situ* into anhydrides using pivalic anhydride, and consequently reduced with sodium hypophosphite in the presence of a palladium catalyst.

The same principle was utilized in our new ketone synthesis, in which carboxylic acids are coupled with boronic acids. Three reaction variants were developed, with the activating agents pivalic anhydride, dimethyl dicarbonate and disuccinimidyl carbonate. This reaction is the first to give convenient access to a number of functional ketones directly from the corresponding carboxylic acids.

Acyl-palladium complexes decarbonylate at elevated temperatures. This behavior was exploited in a new decarbonylative Heck olefination of carboxylic acids. In this process, aromatic carboxylic acids can be converted to vinyl arenes in the presence of di-*tert*-butyl dicarbonate. Furthermore, a decarbonylative Suzuki coupling was developed that allows the synthesis of biaryls from aromatic carboxylic anhydrides and arylboronic acids. We have also recently found a palladium catalyst that allows the conversion of aliphatic carboxylic acids to alkenes *via* a decarbonylative elimination reaction.

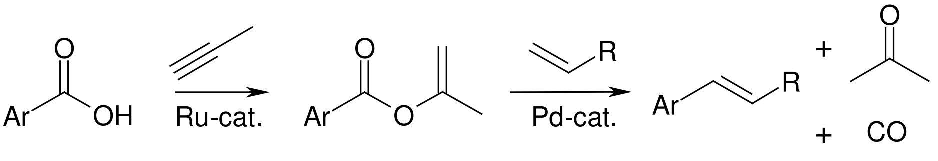
With especially developed palladium catalysts, even poorly reactive carboxylates were utilized as substrates for decarbonylative Heck olefinations. Hence, various esters of electron-deficient phenols were coupled with olefins to give the vinyl arenes, along with CO and the corresponding phenols. These were then recycled into the starting materials in an esterification step with fresh carboxylic acid. Thus, it was experimentally demonstrated for the first time that the production of waste salts is avoidable in Heck olefinations (Scheme 2).



Scheme 2. Salt-free Heck olefination

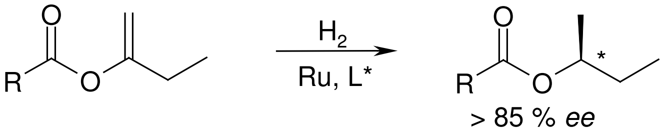
Further development of the catalysts enabled the decarbonylative Heck olefination of aryl isopropenoates to give the vinyl arenes, CO, and acetone. Combined with the formation of the isopropenyl esters from the carboxylic acids and propyne – a side product in oil refining – this also becomes a salt-free overall process (Scheme 3). Besides CO, acetone is the only byproduct, and can be incinerated without a negative impact on the environment. Thus, a recycling of the byproduct is no longer necessary.

This synthetic sequence was significantly facilitated by the development of new ruthenium catalysts for the addition of carboxylic acids to alkynes. These allow a preparatively simple, highly regioselective preparation of either the alk-1-en-2-yl esters or the (*Z*)-alk-1-en-1-yl esters.



Scheme 3. Salt-free Heck olefination

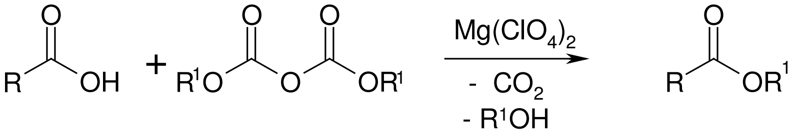
Since the new reaction allowed an easy access to these compounds, we then investigated the synthetic utility of alk-1-en-2-yl esters. In this context, we found that they can be reduced in a highly enantioselective fashion in the presence of a ruthenium catalyst bearing novel sugar-based chiral phosphite ligands.



Scheme 4. Asymmetric reduction of enol esters

In reductions of the type shown in the general Scheme 4, *ee* values of more than 95 % were achieved, a new record for this substrate class. Thus, a synthetic sequence consisting of the addition of a carboxylic acid to an alkyne, followed by an asymmetric hydrogenation of the enol ester, appears to be a valuable alternative to the asymmetric reduction of dialkyl ketones (i.e. methyl ethyl ketone) followed by esterification.

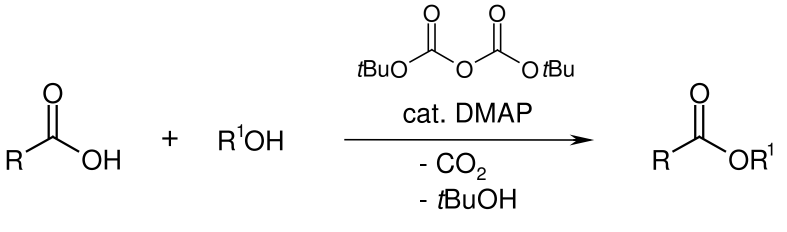
Furthermore, new processes were developed for the esterification of carboxylic acids, which is one of the most widely used transformations in organic chemistry. The carboxylic acids were converted *in situ* to the mixed anhydrides with dialkyl dicarbonates, which then decarboxylate in the presence of suitable catalysts (Scheme 5). Mild Lewis acids, such as $Mg(ClO_4)_2$, proved to be significantly more active and selective catalysts than the previously employed DMAP.



Scheme 5. Decarboxylative esterification

Particular advantages of this esterification method are its compatibility with many functional groups along with the fact that solely volatile byproducts are formed.

The low reactivity of tertiary alcohols was used in the conversion of carboxylic acids to the esters of primary or secondary alcohols in the presence of $(BOC)_2O$ and a catalytic amount of DMAP (Scheme 6).



Scheme 6. Esterification in the presence of $(BOC)_2O$

The esters of the sterically less hindered alcohols were formed selectively, while none of the *t*-butyl esters were detected. In contrast to the traditional process using DCC as the coupling reagent, only volatile byproducts are formed, thus significantly simplifying the work-up.

In parallel to our experimental work, we also investigated the mechanism of palladium-catalyzed coupling reactions in general, and of our new reactions in particular, by means of DFT calculations and *in situ* spectroscopy. In this context we found an energetically favourable mechanism for the oxidative addition of aryl halides to Pd-catalysts *via* a stable four-coordinate anionic intermediate. This simple mechanism offers an alternative explanation for the complex experimental observations in cross-coupling reactions, without involving five-coordinate Pd-intermediates (Figure 1).

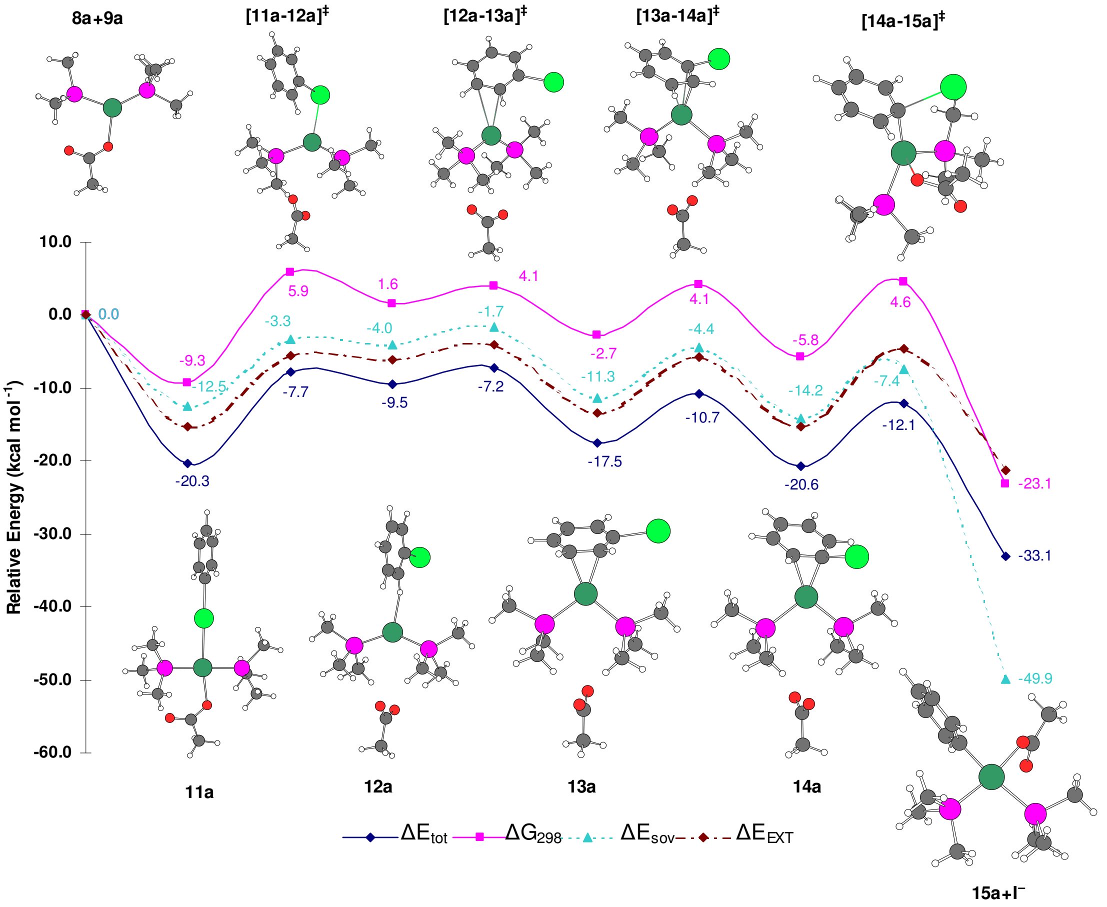


Figure 1. Calculated reaction path for the oxidative addition of iodobenzene to $[Pd(PMe_3)_2OAc]^-$

Publications resulting from this research area: 52, 53, 54, 55, 56, 57, 214, 215, 263, 352, 353, 354, 355, 356

External funding: DFG Go 853/2-1; DFG Go 853/3-1; DFG Go 853/4-1; Liebig fellowship of the Fonds der Chemischen Industrie; BMBF/FCI 661133, research funds from Umicore and Bayer AG

Cooperations: H.-J. Altenbach (Wuppertal, DE); M. T. Reetz (Mülheim/Ruhr, DE); W. Thiel (Mülheim/Ruhr, DE); A. R. Ferwanah (Gaza, Palestine)

2.1.9 Research Area "Hydrogenation/Hydrogenolysis of Bituminous Coals with Homogeneous Borane Catalysts" (M. W. Haenel)

Involved: J. Narangerel, U.-B. Richter, A. Rufińska

Objective: The prospect that the world's petroleum reserves will eventually deplete in a few decades let the oil price escalate. Hence the more abundant coal might become economically competitive as a source for liquid fuels and chemicals. With the *Bergius* direct coal liquefaction and the indirect liquefaction consisting of coal gasification and *Fischer-Tropsch* synthesis two fundamental technologies to liquefy coal have been available since the first half of the last century. The direct liquefaction is a hydrocracking process by which coal is converted at 450 °C under hydrogen pressures of > 30 MPa in the presence of a process-derived solvent and a solid iron oxide catalyst. The catalytic efficiency is low, mainly because a solid catalyst cannot penetrate into the macromolecular network structure of insoluble coal. The much better promise a homogeneous catalyst would show in this regard prompted us some time ago to investigate the hydrogenation/hydrogenolysis of coals with homogeneous borane catalysts. This let us accomplish a first case of a homogeneous hydrogenation of coal.

Results: High-rank bituminous coals such as medium-volatile bituminous coal (mvb coal, coking coal, Fettkohle), low-volatile bituminous coals (lvb coals, Ess- and Magerkohlen) and even anthracite were hydrogenated in suspension in toluene using dialkyliodoboranes or iodohydroboranes as catalysts (15-25 MPa hydrogen, 280-350 °C, 12 - 48 h). Iododihydroborane simply could be generated *in situ* from sodium tetrahydridoborate and iodine: $NaBH_4 + I_2 \rightarrow NaI + H_2BI + H_2$. The solid products obtained by hydrogenation were highly soluble in pyridine (up to 90%), which is attributed to partial hydrogenation of polycyclic arenes as well as to hydrogenolytic cleavages of C_{aryl}–C_{alkyl} bonds disrupting the network structure of coal. 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} was increased from 11/89 in an original lvb coal (Magerkohle) and from 5/95 in an original anthracite to 60/40 in both coal products.

The *Bergius* hydrocracking process and all further developments thereof can be used to liquefy only lignites (brown coals), subbituminous coals and low-rank bituminous coals such as high-volatile bituminous (hvb) coals, whereas high-rank bituminous coals (rank from mvb or coking coals to lvb coals), semi-anthracite and anthracite are not reactive enough for such hydrocracking processes. On the other hand, just these high-rank bituminous coals are most appropriate for the borane-catalyzed hydrogenation. As the result the aliphatic portion of these coals is increased to such an extent that the subsequent hydrocracking into liquid products becomes possible. The feasibility of such a two-stage liquefaction process of high-rank coals was shown for the example of a German Magerkohle (lvb coal).

Our research on coal hydrogenation was expanded to include also boron-free catalysts. In the context of mechanistic studies polycyclic aromatic hydrocarbons and 1,2-diarylethanes were used as simple coal models. Their hydrogenation with different catalyst systems containing boron and iodine revealed remarkable differences in yields and product distributions, which are considered to be important keys in the further development of the catalysts. In view of the escalating oil price, the development of new processes for the conversion of coal to liquids represents still one promising option for fuels in the future.

Publication resulting from this research area: 211

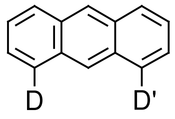
External funding: DFG 446 MON 112/11/02

Cooperations: none

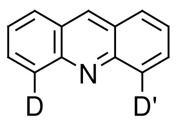
2.1.10 Research Area "Development of Thermostable Homogeneous Catalysts Based on Polycyclic Arenes and Heteroarenes" (M. W. Haenel)

Involved: C. W. Lehmann, R. Mynott, E. Roßkamp, M.-A. Schneider, F. Sedlatzek, C. Wirtz, E. Wöstefeld

Objective: Thermally robust homogeneous catalysts have three major advantages: 1) catalytic conversion of less reactive substrates, for which the kinetics require high temperatures; 2) the extension of homogeneous catalysis to endothermic processes, for which the thermodynamics require high temperatures; 3) a facile catalyst separation by distillation of educts and products. Our concept to achieve the high demands on the catalytically active metal complexes makes use of robust aromatic ligand frameworks and extremely strong ligand-to-metal bonding by tridentate coordination. Accordingly the project aims to synthesize bifunctional phosphine/amine compounds of 1,8-disubstituted anthracenes **A** and 4,5-disubstituted acridines **B**, to investigate their properties for the tridentate coordination of transition metals forming metal complexes **C** and **D**, and to test these complexes for possible applications in homogeneous catalysis. In our previous work it was shown that compounds **A** and **B** generally can be synthesized by nucleophilic substitution of the 1,8-difluoroanthracene **1** and 4,5-difluoroacridine **2** by alkali metal phosphides or amides, respectively.

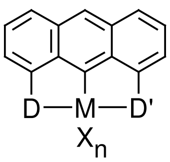


A

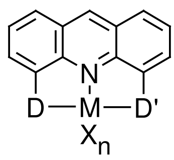


B

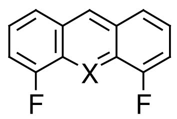
D,D' = PR_2 or NR_2



C

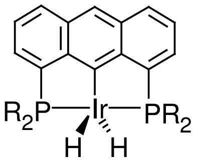


D

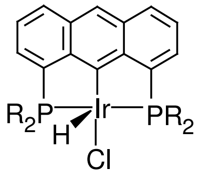


1: X = CH
2: X = N

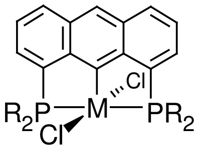
Results: A main effort concerned the development of homogeneous catalysts to activate alkanes for the endothermic (by 33 kcal mol^{-1}) dehydrogenation into alkenes and hydrogen. A thermostability unique for an organometallic compound recently was observed for the anthraphos(*t*bu) $Ir(H)_2$ **3**, which catalyses the dehydrogenation of cylododecane into *E*/*Z*-cyclododecene and hydrogen at 250 °C (initial TOF 40 h^{-1}, TON 146 after 144 h). However, the synthesis of **3** could not simply applied for other anthraphos $Ir(H)_2$ complexes such as **4** and **5** or corresponding rhodium complexes. Whereas from anthraphos(*t*bu) and $IrCl_3$ solely complex **6** was obtained, the reaction of anthraphos(*i*pr) and $IrCl_3$ under identical conditions yielded a mixture of the complexes **7** and **10,** and in addition, the intermediary formation of the coordination complex **13** and the two carbene complexes **14** and **15** were observed. By modifying the conditions it was possible to prepare the complexes **7**, **10**, **13**, **14** and **15** individually from anthraphos(*i*pr) and $IrCl_3$ in high yields. With this expertise also individual and effective syntheses of the iridium or rhodium complexes **8**, **11**, **9** and **12** could be elaborated.



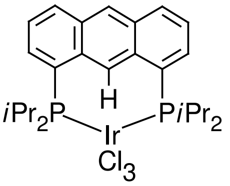
3: R = *t*Bu
4: R = *i*Pr
5: R = Ph



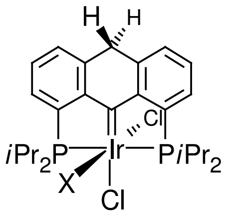
6: R = *t*Bu; M = Ir
7: R = *i*Pr; M = Ir
8: R = Ph; M = Ir
9: R = *i*Pr; M = Rh



10: R = *i*Pr; M = Ir
11: R = Ph; M = Ir
12: R = *i*Pr; M = Rh

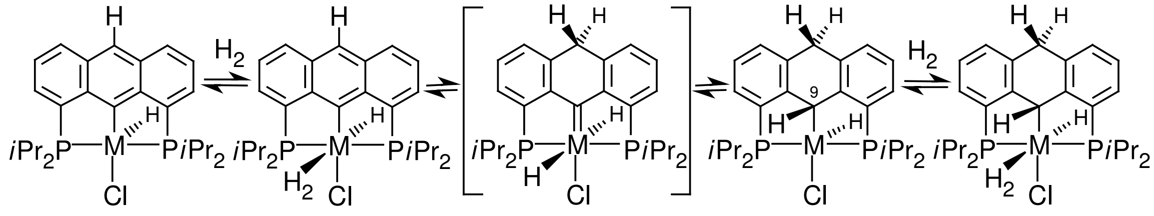


13



14: X = H
15: X = Cl

Interestingly the chlorohydrido complexes **7** and **9** reversibly added hydrogen (2-3 bar) via the hydrogen complexes **16** and **17** and the postulated carbene complexes **18** and **19** to form the complexes **20** and **21** having 9,10-dihydroanthracene units. The rhodium complex **21** shows a dynamic process causing at 25 °C the fast exchange of anthryl-9-H and Ir-H ($\Delta G^{\ddagger} \approx 12$ kcal mol^{-1}). In the case of the iridium complex **20** the barrier is higher ($\Delta G^{\ddagger} > 18$ kcal mol^{-1}) which is considered to be the reason that a further hydrogen molecule is coordinated under formation of complex **22**. The reaction sequences and the exchange processes presently are investigated in detail by density functional theory (DFT) techniques (cooperation with M. B. Hall).



7: M = Ir
9: M = Rh

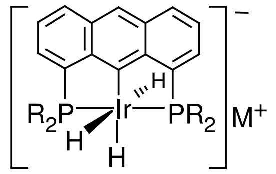
16: M = Ir
17: M = Rh

18: M = Ir
19: M = Rh

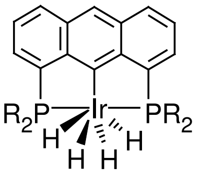
20: M = Ir
21: M = Rh

22: M = Ir

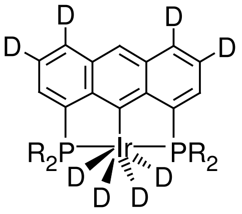
The reaction of the chlorohydrido complexes **6**, **7** and **8** with sodium or potassium hydride and hydrogen led to anionic anthraphos trihydridoiridate(III) complexes **23**-**28**.



23/**24**: R = *t*Bu; M = Na/K
25/**26**: R = *i*Pr; M = Na/K
27/**28**: R = Ph; M = Na/K



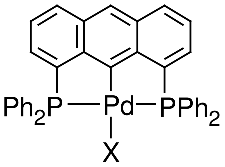
29: R = *t*Bu
30: R = *i*Pr
31: R = Ph



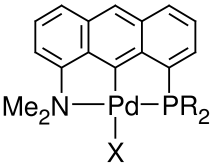
32: R = CH(CD_3)$_2$

Protonation with water cleanly converted **23**-**26** to anthraphos Ir(H)$_4$ complexes **29** and **30**, whereas **27** did not give **31**, but a complex mixture of compounds. In contrast to anthraphos(*t*bu) Ir(H)$_4$ **29** which forms a reversible equilibrium with anthraphos(*t*bu) Ir(H)$_2$ **3** and hydrogen, hydrogen could not be eliminated from anthraphos(*i*pr) Ir(H)$_4$ **30** without decomposing the complex. However, compound **30** self turned out to be a very "hot" catalyst for the activation of aromatic C–H bonds, as it was revealed by the reaction with [D$_6$]benzene at 25 °C to the deuterated complex **32** (relative rates of H/D exchange: Ir(H)$_4$ >>3,6-H > CH_3 > 4,5-H). **30** starts to become catalytically active for the dehydrogenation of alkanes also at much lower temperatures than catalyst **3**, and more detailed studies to compare the activities of both catalysts are currently under way.

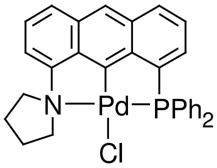
The anthraphos Pd(II) complexes **33**/**34** and the complexes **35**-**40**, which are derived from anthraphos Pd(II) complexes by replacing one or both phosphino groups by dialkylamino groups, are catalysts for the *MIZOROKI-HECK* reaction of bromobenzene and alkyl acrylates to form alkyl *E*-cinnamates with high yields (NaOAc or Na_2CO_3 as base, NMP or DMA, 140 °C, TON up to 76000), but no reaction was observed with chlorobenzene. The catalysts were not decomposed at 180 °C, and the reaction solution maintained the yellow colour of the palladium complexes. Some observations seem to indicate that the catalytic reactions with **33**-**40** involve Pd^{II}/Pd^{IV} cycles.



33: X = Cl
34: X = Br

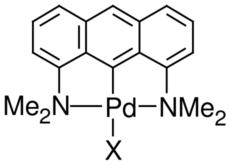


35: R = Ph; X = Cl
36: R = Ph; X = Br
37: R = Cy; X = Cl



38

Cy = cyclohexyl



39: X = OAc
40: X = Cl

Publications resulting from this research area: none

External funding: DFG HA2167/1-2; DFG HA2167/1-3

Cooperations: W. C. Kaska (Santa Barbara, USA); M. B. Hall (Texas A&M, USA)

2.1.11 Research Area "Supercritical Carbon Dioxide as Reaction Medium for Catalysis" (W. Leitner / N. Theyssen)

Involved: A. Brinkmann, D. Giunta, G. Franció, Z. Hou, K. W. Kottsieper, M. McCarthy, C. Pallazi (AK Bolm), M. Solinas, H. Stemmer, L. Winkel, W. Wiesenhöfer

Form of organisation: A close cooperation between the Max-Planck-Institut für Kohlenforschung and RWTH Aachen has been created with the change of Dr. W. Leitner to the chair of Technical Chemistry and Petrochemistry at RWTH Aachen (successor to Prof. Keim) in February 2002. In December 2002 Prof. Dr. W. Leitner was appointed External Scientific Member of the Max-Planck-Institut für Kohlenforschung. Dr. N. Theyssen, a former PhD-student of Prof. Dr. W. Leitner, became the group leader of the local scientific subgroup in July 2003 and also the head of the Service Department "Technical Laboratoaries".

Objective: The use of compressed carbon dioxide (subcritical and supercritical) as an alternative solvent for advanced reaction technologies is receiving continuously growing attention in both academia and industry. The unique properties of carbon dioxide in terms of toxicology, safety, variable solvency and mass transport capacity are seen as highly potent to fulfil a variety of demands arising from the steadily increasing need for environmentally benign chemical synthesis ("Green Chemistry"). We focus on the use of carbon dioxide as a reaction medium for homogeneously, heterogeneously, and enzymatically catalysed reactions, whereby aerobic oxidations and olefin ring closing metathesis reactions were investigated in particular. The development of efficient continuous flow processes was a major aspect in the period covered by the present report.

Results: Supercritical fluids have the unique property to be fully miscible with other gases which makes them highly attractive for reactions with gaseous reactants. Carbon dioxide, as a final product of deep oxidations, behaves fully inert under oxidizing conditions making this reaction medium especially attractive for aerobic oxidations. In addition, its high specific heat capacity ensures efficient heat transfer in these mostly highly exothermic oxidation reactions.

We could show that the use of compressed carbon dioxide enables significantly higher conversions in the selective alkane oxidation reactions using molecular oxygen as a primary oxidant and acetaldehyde as a coreductant when compared to other inert gases such as nitrogen or argon under identical optimised reaction conditions. The reaction is triggered heterogeneously by the stainless steel walls of the reactor which are responsible for the formation of peroxo acyl radicals. Remarkable conversions and keto to alcohol selectivities for secondary carbon atoms could be observed whereby β-scission reactions of oxidised tertiary carbon atoms occur only to a very low extent. High pressure ATR-FT-IR online spectroscopy turned out to be an excellent tool for determination of reaction profiles, even in these multiphase systems.

In a more recent project we developed a novel catalytic system for the selective aerobic oxidation of alcohols utilizing highly dispersed Pd-nanoparticles in poly(ethyleneglycol) (PEG) as the catalyst matrix and supercritical carbon dioxide ($scCO_2$) as the substrate and product phase. This catalytic system shows high activity, selectivity, and stability in the conversion of structurally diverse primary and secondary alcohols to their corresponding aldehydes and ketones (Figure 1 and 2).

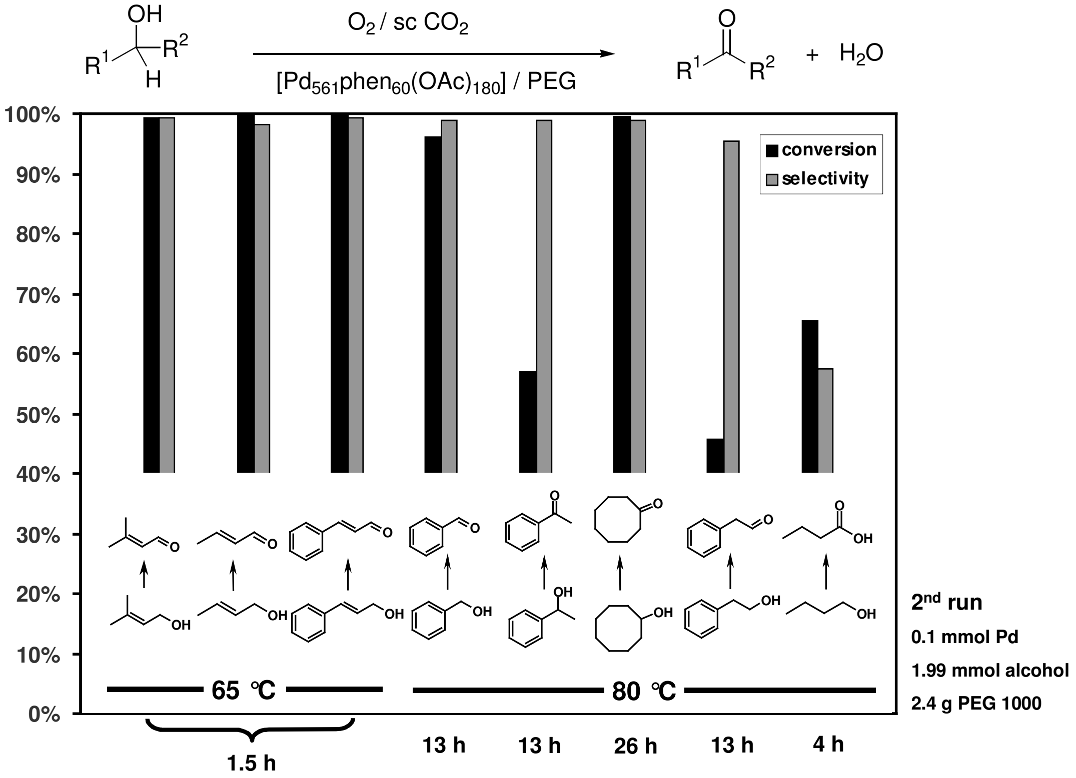


Figure 1. Biphasic catalytic oxidation of alcohols using PEG-stabilized palladium nanoparticles in $scCO_2$

The catalytically active particles can be formed from palladium sources such as $[Pd_{561}phen_{60}(OAc)_{180}]$ or $[Pd(acac)_2]$ / PEG / *Brij® 35*, whereby their dispersion within the matrix is aided by the presence of the supercritical reaction medium. The PEG matrix effectively stabilizes and immobilizes the catalytically active particles whereas the unique solubility and mass transfer properties of $scCO_2$ allow for continuous processing at mild conditions even with low volatile substrates (Figure 2).

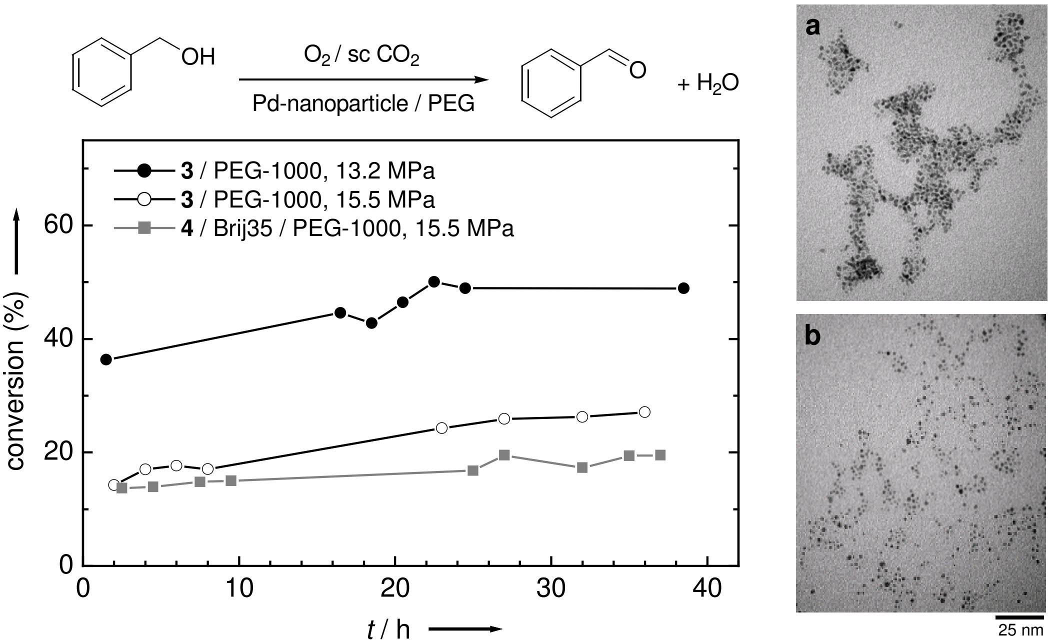


Figure 2. Continuous-flow aerobic oxidation of benzylic alcohol in $scCO_2$ using PEG (3.5 g) stabilized Pd-nanoparticles (0.1 mmol Pd) formed from $[Pd_{561}phen_{60}(OAc)_{180}]$ and $[Pd(acac)_2]$ / *Brij® 35*, respectively ($T = 80$ °C, $p(CO_2/O_2, 92/8) = 15.5$ MPa and 13.2 MPa, respectively; flow rates: alcohol: 0.5 mL/h; exit flow: 5 L/h); TEM images of the catalytically active material formed from the giant palladium cluster and PEG-1000 in the initial phase (a) and at the end (b) of the selective biphasic oxidation

As can be seen from Figure 2, a small but continuous enhancement in activity occurs for both catalytic materials over the course of 40 h continuous operation. TEM measurements of the catalytic system at different stages of the reaction show an increasing dispersion of Pd-nanoparticle throughout the whole PEG matrix with time on stream. Most probably the number of accessible active centres is thereby increased.

Another focus of our current research using supercritical carbon dioxide is directed towards olefin ring closing metathesis reactions, carried out in close cooperation with industrial partners. Basic experience concerning catalyst immobilisation strategies for continuous flow processes were gathered with 1,7-octadien as a model substrate. Beside fixed bed technologies, the use of ionic liquids (IL) as a catalyst immobilizing matrix for homogeneous Ru-precatalysts turned out to be very powerful for biphasic operation.

In our most sophisticated contribution we have developed a very active olefin ring closing metathesis (RCM) for the macrocyclisation of a pharmaceutical precursor using Hoveyda-type catalysts. Due to its high molecular weight and polar functionalities the use of high CO_2 densities were necessary to achieve dissolution in the supercritical phase leading to reaction pressures of up to 400 bar at 70 °C (Figure 3). Appropriate technology can now be operated routinely under continuous-flow conditions.

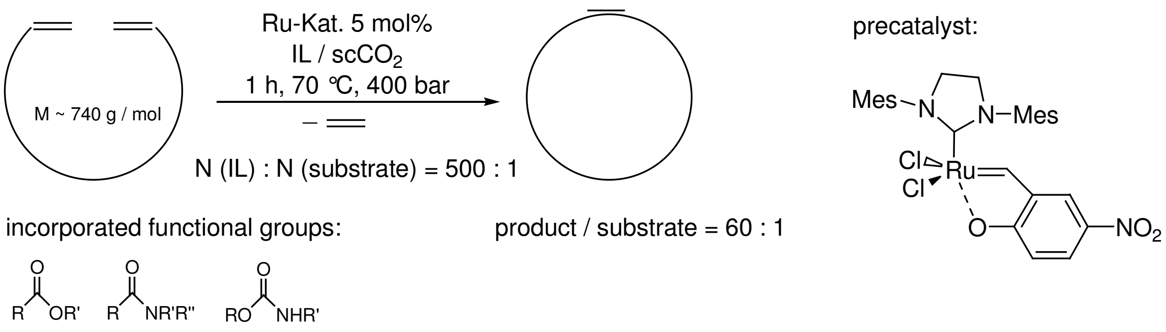


Figure 3. Macrocyclisation of a pharmaceutical precursor by RCM in a $scCO_2$ / IL biphasic system

Other scientific projects in the field of $scCO_2$ which have been or are currently investigated in the period covered by the present report are the following:

- Biphasic enzymatically catalysed kinetic resolutions
  In collaboration with the Reetz group, lipase catalysed transesterification was studied in a ionic liquid/scCO2 biphasic system. In particular, it was demonstrated that kinetic enzymatic resolution can be coupled efficiently with SCF-based mass separation to isolate the two enantiomers of racemic secondary alcohols (as the free alcohol and ester, respectively) continously in a single process unit.
- Mechanistic studies in methanol-synthesis (with the Schüth group)
- Aerobic oxidations of olefins using a PEG-immobilized Fe-catalyst
- Depolymerisation of ADMET-polymers by Ru-catalysts and enzymatic depolymerisations of polyesters
- Production of resorcinol-formaldehyde-aerogels (RF-aerogels) and supramolecular organometallic aerogels by Supercritical Fluid Extraction (SFE) (with the groups of Schüth and Dötz (Bonn), respectively)
- Crystallisation of polymorphic caffeine-CO_2-adducts (with Lehmann)

Publications resulting from this research area: 17, 62, 79, 82, 83, 92, 95, 114, 135, 154, 239, 240, 271, 288

External funding: Boehringer Ingelheim Pharma; Symrise; RWTH Aachen; DFG (Gerhard-Hess-Program); bmb+f (CoNeCat Lighthouse project "Regulierbare Systeme für die Mehrphasenkatalyse – smart solvents/smart ligands", transferred to RWTH Aachen in 2002)

Cooperations: F. Faraone (Messina, IT); D. Ballivet-Tkatchenko (Dijon, FR); K.-H. Dötz (Bonn, DE); C. Bolm (Aachen, DE); P. Wasserscheid (Aachen/Erlangen, DE); C. W. Lehmann (Mülheim/Ruhr, DE); M. T. Reetz (Mülheim/Ruhr, DE); F. Schüth (Mülheim/Ruhr, DE); B. Tesche (Mülheim/Ruhr, DE)

2.2 Department of Homogeneous Catalysis

Director: NN

Further group leaders:

Klaus Jonas (born 1941)
Publications: none

Benjamin List (born 1968)
in the Institute since May 2003
Publications: 360, 361, 362, 378-381, 430, 434

Klaus-Richard Pörschke (born 1949)
Publications: 96, 149, 306

Research in the Department of Homogeneous Catalysis

Although the position of the head of this Department is still vacant (formerly Professor A. Pfaltz), the research activities in the field of homogeneous catalysis have been significantly enlarged during the report period.

Thus, the appointment of Professor List in 2003 has expanded the portfolio of the Department beyond metal catalyzed reactions and the organometallic chemistry associated with them, which are traditional and well established areas of interest at the Institute. Professor List's research activities spearhead the timely field of "organocatalysis", i.e. the use of small organic molecules as catalysts for a variety of enantioselective transformations. As will become evident from his report, the systematic exploitation of the "enzyme-like" reactivity profile of molecules as small as proline or related compounds, the design of novel organocatalysts, and the understanding of the guiding principles presently constitute the major lines of research in his group.

In addition, the groups of Professor Pörschke and Professor Jonas continue their research programs in the field of metal-based molecular catalysts. Thereby, priority is given to the understanding of the elementary steps of catalytic transformations and the insight into the structure and reactivity of the intermediates of relevant catalytic cycles. This knowledge is used to design catalytic transformations which ensure high "atom economy" and proceed under notably mild conditions. Moreover, the preparation of metal complexes with novel structures, unconventional ligand sets, and/or largely unprecedented reactivity is actively pursued. Close collaborations with the Theory Department and various Scientific Service Units are necessary to achieve these goals.

2.2.1 Research Area "Mononuclear and Polynuclear Transition Metal Complexes with Pentalene and Related Polycycles as Ligands" (K. Jonas)

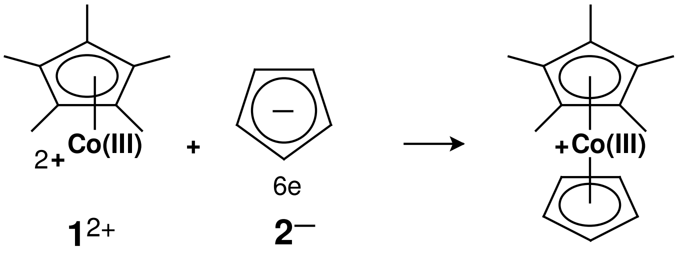
Involved: M. Hannappel, U. Nienhaus

Objective: Our group investigates the chemistry of metal complexes in which pentalene or substituted pentalene is bound to a single metal atom or functions as a bridging ligand between two metal atoms. The synthetic work is mainly directed towards the development of efficient pathways to such complexes, but it also includes the preparation of new organic compounds to be used as precursors for substituted pentalene ligands. The thorough elucidation of the structures and structure dynamics of the metal pentalene complexes is carried out in close collaboration with various analytical Departments of the Institute. A further aspect of our work is to determine the reactivity of the complexes prepared. The so far observed reactivity of the pentalene complexes accounts for the growing importance of this research area in our group.

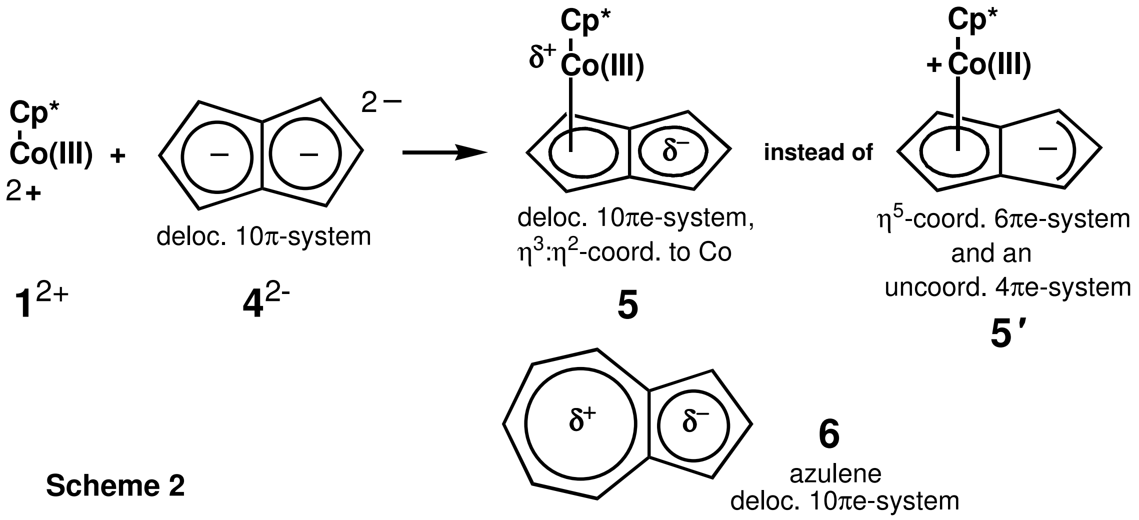
Results: For the last few years our efforts have focused on the mononuclear *late* transition metal pentalene complex pentalene(pentamethylcyclopentadienyl)cobalt(III) (**5**) and the chemistry derived from it. These investigations have been very rewarding since they have helped us to develop a methodology which allows the successive incorporation of up to four identical or different alkyl substituents on the C_α carbon atoms of the pentalene dianion.

1. Revised Representation of the Structure and Bonding of Pentalene(pentamethylcyclopentadienyl)cobalt(III) (5)

The cobalt atom of the dicationic 12e-fragment $\mathbf{1}^{2+}$ requires six valence electrons to achieve the noble gas configuration. If it were up to the monoanion $\mathbf{2}^{-}$ to achieve stabilization of $\mathbf{1}^{2+}$, one would obtain the monocation $\mathbf{3}^{+}$, being a derivative of Cp_2Co^+. Yellow Cp_2Co^+, which is isostructural and isoelectronic to ferrocene, is known to be of very low reactivity. It is is attacked by nucleophiles only if these are very strong, and its resistance toward electrophiles is proverbial.



Scheme 1 $\mathbf{1}^{2+}$ $\mathbf{2}^{-}$ $\mathbf{3}^{+}$

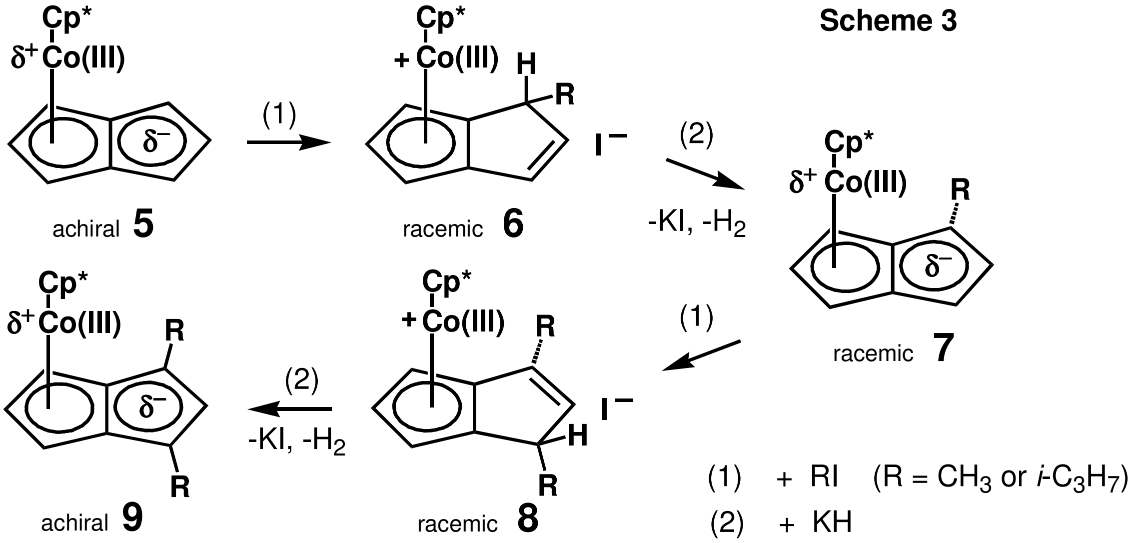


Scheme 2

Originally we had assigned to the dark blue mononuclear cobalt complex **5** — prepared from $[Cp^*CoCl_2]_2$ and $Li_2[C_8H_6]$ (Li_2[**4**]) — a zwitterionic structure, with a positive charge on the metal and an entire negative charge on the noncoordinated part of the pentalene ligand (see **5′** in Scheme 2). However, after re-examination of the geometrical parameters and the NMR data of **5**, along with the examination of the data of a series of reference compounds, we now consider that the structure and bonding of this dipolar pentalene complex are represented more precisely by a formulation according to **5**. The fused monocycles of the pentalene ligand — one of them has a distorted η^5-coordination (η^3:η^2) and the other one three carbons noncoordinated — are integrated elements of an aromatic 10-π-electron system and as such contribute both to the overall aromaticity of the dianionic pentalene ligand. The relationship between the cobalt-coordinated [5,5]-bicycle **5** and the [7,5]-bicycle of azulene (**6**) is conspicuous. The azulene molecule, being aromatic with 10 π-electrons but metal-free, is also polarized, in contrast to the dianion of pentalene ($\mathbf{4}^{2-}$) and the neutral naphthalene molecule.

2. Monoalkyl Derivatives of 5, Prepared by a Simple Two-Step Procedure, and the Extension of this Procedure to Synthesize Dialkyl Derivatives

The conversion of the dipolar pentalene complex **5** into compounds having one or two alkyl groups attached to the uncoordinated pentalene part requires two types of reagent. Needing an electrophilic alkylation reagent as well as a base, we have used the carbon electrophiles RI [(1) in Scheme 3] for the alkylation reactions and potassium hydride [(2) in Scheme 3)] as a base. Its basicity was found to be by far sufficient to deprotonate the intermediate air-stable, light yellow cobalticenium salts (derivatives of **3**).



Scheme 3

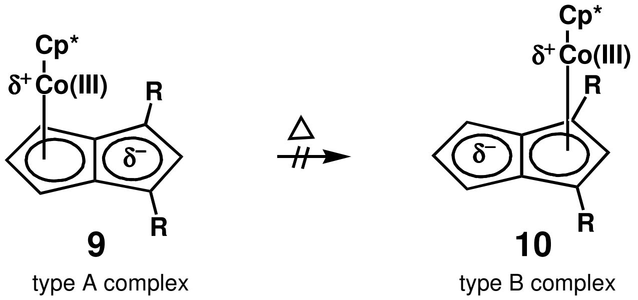
(1) + RI (R = CH_3 or *i*-C_3H_7)
(2) + KH

In their reactions with RI (1), and in the products resulting thereof (**6**, **8**), the complexes **5** and **7** are strongly reminiscent of how amines and phosphines behave toward electrophiles. Although these nucleophiles stand for heteroatom nucleophiles, their reactions with alkyl halides are also *addition* reactions with two nonionic reactants on the educt side and an ionic compound (onium salt) on the product side. The alkylation of the ambident carbon nucleophile **5** with RI is stereoselective, affording a racemic stereoisomer that has the alkyl group in the less hindered *exo*-position (**6**). Deprotonation of **6** with KH (2) gives the racemate **7**, which at the same time is the conjugate base of **6** and a monoalkyl derivative of the parent **5**. For racemic **7** (a type A alkyl derivative of **5**) the alkylation is stereoselective *and* regioslective; that is, in the isolated product **8** the stereoisomer that would be formed by electrophilic attack at the ipso position is not detected. This finding clearly demonstrates the striking directing influence that an alkyl substituent already present in the ambident nucleophile has on the positional selectivity. The end of the overall reaction sequence is given by the deprotonation of **8** to give the final **9** (also a type A alkyl derivative of **5**) which is achiral just as **5**.

3. Conversion of Alkyl Derivatives of 5 (Type A Complexes) into their Positional Isomers (Type B Complexes) by Electron-Transfer-Chain Catalysis

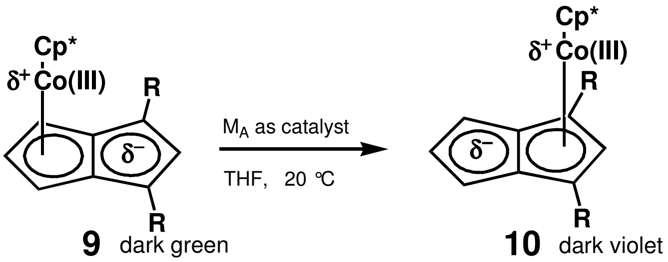
A characteristic property of the neutral cobalt pentalene complexes **5**, **7**, and **9** is their high thermal stability. They do not decompose when heated in THF or xylene (120 °C!) even for prolonged periods, nor do the alkyl-substituted complexes **7** and **9** (type A complexes) undergo a thermal inter-ring haptotropic rearrangement to yield the positional isomers (type B complexes, see Scheme 4) or a mixture of both isomers.

Scheme 4



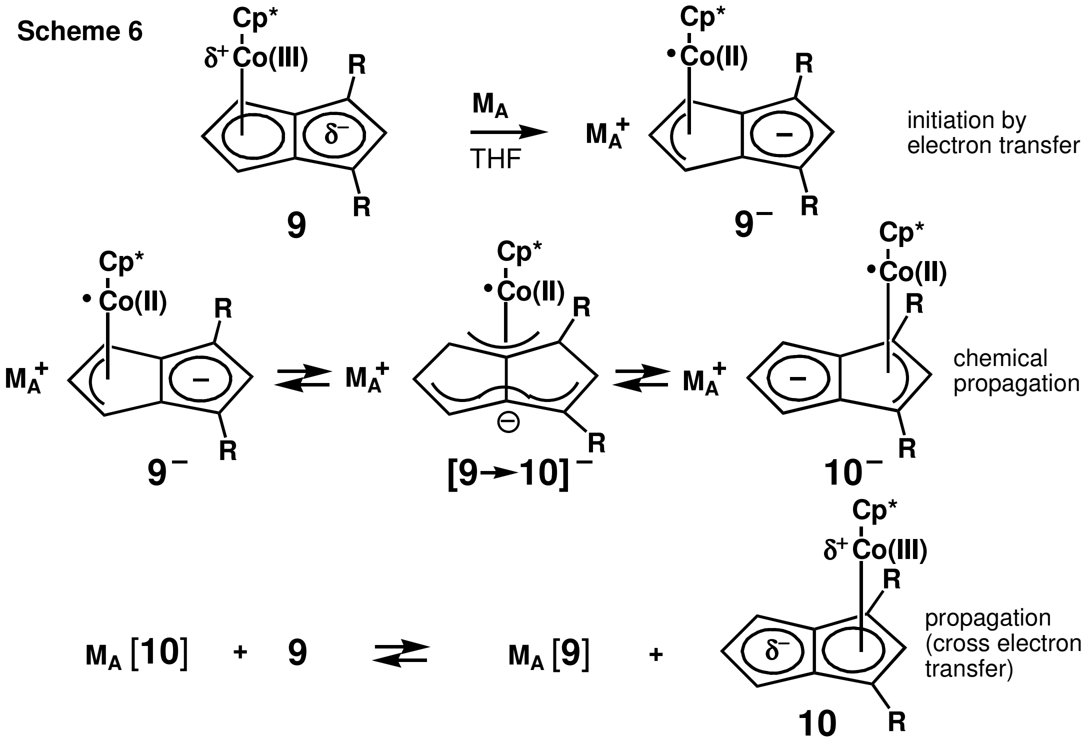
Decisive for the progress of our work was the discovery that the compounds **7** and **9** (type A complexes) readily isomerize in the presence of a catalytical amount of alkali metal M_A (Li, K) and when dissolved in tetrahydrofuran at room temperature, and that for all pairs of the investigated isomers the equilibrium of isomerization lies far to the side of the isomer which has the alkyl group(s) bonded to the *coordinated* pentalene ring (Scheme 5).

Scheme 5



Concerning the overall mechanism, the alkali metal (or electron) catalyzed isomerization can be classified as a chain reaction, which comprises an initiation step and two propagation steps.

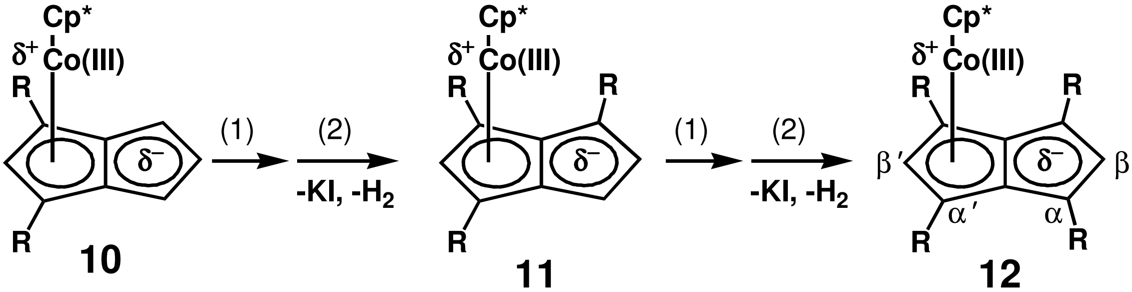
Scheme 6



DFT calculations carried out by M. Bühl of this institute have revealed that the activation energy of the process which comprises the migration of the Cp*Co fragment between the two five-membered rings (chemical propagation, see Scheme 6) decreases considerably when cobalt is caused by one-electron reduction to reduce its oxidation state from III to II. With cobalt(II) instead of cobalt(III) the inter-ring rearrangement is facile and has an allyl cobalt(II) species as an intermediate ($[\mathbf{9}\rightarrow\mathbf{10}]^-$) in Scheme 6), whereas the intermediate of the noncatalyzed isomerisation, which was experimentally not observed, has been calculated to be a cobalt(III) species with a trimethylene-methane-like bonded pentalene ligand.

4. From Dialkyl Derivatives of 5 (Type B Complexes) to Tri- and Tetraalkyl Derivatives (Type C and D Complexes)

As expected, for the conversion of the type B complexes having an alkyl-disubstituted pentalene ligand (**10**) into complexes with one alkyl group more (type C complexes) or ultimately into complexes having both pentalene rings alkyl-disubstituted (type D complexes), exactly the same reagents (1) and (2) and the same two-step procedure can be used as for the preparation of the type A complexes.



Scheme 7

Apart from the preparation of the two compounds **12** (R = CH_3 or i-C_3H_7), both of which have a set of four identical alkyl substituents, we have also accomplished the synthesis of several complexes in which the C_α and C_α' carbon atoms of the bicyclic ligands bear *different* alkyl substituents (type D′ complexes). Figure 1 displays the crystal structure of such a complex. In this compound the [5,5]-bicycle bears two methyl substituents in the coordinated part and two isopropyl substituents in the noncoordinated part.

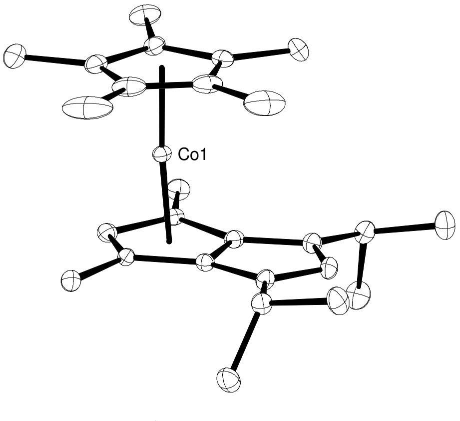
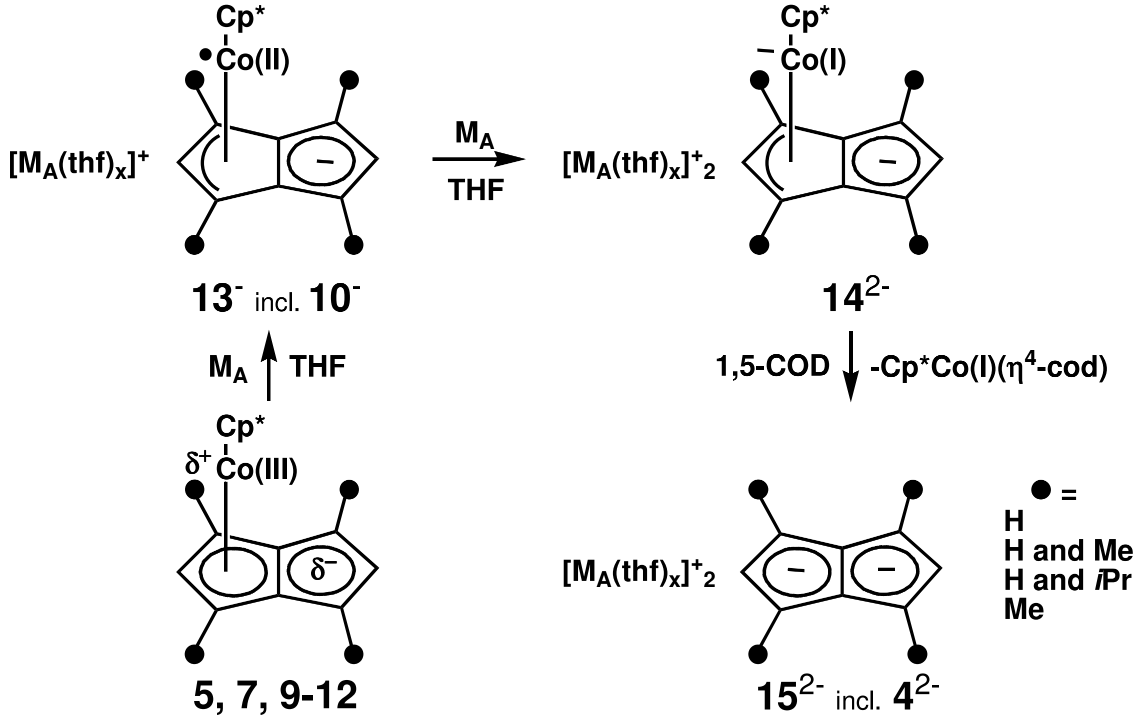


Figure 1

It is true that the synthesis of the complexes **12** (type D; R = CH_3 or i-C_3H_7) and of the type D′ complexes starting from the parent compound **5** are all multi-step syntheses, comprising four alkylations, four deprotonations and one isomerisation, but all the individual steps are experimentally easy to carry out. Furthermore, the overall yields are higher than 50% with respect to **5**. For example, starting from 25 g of **5** one ends up with more than 16 g of **12** (R = CH_3).

5. Synthesis of Alkali Metal Dihydropentalenediids with One to Four Alkyl Substituents by Reductive Degradation of Alkyl Derivatives of 5

On treatment with alkali metal in THF the neutral parent compound **5** and all its alkyl derivatives undergo an one-electron reduction (Scheme 8, see also Schemes 5 and 6 in section 3), and the same holds also for the respective paramagnetic monoanions that are formed (in form of their alkali metal compounds $M_A(thf)_x$[**10**] and $M_A(thf)_x$[**13**]; of these ate complexes the TMEDA derivative Li(tmeda)[Cp*Co(II)(η^3-$C_8H_2(CH_3)_4$] has been characterized by X-ray crystallography!). The products of the exhaustive alkali metal reduction (*two* one-electron reductions) are diamagnetic dianionic cobalt(I) complexes of the composition $(M_A(thf)_x)_2$[**14**], being presumably contact triple ions.



Scheme 8

Of great importance with regard to synthetic applications is the finding that the alkali metal cobalt complexes $(M_A(thf)_x)_2$[**14**], composed of a dianionic part with cobalt in the relevant oxidation state I and two alkali metal counterions, can be directly used as precursors for the high yield synthesis of pentalene dianions (in form of their alkali-metal salts $(M_A(thf)_x)_2$[**15**]) that have a well-defined pattern of alkyl substitution. It is only needed to simply mix the appropriate dianion **14** with a compound (e.g., 1,5-cyclooctadiene) that is known to be coordinated strongly enough to the neutral Cp*Co(I) fragment (**1**) (Scheme 8).

6. *First Applications of the New Alkali Metal Dihydropentalendiids as Reagents in Organometallic Synthesis*

Having made the precious reagents $(M_A(thf)_x)_2$[**15**] accessible, we decided to test them first as starting materials for the synthesis of transition metal complexes whose parent compounds had already been prepared by us. Earlier we had learnt that with the group IV transition metals it is possible to prepare homoleptic complexes with two η^8-coordinated pentalene or 2-methylpentalene ligands, i. e., $(\eta^8\text{-}C_8H_6)_2M$ (M = Ti, Zr, Hf; **16a–c**) and $(\eta^8\text{-}C_8H_5CH_3)_2M$. The six analogous complexes, which have also been the topic of several theoretical investigations, are afflicted by the deficiency that their crystal structures and thus their geometrical data are not known. We have now been able to accomplish the synthesis of the highly alkylated pentalene zirconium complexes $(\eta^8\text{-}C_6H_2(CH_3)_4)_2Zr$ (**17a**), $(\eta^8\text{-}C_8H_2(CH_3)_4)Zr(\eta^8\text{-}C_8H_4(CH_3)_2)$ (**17b**) and $(\eta^8\text{-}C_8H_2(CH_3)_4)Zr(C_8H_4(i\text{-}C_3H_7)_2)$ (**17c**). It has been possible to characterize all of them by X-ray crystallography. Figure 2 depicts the crystal structure of **17a** viewed from the side and Figure 3 the structure viewed from above a tetramethylpentalene ligand.

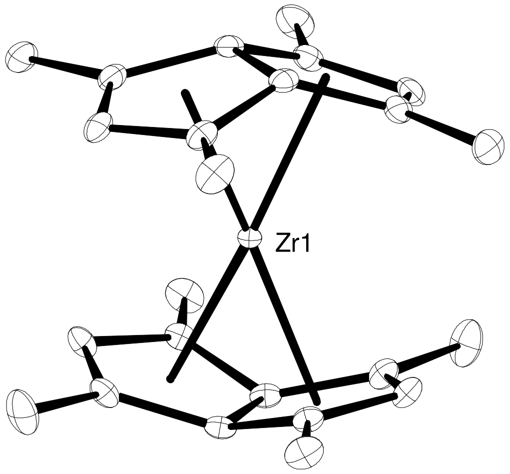


Figure 2

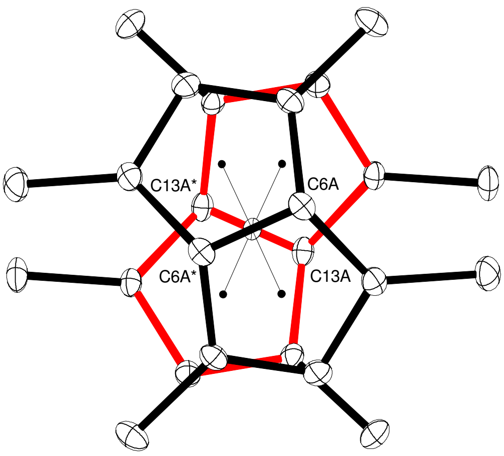


Figure 3

The novel sandwich complex **17a** has crystallographic C_2 point symmetry with the C_2-axis passing through the Zr atom and both centers between the bridgehead carbon atoms. The angle of torsion between the two ligands is at 48.8°, and the angles of folding within the bicyclic ligands along the bonds between the bridgehead carbon atoms amount to 148° and 146°, respectively. It should be noted that these data are in excellent agreement with the calculated data which R. Gleiter et al. had obtained by applying the RHF method for the parent compound $(\eta^8\text{-}C_8H_6)_2Zr$ (**16b**) in the gase phase (51° and 152°).

Publications resulting from this research area: none

External funding: none

Cooperations: R. Gleiter (Heidelberg, DE); M. Bühl (Mülheim/Ruhr, DE); R. Mynott (Mülheim/Ruhr, DE); C. W. Lehmann (Mülheim/Ruhr, DE)

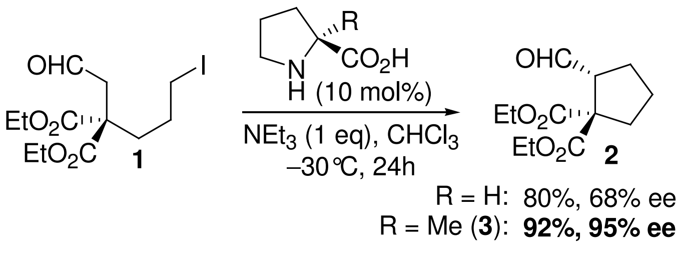
2.2.2 Research Area "Organocatalytic Asymmetric α-Alkylation of Aldehydes"

(B. List)

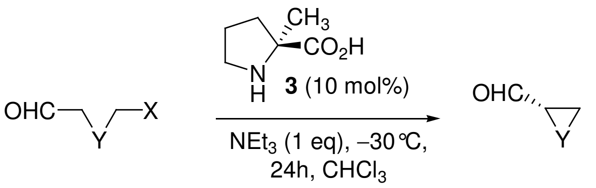
Involved: N. Vignola, A. Majeed Seayad

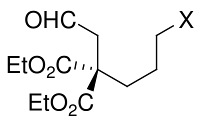
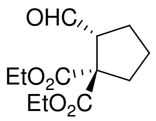
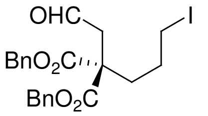
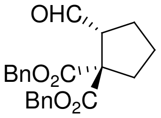
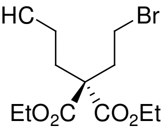
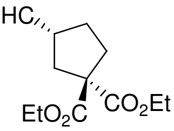
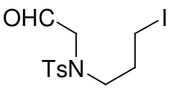
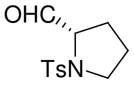
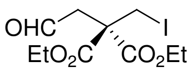
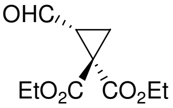
Objective: α-Alkylations of carbonyl compounds are central carbon-carbon-σ-bond forming reactions in organic synthesis. Asymmetric variants generally rely on the use of chiral auxiliaries and a variety of efficient examples have been reported in the last three decades. Despite its potential as a broadly useful synthetic methodology, the development of a general catalytic asymmetric α-alkylation reaction has proven extremely challenging and the only two reported strategies are limited in scope. Although chiral α-branched aldehydes are particularly valuable synthetic intermediates, neither direct nor indirect catalytic asymmetric α-alkylations of aldehydes have previously been described. The aim of this project has been to develop the first, efficient, and highly enantioselective direct aldehyde α-alkylation reactions.

Results: Based on our previous successful use of proline enamine catalysis of a variety of asymmetric reactions, we initially investigated the intermolecular α-alkylation reaction of cyclohexanone and propionaldehyde with benzylbromide catalyzed by proline in the presence of triethylamine. Not surprisingly however, we only identified products of proline benzylation. We then studied intramolecular alkylations of aldehydes and to our excitement found these reactions to work quite well. For example, the proline-catalyzed intramolecular alkylation of aldehyde **1** gave cyclopentane derivative **2** in 80% yield and in promising 68% *ee*. After optimizing the reaction conditions, and screening several proline derivatives and other amines as alternative catalysts, we found that commercially available (S)-α-methyl proline (**3**) significantly improved both rate and enantioselectivity of the reaction. Treating aldehyde **1** with catalyst **3** (10 mol%) in chloroform at –30 °C in the presence of triethyl amine furnished cyclopentane carbaldehyde **2** in excellent yield (92%) and enantioselectivity (95% *ee*).



We also studied the scope of this novel reaction. Varying the leaving group (I, Br, OTs) furnished product **2** in similar high enantioselectivities although the cyclization of tosylate **5** was particularly slow. Replacing ethyl- with benzyl groups as in ester **6** furnished the corresponding product (**7**) in almost identical enantioselectivity and yield.



Substrate	Product	Yield (%)	ee (%)
			
1 (X = I)	**2**	92	95
4 (X = Br)	**2**	90	94
5 (X = OTs)	**2**	20	91
 **6**	 **7**	94	95
 **8**	 **9**	92	97
 **10**	 **11**	52	91
 **12**	 **13**	70	86

If structural isomer **8** was treated with catalyst **3**, aldehyde **9** was obtained in 92% yield and 97% *ee*. Much to our delight we found that extending this new reaction to the synthesis of heterocycles worked equally well. Thus subjecting amino aldehyde **10** to the reaction conditions furnished (*S*)-*N*-tosyl prolinal (**11**) in high enantioselectivity. Furthermore, we were able to extend our methodology to alternative cyclization modes such as the 3-exo-tet cyclization of aldehyde **12** to cyclopropane **13** in high yield and enantioselectivity.

Our process represents the first catalytic asymmetric α-alkyation of aldehydes and we are currently expanding the substrate scope of the reaction and develop an intermolecular variant.

Publication resulting from this research area: 430

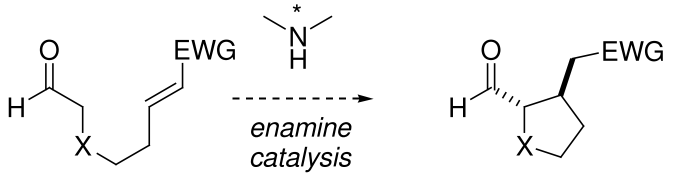
External funding: none

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

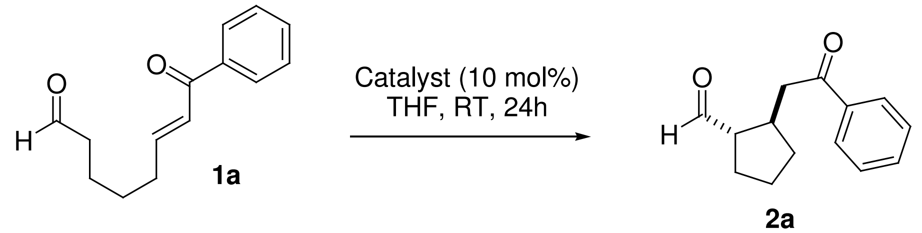
2.2.3 Research Area "Organocatalytic Asymmetric Intramolecular Michael Reaction of Aldehydes" (B. List)

Involved: M. H. Fonseca, D. Monge Fernández, J. Seayad

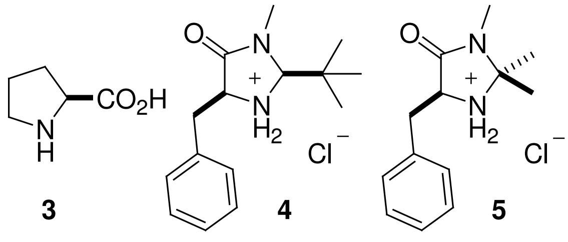
Objective: We have recently developed novel organocatalytic asymmetric cyclization reactions of aldehydes, including a new enolexo-aldolization and an α-alkylation reaction. In this context we realized that although there are a number of reports on elegant catalytic enantioselective intermolecular Michael reactions, *intramolecular* catalytic asymmetric Michael reactions of aldehydes are unknown. We felt such a process to be of high value, particularly if included in strategic reaction sequences such as the Robinson annulation. The aim of this project was to develop an efficient catalytic enantioselective cyclization of formyl enones in a process that constitutes the first catalytic asymmetric intramolecular Michael reaction of aldehydes.



Results: As a model reaction we studied the amine-catalyzed Michael cyclization of formyl enone **1a** to give keto aldehyde **2a**. This reaction was catalyzed by (*S*)-proline (**3**, 10 mol%, RT, DMF, 3d) but as expected, both diastereoselectivity and enantioselectivity were low. Next, we studied MacMillan's commercial imidazolidinone catalysts **4** and **5**. Although they have not previously been used in enamine catalysis**,** we found them to effectively catalyze the cyclization reaction. Interestingly, while the more reactive catalyst **4** provided the product in very high yield (99%) and only 39% *ee*, catalyst **5** gave the product with the same yield and *in excellent 97% ee*.



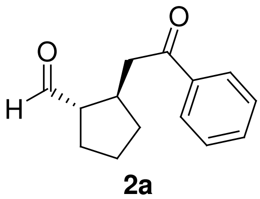
1a **2a**



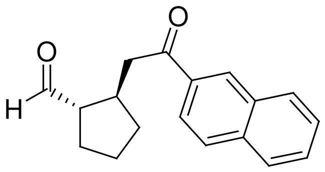
3 **4** **5**

Cat	Yield	*dr* (*anti*:*syn*)	*ee* (*anti*)
3	85%	2:1	15%
4	99%	19:1	39%
5	99%	24:1	97%

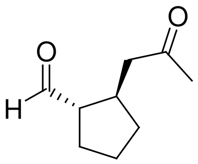
We have extended this reaction to a variety of different substrates that all furnished the desired products in high yields and diastereo- and enantioselectivities. In addition, the reaction could be used in tandem with an intramolecular aldolization to give enone **6**. We are currently using enones such as **6** in a novel approach toward artificial steroids.



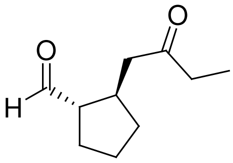
2a
99% Yield, 97% *ee*



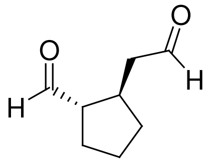
2b
99% Yield, 97% *ee*



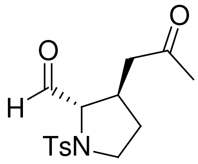
2c
99% Yield, 93% *ee*



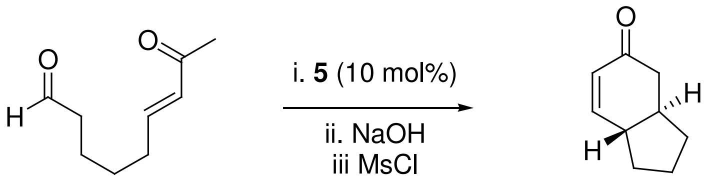
2d
99% Yield, 94% *ee*



2e
85% Yield, 80% *ee*



2f
90% Yield, 93% *ee*



1c

6
88%, 94% *ee*

Publication resulting from this research area: 361

External funding: none

Cooperation: W. Schrader (Mülheim/Ruhr, DE)

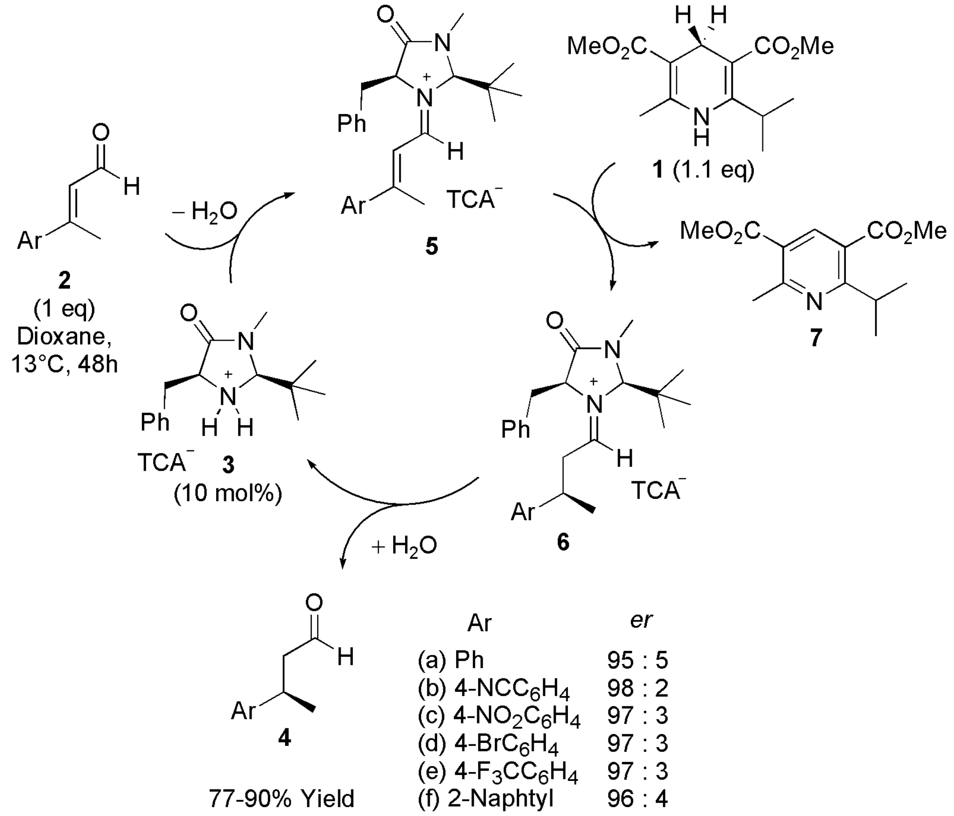
2.2.4 Research Area "Metal-Free Catalytic Hydrogenation" (B. List)

Involved: J. W. Yang, M. H. Fonseca, N. Vignola

Objective: Hydrogenation is arguably the single most important catalytic reaction for the synthesis of enantiomerically pure compounds and is crucial for all living organisms. Previous chemical and biological catalytic asymmetric hydrogenations require metals. 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 has been the development of methodology for the catalytic asymmetric and non-asymmetric transfer hydrogenation of α,β–unsaturated aldehydes via iminium catalysis.

Results: Recently catalysis with small organic molecules has become a rapidly growing area of research and one of its advantages is the general lack of metals. While hydrogenations or transfer hydrogenations have not been catalyzed previously with organic compounds only, we reasoned that a completely metal-free hydrogenation may be realized if organocatalysis would be used in combination with a suitable purely organic hydrogen donor. Specifically, we hoped that asymmetric catalysis of the conjugate reduction of α,β-unsaturated carbonyl compounds may be realized via catalysis with secondary ammonium salts via iminium ion intermediates. Iminium catalysis has recently been introduced as a powerful organocatalytic method for carbonyl transformations such as conjugate- and cycloadditions. As potential hydrogen donor we identified Hantzsch dihydropyridines. Dihydropyridines have been used in hydrid- or hydrogen transfer reactions as synthetic NADH models for the reduction of carbonyl compounds, olefins, and imines. However, while chiral Hantzsch esters have been employed stoichiometrically, the potential of their simple achiral derivatives as cofactors in catalytic asymmetric reductions has never been explored.

After an extensive screening of several synthetic Hantzsch dihydropyridines and chiral ammonium salt catalysts, we found that upon treating aromatic, trisubstituted α,β-unsaturated aldehydes **2** with a slight excess of dihydropyridine **1** and a catalytic amount of imidazolidinone salt **3** at 13 °C in dioxane, the corresponding saturated aldehydes **4** were obtained in high yields and enantioselectivities.

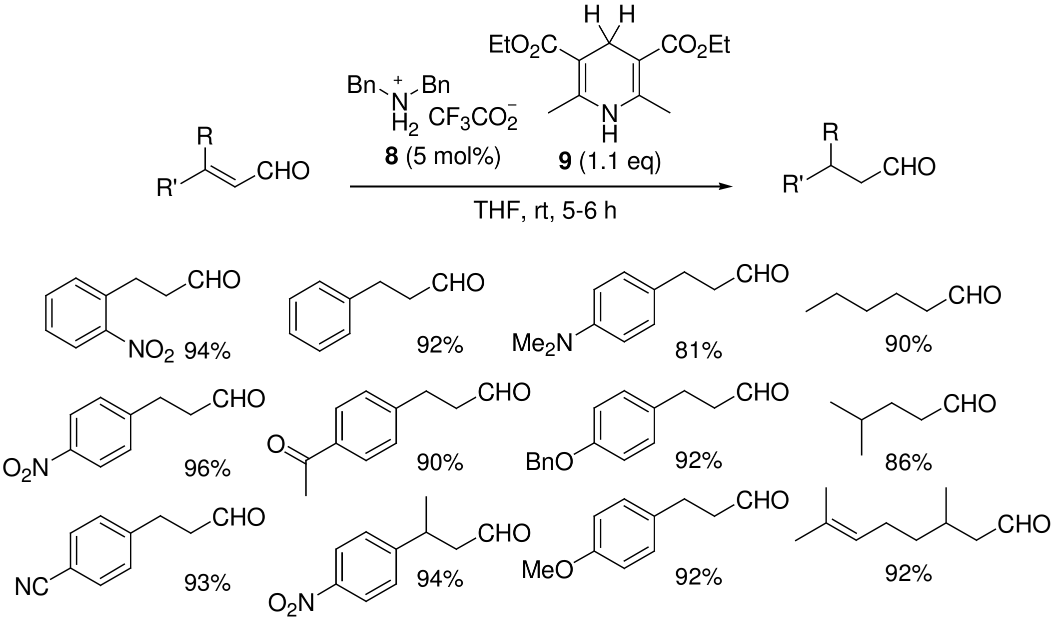


Ar	er
(a) Ph	95 : 5
(b) 4-NCC_6H_4	98 : 2
(c) 4-$NO_2C_6H_4$	97 : 3
(d) 4-BrC_6H_4	97 : 3
(e) 4-$F_3CC_6H_4$	97 : 3
(f) 2-Naphtyl	96 : 4

The reactions are generally clean and highly chemoselective and carbonyl reduction products have not been detected. We also investigated the influence of the olefin geometry. Remarkably, when we subjected both the isolated pure (*E*)- or (*Z*)-isomers of 4-nitro-substituted derivative **2c** to our reaction conditions, the same (*R*)-enantiomer of product **4c** was obtained and with the same enantioselectivity of 97:3 *er*. Similarly, (*E*)/(*Z*)-mixtures always gave the same result and, independent of their exact ratio, all furnished (*R*)-**4c** in 97:3 *er*. Thus, our process is *enantioconvergent*, a highly desirable yet rare feature of a catalytic asymmetric reaction, where a mixture of stereoisomers furnishes only one product enantiomer. Mechanistically, we assume the reaction to proceed via the formation of iminium ion **5**, which accepts a hydride and a proton from dihydropyridine **1** to give iminium ion **6** and pyridine **7**, and upon hydrolysis saturated aldehyde **4**. The enantioconvergence is explained with a fast (*E*)/(*Z*)-isomerization at the stage of the iminium ion, presumably via the formation of a dienamine intermediate.

In summary we have described the first completely metal-free catalytic asymmetric hydrogenation. In our iminium catalytic reaction α,β-unsaturated aldehydes are highly efficiently reduced via transfer hydrogenation from a dihydropyridine. Attractive features of the process are (a) its high yields, chemo-, and enantioselectivities, (b) its enantioconvergence, and (c) its simplicity and practicality. Applications in the synthesis of chiral pharmaceuticals may be envisioned.

In addition to this asymmetric variant we have previously established a non-asymmetric, though highly efficient and chemoselective version, in which we use dibenzyl ammonium salt **8** as the catalyst and commercially available Hantzsch ester **9** as hydride donor.



Publication resulting from this research area: 434

External funding: none

Cooperations: none

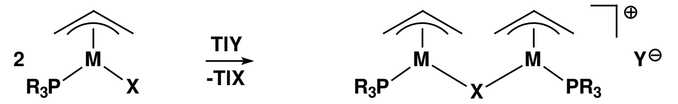
2.2.5 Research Area "Allyl Complexes of the d^{10}-Metals Nickel and Palladium"

(K.-R. Pörschke)

Involved: D. Alberti, Y. Ding

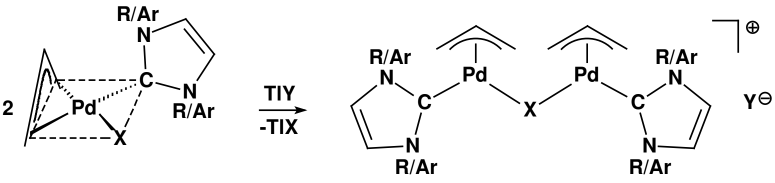
Objective: M–allyl complexes have been known since long as highly efficient catalysts or catalyst precursors for numerous transformations of organic substrates. There has been much speculation as to whether (η^3-C_3H_5)M(L)X complexes (M = Ni, Pd; L e.g. phosphane; X = halide) can be activated with Lewis acids to generate highly electron deficient ionic 14e [(η^3-C_3H_5)ML]Y complexes with a noncoordinating counterion Y. In an attempt to develop new M–π-allyl based catalysts (M = Ni, Pd) for hydrosilylation reactions we have studied the reaction of (η^3-C_3H_5)M(L)X complexes with halide abstracting reagents in detail.

Results: When the complexes (η^3-C_3H_5)M(PR_3)X (M = Ni, Pd; PR_3 = P^iPr_3 or P^tBu_3) and (η^3-C_3H_5)Pd(NHC)X (NHC = N-heterocyclic carbene) are reacted with TlY (Y = PF_6, $B(C_6F_5)_4$, $B\{3,5\text{-}C_6H_3(CF_3)_2\}_4$) in a noncoordinating solvent (CH_2Cl_2), only half of an equivalent of TlY is consumed to precipitate TlX. From the resulting solutions the novel dinuclear, single halide-bridged ionic complexes [{(η^3-C_3H_5)M(PR_3)}$_2$(μ-X)]Y (**1**) and [{(η^3-C_3H_5)Pd(NHC)}$_2$(μ-X)]Y (**2**) are isolated.



(1)

M = Ni, Pd; X = Cl, Br; R = ^{i}Pr, ^{t}Bu

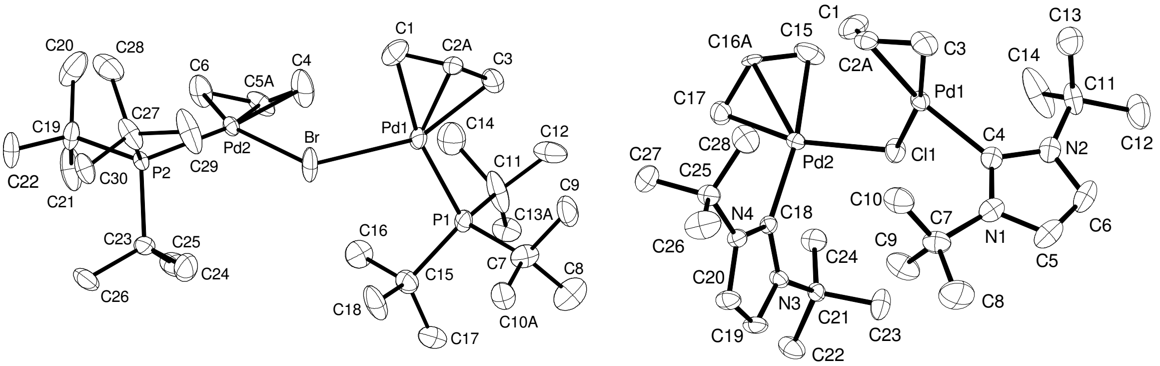


(2)

X = Cl, I; R = ^{t}Bu, Ar = C_6H_3-2,6-^{i}Pr_2

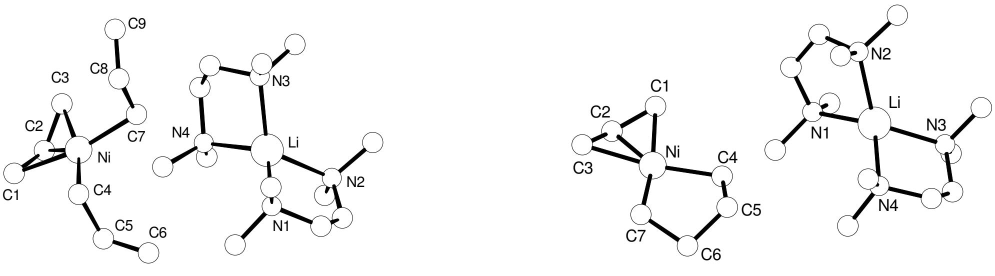
As a consequence of chirality of the individual (η^3-C_3H_5)M(L)X moieties, the dinuclear complexes **1** and **2** exist as mixtures of diastereomers. Thus, two sets of solution NMR resonances are observed at low temperature (–30 to –80 °C), evidencing also non-dynamic coordination of the ligands at the Pd centers (rotations about the M–μ-X bonds are, however, possible). The M–μ-X–M bond strength increases in the series Cl < Br < I and Ni < Pd, and the bonds appear more stable for NHC than for phosphane ligands. Thus, the Pd complexes are stable also for Y = OTf as a weakly nucleophilic anion (i.e., no attack of OTf occurs at the Pd center), whereas in the case of Ni transient Ni–μ-X–Ni moieties are cleaved by OTf to afford mononuclear (η^3-C_3H_5)Ni(PR_3)(OTf).

For $[\{(\eta^3\text{-}C_3H_5)Pd(P^tBu_3)\}_2(\mu\text{-}Br)][B(C_6F_5)_4]$ (**1a**) and $[\{(\eta^3\text{-}C_3H_5)Pd(C(N(^tBu)\text{-}CH)_2)\}_2(\mu\text{-}Cl)][PF_6]$ (**2a**) the crystal structures have been determined. The structure of the bromide **1a** is of particular interest, since the coordination planes of the two Pd atoms are almost perpendicular to one another at bromine, suggesting substantial pπ–dπ bonding for the Pd–μ-Br-Pd core. The study shows that ionic, halide-free 14e $[(\eta^3\text{-}C_3H_5)ML]Y$ complexes are not accessible from halide-containing precursor complexes.



Molecular structures of the cations of **1a** and **2a**

In an affiliated project LiC_3H_5 has been *added* to $M(\eta^3\text{-}C_3H_5)_2$ (M = Ni, Pd) to afford the first homoleptic allyl–metallate(II) complexes $[Li(tmeda)_2]^+[(\eta^3\text{-}C_3H_5)M(\eta^1\text{-}C_3H_5)_2]^-$ (M = Ni, Pd; **3a,b**). The complexes are *fluxional in the solid* above –90 °C (!), undergoing rapid π–σ-allyl isomerization of all ligands. In contrast, by reaction of $M(\eta^3\text{-}C_3H_5)_2$ with $Li_2C_4H_8$ the same LiC_3H_5 is *eliminated* to yield mixed allyl–alkyl–metallate(II) complexes $[Li(tmeda)_2]^+[(\eta^3\text{-}C_3H_5)M(1,4\text{-}C_4H_8)]^-$ (M = Ni, Pd; **4a,b**).



Molecular structures of **3a** and **4a**

Publication resulting from this research area: 149

External funding: Industrial

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

2.2.6 Research Area "Stereochemical Nonrigidity of Ni- and Pd-allyl Complexes"

(K.-R. Pörschke)

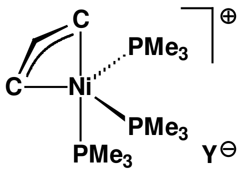
Involved: W. Ben Mustapha

Objective: Since their discovery Ni– and Pd–π-allyl complexes have been of fundamental importance with respect to their structure, bonding properties, and reactivity. We have observed that certain ionic Ni–π-allyl complexes form a plastically crystalline phase, a property which has hardly ever been reported in organometallic chemistry.

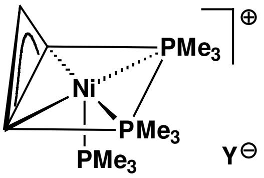
Results: In continuation of the project described in the previous report we have synthesized a series of pentacoordinate, ionic 18e complexes $[(\eta^3\text{-}C_3H_5)Ni(PMe_3)_3]Y$ (**1a–d**) and $[(\eta^3\text{-}C_3H_5)Ni\{P(OMe)_3\}_3]Y$ (**2a–d**) with the counterions Y = OTf, PF_6, Br, and I. The high structural fluxionality of the complexes in solution (NMR) led us to study also their solid state properties.

The solid-state ^{31}P NMR spectra are very characteristic for the coordination geometries of the complexes. For example, in the case of *TBP*-5 geometry large *J*(PP) coupling constants are observed for the equatorial phosphorus ligands ranging from 132 Hz (**1a**) to 211 Hz (**2b**), whereas they are much smaller for *SPY*-5 geometry (≈50 Hz). In fact, the first hints as to the structures of the complexes were obtained from solid state ^{31}P NMR and were just verified by X-ray structure analysis.

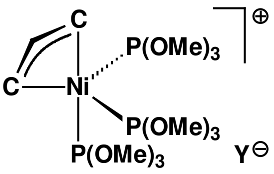
Solid state ^{13}C and ^{31}P NMR spectra and X-ray single-crystal structure determinations (–173 °C) indicate that the cations in **1a,b** and **2b,d** assume C_1 symmetrical, distorted trigonal bipyramidal (*TBP*-5) molecular geometries with the allyl group taking up axial and equatorial sites at the Ni^{II} center. In contrast, the structure of the cation in **2c** is square pyramidal (*SPY-5*) with the allyl group in the basal plane, presumably due to fixation of this structure by ion-pair interaction with the bromide. The assignment of *SPY-5* geometry to the microcrystalline **1c,d** is based solely on solid state NMR. For **2a** the ground state structure could neither be determined by crystallography, nor by solid state NMR, presumably due to high fluxionality in the solid.



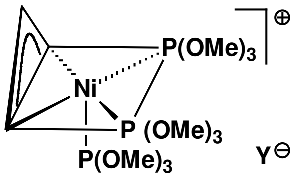
Y = OTf 1a , PF_6 1b
(NMR, X-ray)



Y = Br 1c , I 1d
(solid state NMR)



Y = PF_6 2b , I 2d
(NMR, X-ray)



Y = Br 2c
(NMR, X-ray)

DSC shows that complexes **1c,d** and **2a,b** are allotropic, i. e., these complexes form various solid phases. The PMe_3 complexes **1c,d** display enantiotropism and (reversibly) undergo transitions between two monoclinic crystalline phases at –18 and –56 °C, respectively, which is not an unusal property for crystalline compounds. The $P(OMe)_3$ complex **2b** (X-ray) converts monotropically (irreversibly) and endothermically at 47 °C into a modification **2b′** (NMR), which initially resides in its low temperature phase (see Figure 2). **2b′** is likewise allotropic. Unexpectedly, when the crystalline low temperature phases of **2a** and **2b′** are heated the complexes form plastically crystalline mesophases at –16 °C (Figure 1) and 53 °C (Figure 2). For these mesophases the reassumption of the ordered crystalline low-temperature phases is associated with a large supercooling of 14 and 70 K (!), respectively, due to retarded nucleation.

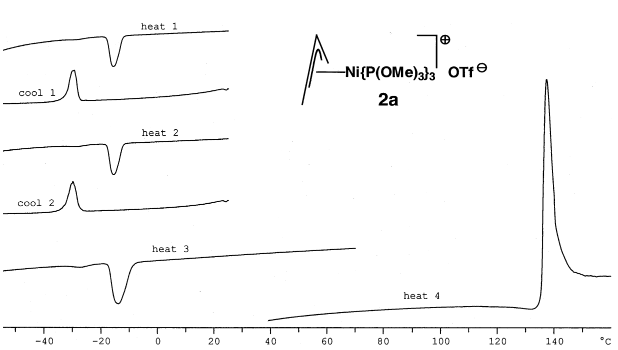


Figure 1. DSC Spectrum of **2a**

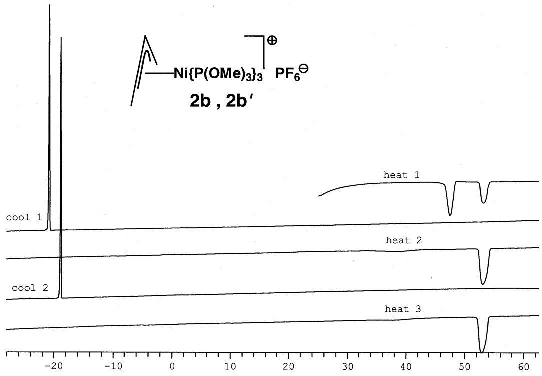
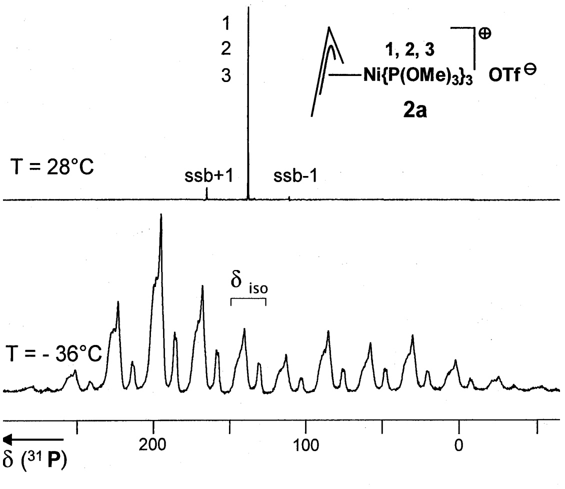


Figure 2. DSC Spectrum of **2b**

Conclusive evidence for the occurrence of plastically crystalline phases for **2a** and **2b/2b′** stems from the variable temperature solid state NMR spectra and from X-ray powder diffractometry. According to ^{31}P CP-MAS NMR complex **2a** is either dynamic or highly disordered in its low temperature phase, whereas the metastable **2b** is fully rigid and **2b′** in its low temperature phase is slightly dynamic. When **2a** is heated from –36 to 28 °C (Figure 3) and **2b** or **2b′** is heated from ambient temperature to 50 °C (Figure 4), the ^{31}P CP-MAS spectra collapse into a sharp single line with small satellites, just as it is otherwise typical for a solution NMR spectrum. Note that this change does not represent a coalescence of the primary resonances, but that the various signals are attributable to different phases. Figure 4 illustrates that the (ordered crystalline) low temperature phase and the (plastically crystalline) high temperature phase coexist at 45 °C, and within a 5 K temperature increase a complete conversion into the mesophase occurs. These phase changes are reversible. That fact that no supercooling is observed in the solid state NMR spectra (in contrast to DSC) is explained by the action of shear stress imposed by rotation of the sample; the shear stress causes rapid nucleation.



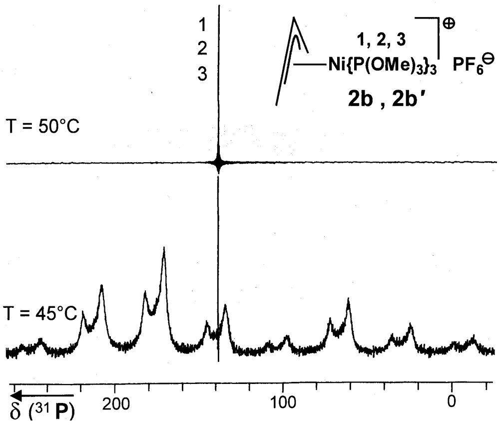


Figure 3. VT ^{31}P CP-MAS NMR of **2a**

Figure 4. VT ^{31}P CP-MAS NMR of **2b**

The equilibration of the ^{31}P NMR resonances is attributed to turnstile rotation of the three phosphorus ligands. Moreover, NQS ^{13}C CP-MAS NMR (NQS = non-quaternary suppression) indicates that in the mesophases of **2a** and **2b/2b′** the allyl group is also mobile. As a consequence, all ligands of the cation and, hence, the complete cation is in a virtual rotatory motion and any long-range orientational order is lost.

The X-ray powder diffraction data observed for **2b** at ambient temperature correspond to the single-crystal crystallographic data. When **2b** is heated to 60 °C a drastic simplification of the pattern occurs, which has been indexed with a cubic primitive cell. Cooling the sample again to ambient temperature gives rise to a new powder diffraction pattern which has been assigned to the low temperature crystalline phase of **2b′**. Similar results have been obtained for **2a**. The formation of a cubic primitive (or hexagonal) cell appears as one of the characteristics of the plastically crystalline state.

Plastic crystals are quite common in organic (neopentane) and inorganic chemistry (NH_4ClO_4), where they are observed for globular molecules. Phenomenologically, plastic crystals and liquid crystals together constitute the general class of mesogens and here more specifically metallomesogens. Although clearly solids, plastic crystals in their properties are much closer to liquids than to (ordered) crystals.

Publications resulting from this research area: none

External funding: none

Cooperations: A. Rufińska (Mülheim/Ruhr, DE); C. Weidenthaler (Mülheim/Ruhr, DE); R. Goddard (Mülheim/Ruhr, DE); M. Bühl (Mülheim/Ruhr, DE)

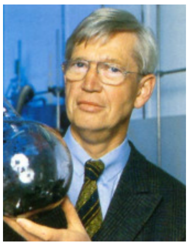
2.3 Department of Heterogeneous Catalysis

Director:

Ferdi Schüth (born 1960)
Publications: 1, 26, 67, 73-75, 89, 117, 122-127, 129, 143, 146, 159, 167, 168, 185, 221, 224, 228, 231-233, 238, 246-249, 275-278, 291, 292, 294, 295, 300-302, 310, 331, 339, 367, 371, 373, 376, 383-387, 422-424, 431, 433, 436-439

Further group leaders:

Helmut Bönnemann (born 1939)
retired from the Institute in November 2004
Publications: 3, 10-14, 19, 94, 116, 138, 151, 163-166, 217, 255, 293, 312-318, 386, 393, 413



Stefan Kaskel (born 1969)
left the Institute in March 2004
Publications: 2, 70-72, 87, 177, 226, 227, 333, 334, 365-367, 372, 416

Frank Marlow (born 1960)
Publications: 30, 67, 88, 91, 117, 143, 188, 189, 219, 220, 224, 244, 253, 390, 417

Other publications: 15, 16, 28, 86, 118, 119, 142, 147, 169, 190, 191, 192, 241, 242, 245, 273, 285, 305, 309, 319, 343, 394, 435

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

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-	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-	Chairman of the Dechema Arbeitsausschuß "Zeolithe"
1999-	Founder, Chairman of the Board and of the Scientific Advisory Board hte AG
1999-	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-	Member of the Selection Committee Heinz Maier-Leibniz Award
2003-	Managing Director of the Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr
2003-	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

Research in the Department of Heterogeneous Catalysis

The development of the Department of Heterogeneous Catalysis over the last three years was again characterized by substantial change on the level of the group leaders, as detailed below. This change is desired, since most of the group leader positions are not permanent and these positions are considered as stepping stones for the next career move of the respective scientists.

The overall mission of the Department, however, has not changed: It is focused on the controlled synthesis of solids (where solid is defined in a rather broad sense, i.e. starting already with metal clusters) with a primary application field in catalysis. Around this main thrust are grouped several supporting research fields, such as understanding the formation of the catalytic materials, the development of high throughput methodologies, the development of catalyzed hydrogen storage materials, and the use of the solids for other applications, for instance in the development of optically functional materials. Over the reporting period, the Department consisted on average of four groups, Prof. Dr. F. Schüth (director), Prof. Dr. H. Bönnemann (retired end of November 2004), Dr. S. Kaskel (was promoted to group leader in 2002 and left the institute in 2004 to become full professor of inorganic chemistry at the Technical University of Dresden), Dr. habil. F. Marlow, and Dr. G. Veser (left the institute in 2002 and is now associate professor in the Chemical Engineering Department at the University of Pittsburgh). Presently, there are three groups in the Department, since a new Habilitand (corresponds to assistant professor), Dr. Oliver Trapp, has joined the Department in November 2004. It is not clear, yet, whether the original structure of several independent groups will be continued in the future, or whether we will try to work more with younger, advanced post-docs instead of well established group leaders on the associate professor level.

In addition to the groups listed above, Prof. B. Bogdanović 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, Dr. C. Weidenthaler, and Dr. M. Linden (Humboldt fellow), in areas supplementing the fields of expertise covered by the other groups. For historical reasons, the work on the industrial process for electrodeposition of aluminum and magnesium/aluminum from organic electrolytes in close cooperation with two industrial partners also continued in the Department with substantial improvements of the process over the last years. A pilot scale plant went into operation, large scale production plants are being built presently and are expected to start operation in the first half of 2005. However, with the retirement of the research engineer handling this project, this activity is discontinued at the end of 2004, since the process is basically developed, no substantial need for fundamental research is seen, and the research program does not provide a good fit with the rest of the work in the Department.

The major focus of the Department is the synthesis of novel catalytic materials, often using non-standard and innovative techniques for the synthesis of such materials. This line of research was primarily pursued in the groups of H. Bönnemann, S. Kaskel, and F. Schüth, who also operate some specific characterization techniques and test units for several different catalytic reactions. O. Trapp who joined November 2004 is supplementing these activities by the development of novel analytical on-line techniques, such as multiplexing gas chromatography, but also uses and further develops the materials from the synthesis oriented groups as stationary phases in different types of chromatography. These groups are complemented by the group of F. Marlow, which on the one hand uses the expertise of the other groups in synthesizing novel solids to leverage these into the materials field, especially optics, and on the other hands provides the expertise in optical characterization to develop optical tools for the study of catalysts and catalytic reactions.

The activities of the Department cover a wide range, some of which will be introduced in more detail on the following pages. However, not all aspects of the work can be covered on the space available, and some more isolated projects will not be mentioned. Thus the readers are referred to the original publications listed at the end of this report for a complete overview. On the catalyst side, the activities are centered on the development of porous and high surface area materials, although some projects also deal with other types of catalysts. With respect to the synthesis, the focus of the research efforts shifted to some extent away from endotemplating, using molecular entities or supramolecular arrays of surfactants as templates, towards exotemplating strategies, using either disordered activated carbons or carbon aerogels as templates, or ordered mesoporous solids. The potential catalysts created by these methods are predominantly evaluated in oxidation reactions, but also acid catalyzed reactions are studied. Due to the participation of the group of F. Schüth in the DFG center of excellence in Bochum and an internal MPG project funded by the ZEIT-Stiftung, substantial efforts were also devoted to methanol synthesis and methanol steam reforming. The activities of the Bönnemann group are focused on fuel cell catalysts on the one hand, since the clusters developed seem to be ideally suited for such applications, and on the development of magnetic nanoparticles for various applications on the other hand. Several cooperation projects between the Bönnemann and the Schüth groups have been initiated based on the latter activities in order to create magnetic composite materials for catalytic applications.

A major methodological thrust is the development of components for an integrated high throughput approach for the discovery of novel solid catalysts. During the reporting period, the focus shifted away from the development of hardware components and analytical methods – although work continued in these fields to some extent – towards fundamental work to facilitate data management, library design and data mining. This shift was induced by the fact that hardware is becoming more and more commercially available at a high quality level, while there is an obvious lack of techniques for library design going beyond mere statistical tools.

The Department's activities in the development of optical materials and materials for hydrogen storage continued and have even expanded to some extent. Both fields are closely related to the other research directions of the Department, since the developments in optics use the same materials basis and synthetic methodologies as employed in catalysis, i.e. highly porous solids and templating pathways. Work on optical materials is concentrated on photonic crystals, low refractive index films as support for optical chips, and lasers based on porous materials. The hydrogen storage project targets at the development of novel hydrogen storage materials. Light metal alanates need catalyst doping in order to increase the rate of hydrogen release and uptake to technically acceptable levels. Major efforts were devoted to the understanding of the state and mode of action of the catalyst, which is a highly controversial issue in the literature.

The groups in the Department closely interact with the analytical service groups of the Institute, especially with those groups specialized in the analysis of solids. Closer cooperations going beyond routine analysis exist with the mass spectrometry group, the electron microscopy group, and in the field of solid state NMR spectroscopy. With the mass spectrometry group a project with a joint Ph.D. student was initiated to follow the hydrolysis and condensation of alkoxysilanes in situ in real time. Interactions with other Departments include joint projects with the groups of Prof. Fink, Prof. List, and Prof. Thiel.

Most of the groups are linked with many other groups worldwide through formal or informal cooperations, including a EU TMR network (NUCLEUS), a newly established network of excellence (FAME), a EU network of excellence which is in the contract negotiation stage (IDECAT), several BMBF grants, and participation of the Department in DFG Schwerpunktprogrammen (priority programs) and Sonderforschungsbereichen. (centers of excellence). 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: C. Kiener, F. Kleitz, W. C. Li, M. Linden, S. Pelster, I. Ritzkopf, W. Schmidt, S. Vukojevic, A. Wolf, C. M. Yang

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. After initial application to model systems for proof-of-concept they are used to the study the formation of real catalyst systems. In addition, it is attempted to understand the nature of specific interactions in complex catalysts, specifically the creation of metal support interactions. This group of projects is of a rather fundamental character with a correspondingly long time scale.

Results: Electron Spray Ionization Mass Spectrometry (ESI-MS) had been introduced in the last report as a method to obtain information on species present in solution, and the first success in the analysis of a silicate solution could be presented. This method has been developed further to allow time resolved analysis of species present in solution. As a first example, hydrolyzing tetraalkoxysilanes as the relevant precursor solutions for ordered mesoporous silica and silica gels have been studied. Depending on the rate of reaction, the reacting solutions were either injected from a beaker, via a syringe, or taken by a sampling valve from the flow in a tubular reactor and then injected into the mass spectrometer. Figure 1 shows the development of selected

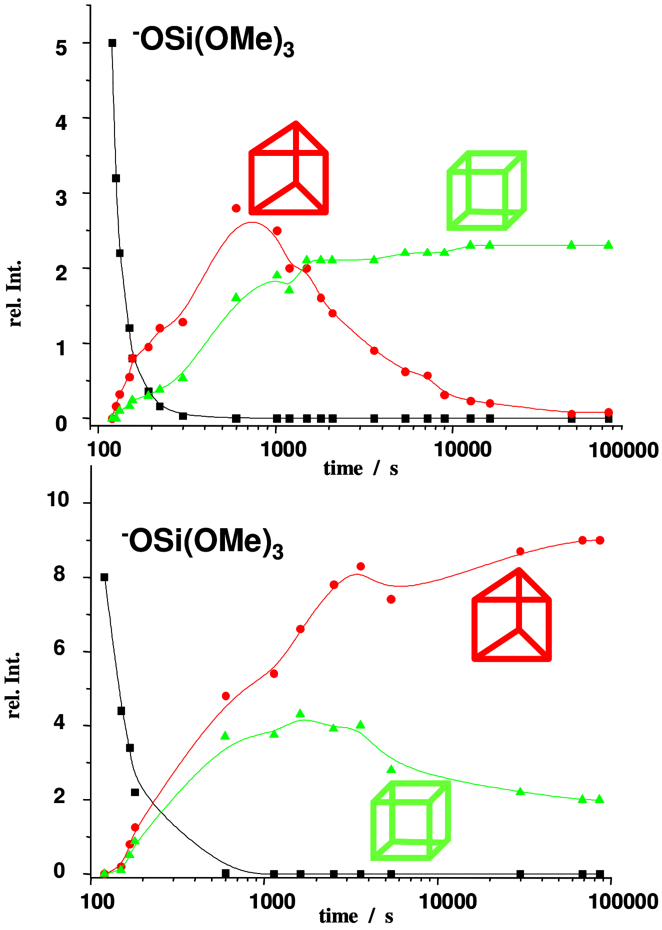


Figure 1. Time dependent speciation in hydrolyzing tetramethoxysilane solutions measured with ESI-MS. Top: system in the presence of TMAOH which stabilizes the double four ring. Bottom: system in the presence of TEAOH which stabilizes the double three ring.

species over time after the start of TMOS hydrolysis. One can see that the different species are all formed initially, but the alkylammonium ions then stabilize specific oligomers within several hours. Such analyses were carried out for various solution conditions and the results allow the extraction of a clearer picture of the processes occurring in hydrolyzing silicate solutions. Interestingly, similar species as reported in Figure 1 are observed also in the absence of alkylammonium ions, and relatively low molecular weight oligmers are present even at fairly low pH very close to the point where precipitation of the silica occurs.

The formation processes of catalytic materials were studied for the Cu/ZnO-system used for methanol synthesis and for gold catalysts active in the low temperature CO-oxidation. Both systems are interesting due to metal-substrate interactions which influence the catalytic activity. For the Cu/ZnO system the hydroxycarbonate precursors were precipitated under strictly controlled conditions and the properties of the resulting catalysts correlated with the catalytic activity which was evaluated in a 49 channel high throughput setup.

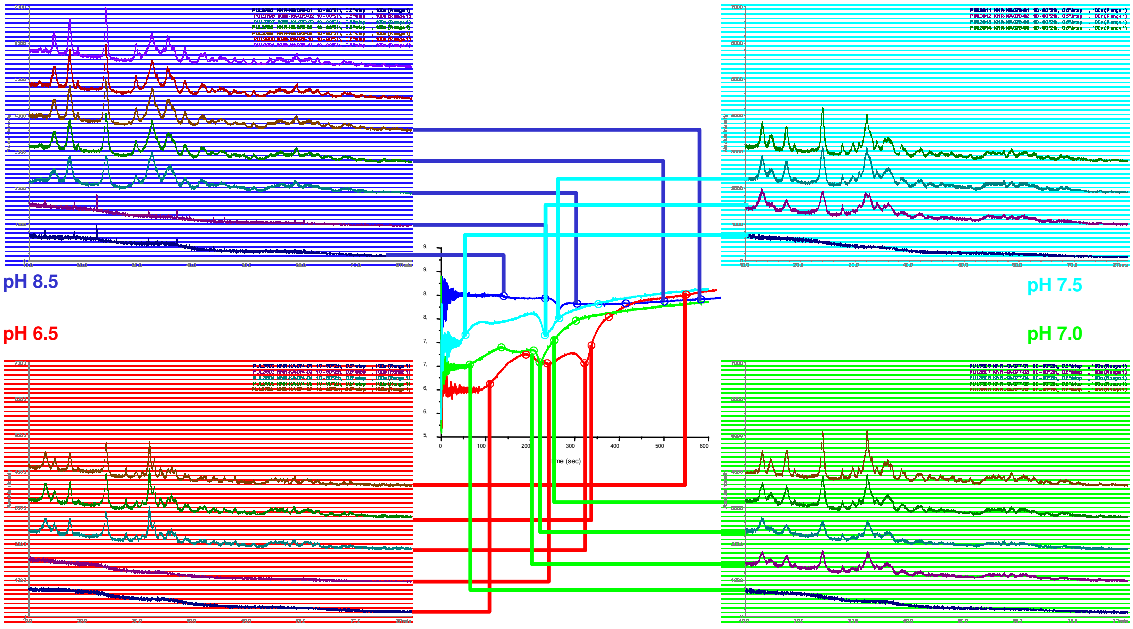


Figure 2. Development of the pH during Cu-Zn-hydroxycarbonate precipitation over time. pH is controlled during precipitation and then left to develop freely. Colors indicate different pH during precipitation. The boxes give diffraction patterns of the precipitates sampled at different times

Figure 2 shows the development of pH after precipitation of the hydroxycarbonates under pH-controlled conditions in the center, and the diffraction patterns of samples withdrawn at different aging times. One can clearly see that crystallization of the precipitate occurs after a sharp drop in pH in the course of aging. However, the catalytic activity of the catalysts obtained after different aging times differs markedly, even if the

XRD patterns of the precursors do not substantially change further. Interestingly, the activity of the catalysts normalized to copper surface area differs by more than a factor of ten between different samples, which clearly shows that other factors are contributing to the activity of methanol synthesis catalysts, in contrast to statements often found in the literature.

Another example where strong metal substrate interactions are suggested to have a strong influence on the catalytic activity are Haruta-type gold catalysts. Such systems were studied extensively in the low temperature CO-oxidation. It is known that lack of reproducibility is a serious problem for such catalysts, and we succeeded by extremely carefully controlling all synthesis and reaction parameters to develop reproducible protocols for the synthesis of highly active catalysts. Although the support material has some influence on the activity, we were able to synthesize very active catalysts also on typically non-interacting supports, such as alumina. Via inverting the charge of silica by grafting of alkylammonium ions to the surface and preventing the growth of gold particles by providing a spatially restrictive pore system, even highly active gold catalysts based on silica as support could be synthesized. These studies clearly demonstrate, that for the CO-oxidation a specific interaction of the gold with the support is not mandatory and differences between supports can be mainly attributed to their different ability to maintain high gold dispersion.

Publications resulting from this research area: 146, 228, 291, 300

External funding: EU; DFG-SFB-Bochum; Zeitstiftung

Cooperations: H. Amenitsch (Graz, AT); R. Catlow (London, GB); D. Frenkel (Amsterdam, NL); D. Fenske (Karlsruhe, DE); M. Muhler (Bochum, DE); J. Rosenholm (Abo, FI); B. Schrader (Mülheim/Ruhr, DE); J. M. Thomas (London, UK)

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

Involved: W. Brijoux, O. Busch, C. Kiener, C. Klanner, T. Kruppa, T. Johann, H. W. Schmidt, A. Taguchi

Objective: High throughput technologies are by now accepted as a research tool supporting the development of novel catalytic materials and for faster evaluation of suitable reaction conditions. Most of the catalytic setups used in the Department are parallelized. Efforts in developing novel reactor technology and analytical tools have been reduced due to the availability of good solutions for most problems, partly due to the research activities of the Department. Some projects in this field, however, were still pursued in the reporting period, because there was a pressing need for the tools. Activities on the development of computational tools have been increased, since commercial solutions are not available, and published approaches only cover part of the problems. Novel reactor concepts, such as short contact time/high temperature systems and microstructured reactors are explored also in some projects in order to realize novel process options.

Results: Over the last years parallel reactor technology has reached a status that the data obtained in a parallelized high throughput reactor are of comparable quality as results from conventional single bed reactors, even for demanding reactions. The 49 channel high pressure reactor for the investigation of methanol synthesis catalysts has been transferred to routine operation, and by comparison with a conventional setup in Bochum the reliability of the data has been ascertained. The most advanced system for high throughput studies of catalysts which has recently been developed allows investigations at temperatures up to 1000 °C and pressures up to 10 bars (50 bars if the temperature is limited to 700 °C). Several of the features realized in the reactors developed in the institute have been transferred to industrial practice at hte AG and other companies.

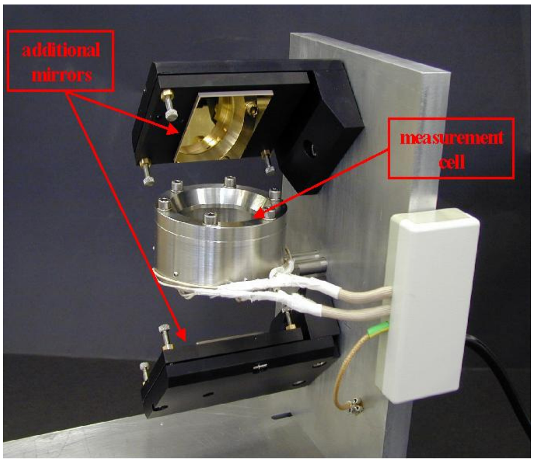


Figure 1. IR cell for simultaneous sorption analysis of eight catalyst samples. The cell is integrated in a FPA detector setup

A focus of the research in this field during the reporting period was the development and implementation of high throughput analysis tools for surface properties of solid catalysts. For this purpose the focal plane array (FPA) detector system has been used, coupled with sorption cells for either CO-adsorption or pyridine adsorption (Fig. 1). With such setups it was possible to analyze in parallel eight samples of zeolites or supported noble metal catalysts. The system works for most types of samples. However, due to the longer beam path, scattering is a more severe problem than in conventional cells, and therefore catalyst particles with sizes in the range of the wavelength of the IR-radiation and unfavorable shapes, such as needles, are difficult to analyze. Nevertheless, the setup appreciably speeds up sample characterization, and the degree of parallelization can further be increased.

Alternatively, a 49 channel reactor operated in reflection mode can be integrated in the FPA setup. This system was used to analyze the reaction products of pentane hydro-isomerization. Even for such a difficult analytical problem with strongly overlapping bands, reliable product analysis was possible. Also this system in principle allows a higher degree of integration, and coupled with rapid scan technology should allow parallel analysis of more than 50 samples in real time.

The most important conceptual development was the work on a descriptor framework for solids. While library design via virtual screening and diversity analysis is well established in the drug industry, such concepts cannot be transferred to heterogeneous catalysis, since no concepts for the representation of solids in a computer program are available as yet. The descriptor concept developed over the last three years relies on the initial description of a complex solid by a vast number of physico-chemical parameters which may or may not be correlated with the catalytic properties. In a calibration step, in which highly diverse solids (diversity judged by chemical intuition) are catalytically evaluated in a target reaction, useful parameters are discovered, the combination of which forms the descriptor vector. The target reaction here was the oxidation of propene. Using this concept, it was possible to predict the performance of catalytic materials in the oxidation of propene at approximately the same level of precision as an experienced catalysis researcher would be able

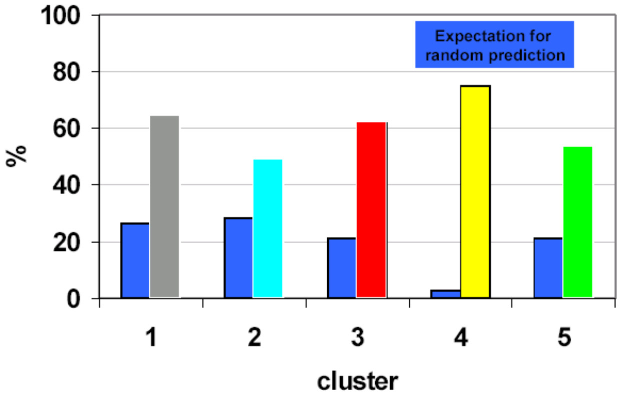


Figure 2. Comparison between prediction of catalytic performance and statistical expectation value (blue). The columns indicate the fraction of correctly classified catalysts in the different performance classes (altogether approximately 120 solids). Grey: low conversion, total oxidation; light blue: medium conversion, total oxidation; red: partial oxidation; yellow: oligomerization; green: high conversion, total oxidation

to. Figure 2 shows the predictions of the computer program based on the descriptors in comparison with the statistical expectation value. Interestingly, the descriptor vector does not contain direct information on the composition of the catalyst. This only enters the descriptor indirectly via the physico-chemical parameters describing the solids. The method developed here can now be used as the basis for a virtual screening of solids for catalytic reactions. Moreover, by inspection of the parameters included in the descriptor vector by many neural networks one can actually draw conclusions on the properties which are relevant to classify catalysts in the target reaction.

Propene oxidation was also the target reaction in a project involving a microstructured reactor. Gaseous hydrogen peroxide was used as oxidant, various titanium containing catalysts were studied in the gas phase reaction of propene to propene oxide. Productivities reached technically relevant levels, and the results from the microstructured reactor could be reproduced in a pilot plant which transfers the relevant dimensions to the technical scale. However, loss of hydrogen peroxide by decomposition on the catalyst renders the process at present inefficient, since only about 45 % selectivity to propene oxide based on the hydrogen peroxide consumed was observed. Nevertheless, this project demonstrated the scalability of microstructure concepts to the technical scale.

Publications resulting from this research area: 26, 67, 73, 123, 124, 224, 231, 275, 331, 371, 373

External funding: two BMBF projects; Zeitstiftung; hte AG

Cooperations: Degussa AG (Hanau, DE); D. Farrusseng (Villeurbanne, FR); D. Hönicke (Chemnitz, DE); Krupp-Uhde GmbH (Dortmund, DE); J. Lercher (München, DE); W. F. Maier (Saarbrücken, DE); R. Schlögl (Berlin, DE)

2.3.3 Research Area "High Surface Area Catalyst Materials" (F. Schüth)

Involved: T. Johann, M. Kalwei, S. Kaskel, F. Kleitz, W. Li, A. Lu, A. Martinez, S. Olejnik, R. Palkovitz, I. Ritzkopf, A. Rumplecker, E. Salabas, W. Schmidt, K. Schlichte, M. Schwickardi, B. Spliethoff, C. Weidenthaler, C. M. Yang, Y. Wang, B. Zibrowius

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, but over the last years the focus has more and more shifted towards carbons. The driving force for such developments are typically catalytic processes for which an advantageous use of such high surface area materials is envisaged. This project group originated in the work on zeolites and ordered mesoporous materials, but recently also other materials were included.

Results: Work on ordered mesoporous oxides has primarily been concentrated on triblockcopolymer templated materials, especially on organically modified materials. These types of modification are important, since the organic groups provide anchorpoints for catalytically active species. Direct functionalization of the silica surface by vinyl-, cyano-, carboxylate-, or thiol-groups has thus been achieved. Interesting results were obtained during the co-condensation of tetraethoxysilane and vinyltriethoxysilane in the presence of the Pluronic 123 template: Increasing the fraction of the vinylsilane leads to a transformation of the hexagonal to the cubic Ia3d-structure. This behavior can be rationalized in terms of the packing parameter, i.e. the increasing hydrophobicity induced by the vinyl groups induces lower curvature of the assembly. If silicas are functionalized by co-condensation routes, the surfactants cannot be removed by calcination. In the course of studies concerning template removal by leaching processes, it was discovered that under suitably chosen conditions ether cleavage of the Pluronics template can be carried out to result in template removal only from the mesopores. The micropores can be made accessible by a gentle calcination procedure, which leaves the grafted groups intact.

A very interesting type of functionalization was achieved by the coupling of a tetraalkylammoniumgroup to the silica surface. This allows charge inversion of the silica so that negatively charged solution species, such as $AuCl_4^-$, can be adsorbed on the silica. Reduction with $NaBH_4$ induces the formation of gold clusters, the size of which is limited by the pore sizes of the silica, as could be demonstrated by TEM tomography. These several nanometer sized gold clusters are active in the room temperature oxidation of CO, which is surprising, since silica is known to be not very prone to interaction with metals supported on it.

The vinyl functionalized Ia3d silica was found to be an excellent hard template for the nanocasting of transition metal oxides. Co_3O_4 was the first oxide to be nanocasted following this pathway, and the material shows interesting magnetic behavior, such as a weak ferromagnetic transition at low temperatures. Also the ferromagnetic $CoFe_2O_4$ could be nanocasted, and this should allow the generation of mutually interpenetrating magnetic frameworks.

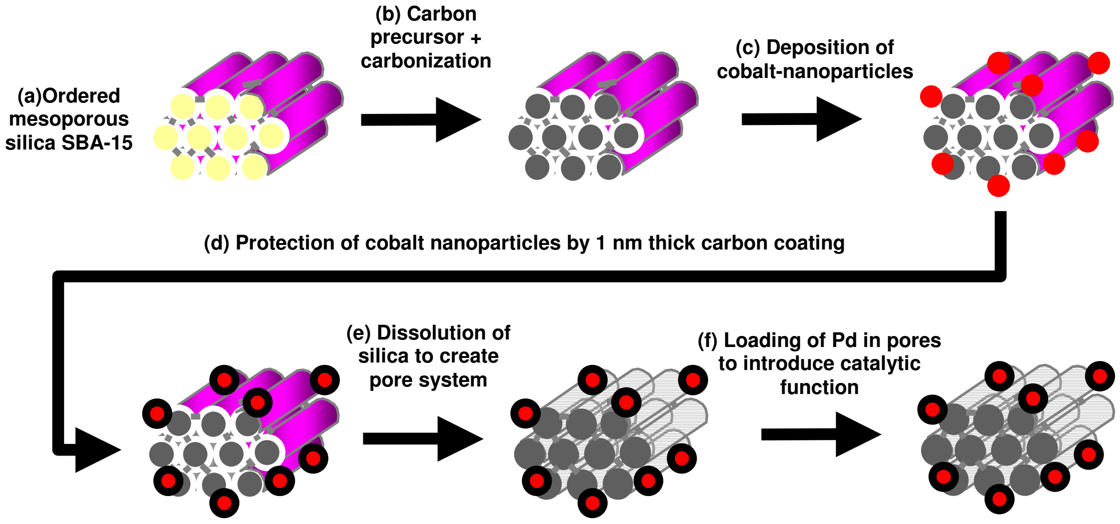


Figure 1. Schematic representation of the process to create magnetic carbon supported Pd-catalysts. The pore system of SBA-15 is filled by carbon (b), then superparamagnetic Co-particles are deposited on the external surface of the carbon (c). These particles are protected by a 1 nm carbon layer (d) before the silica is removed (e). Finally, the active phase can be loaded into the pore system (f).

Although the nanocasting pathway can be used for the synthesis of oxides, it is most valuable for the generation of ordered mesoporous carbons. Using different precursors and different curing conditions, the frameworks of the carbons could be tailored, both with respect to the pore system and to the framework structure and composition, i.e. graphitic, amorphous, or C/N frameworks. By thin layer coating of the silica template walls, pronounced bimodal mesoporous carbons with

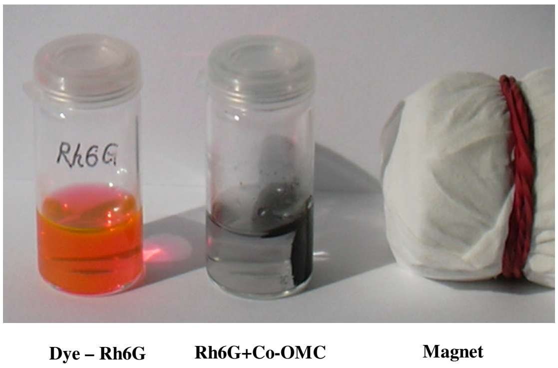


Figure 2. Use of magnetic ordered carbon as magnetically separable adsorbent. On the left a dye solution can be seen, to which the carbon has been added (middle). Within seconds, the dye is adsorbed, the carbon is attracted to the side of the vessel by the magnet on the right side.

surface areas exceeding 2000 m^2/g could be synthesized. By anchoring of superparamagnetic cobalt nanoparticles which were protected by a 1 nm thick carbon layer on the surface of the mesoporous carbons, magnetically separable carbons could be prepared, which can be used as magnetic adsorbents or magnetic catalysts (Figs. 1, 2). A related method was developed for the formation of magnetic silicas. In order to solve this task, a reversible protection strategy for the pore system was used, by which selective functionalization on the external surface of the particles was possible.

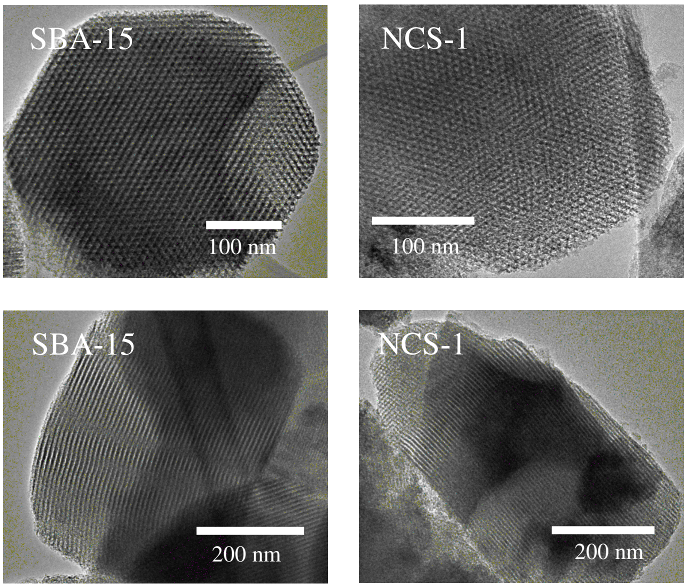


Figure 3. TEM images of the original SBA-15 silica (left) and the NCS-1 silica obtained by double replication via a carbon intermediate (right). One can clearly see that both the mesostructure and the morphology are preserved during this complex process.

In a feasibility study, ordered mesoporous carbon of the CMK-3 type has been used as template for the synthesis of ordered silica. Surprisingly, it could be demonstrated that repeated nanocasting is possible, while maintaining a high degree of structural order. Although slight differences in the textural parameters are observed, such as increased levels of microporosity in the recasted silica, the general quality of the replication is very high. Figure 3 shows TEM images of the original silica and a silica obtained after a first replication as carbon and a subsequent second replication step from this carbon. Transfer to other materials has not been possible so far, but it can be expected that this method will be useful for producing oxides which are otherwise not accessible in mesostructured form.

Not only ordered carbon materials, but also disordered carbons, such as activated carbon or carbon aerogel, are ideal templates for the synthesis of high surface area oxides. For many different binary, ternary or multinary oxides such synthesis pathways have been developed. The reproducibility of such synthesis processes has been studied in detail, since the carbon templates are often derived from natural raw materials with some scatter in their properties. The carbon source was found to play a crucial role in determining the properties of the final products, and different carbons are not equally well suited for all oxide materials. A preselection study of different activated carbons with respect to scale up of the synthesis process was performed and a suitable material was found from which various different oxides with exceptionally high surface areas can be synthesized. For this carbon, a process scale-up has been performed and a system with a productivity of several 10 g per hour in a continuous process is under construction.

Using specifically designed carbon aerogels formed from a resorcinol/formaldehyde resin has made it possible to produce aluminas with surface areas close to 400 m^2/g, which are amorphous after treatment at 600 °C and form glass-like particles. The surface properties of these aluminas are different compared to conventionally prepared samples. These and related materials are evaluated in various catalytic reactions, including DeNOx reactions and in the future also in the reforming of different hydrocarbon feedstocks.

Publications resulting from this research area: 1, 74, 75, 89, 117, 122, 125, 126, 127, 129, 185, 221, 232, 233, 238, 246, 247, 249, 276, 278, 292, 301, 302, 383, 384, 385, 386, 387, 423, 430, 436, 437, 438

External funding: DFG Schm936/3-1; DFG-SFB-Bochum; Zeitstiftung

Cooperations: H. Bönnemann, (Mülheim/Ruhr, DE); K. de Jong (Utrecht, NL); G. Fink (Mülheim/Ruhr, DE); S. Kaskel (Dresden, DE); H. Knözinger (München, DE); F. Marlow (Mülheim/Ruhr, DE); M. Muhler (Bochum, DE)

2.3.4 Research Area "Light Metal Hydrides for Hydrogen and Energy Storage"

(F. Schüth / B. Bogdanović)

Involved: M. Felderhoff, T. Kratzke, M. Mamatha, A. Pommerin, W. Schmidt, N. Spielkamp, B. Spliethoff, A. Taguchi, J. von Colbe de Bellosta, C. Weidenthaler, B. Zibrowius

Objective: With the discovery, that hydrogen adsorption and desorption for $NaAlH_4$ can be catalyzed by the addition of small quantities of transition and rare earth metals, this material became interesting as a hydrogen storage material due to the high storage capacity of theoretically 5.5 wt.%. The objective of this group of projects is to understand the processes occurring during this highly interesting catalytic reaction (Solid-Solid-Gas-Transformation) and to further develop such materials and other light metal hydrides for application as technically useful hydrogen and energy storage material.

Results: $NaAlH_4$ remained in the center of attention, since this system is closest to reach technical benchmark criteria for practical applications. Progress has been made both with respect to the kinetics of the reaction and with respect to rehydrogenation pressure. The doping process has almost completely been changed to ball milling of the hydride in the presence of the catalyst. Following this procedure it was discovered that $TiCl_3$ is almost as efficient as a dopant as the previous best dopant, colloidal titanium. Search for an alternative dopant had become necessary since the synthesis of titanium colloids in large amounts proved to be impractical and excessively expensive. Rehydrogenation times at a pressure of 100 bar are now around 10 minutes, with a reversible storage capacity above 4 wt.% at around 100 °C. These are by far the best parameters compared to any material reported in the literature.

Since for practical applications in cars a rehydrogenation pressure of 100 bar is too high by more than a factor of two, search for alternative catalysts which would accelerate the doping at lower pressures was initiated. In a broad screening of other transition and rare earth elements, it was discovered that scandium compounds are also excellent catalysts. Rehydrogenation times at 50 bar could be reduced to less than one hour, although the gravimetric storage capacity is not satisfying at present with values around 3 wt.%. However, initial results indicate that combinations of various dopants could still improve the system performance significantly, so that there is still substantial potential for further development of the system.

The state of the titanium catalyst after doping and during the hydrogenation/-dehydrogenation cycles had been a matter of strong dispute in the literature since the discovery of the system in 1995. This question could conclusively be solved during the reporting period by the use of several complementary techniques. The results obtained by our group were subsequently confirmed by independent studies of two other groups. It is by now clear that the titanium is present in the zerovalent state immediately after doping and also in all stages of the cycle. EXAFS (Fig. 1) and XANES analysis revealed that the state of the titanium resembles most closely the titanium state in an aluminum/titanium alloy, both in the hydrogenated state and in the dehydrogenated state. This alloy has probably no long range order since it could not be detected by X-ray diffraction. Locally, however, the XAS data could best be fitted by a zerovalent titanium atom surrounded by 12 aluminum atoms.

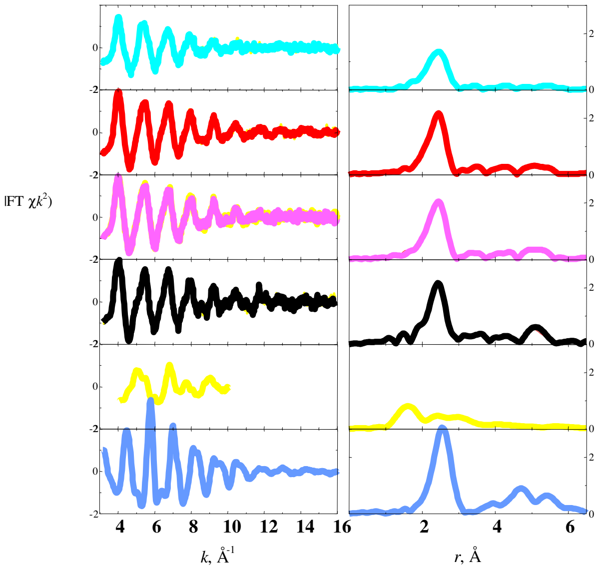


Figure 1. Ti-EXAFS spectra (left) and radial distribution functions (right) for various alanate samples. From top to bottom: ligh blue: after ball milling; red: after 4 cycles dehydrogenated; purple: after 4 cycles rehydrogenated, black: after 100 cycles dehydrogenated; yellow: TiO_2; blue: Ti metal foil.

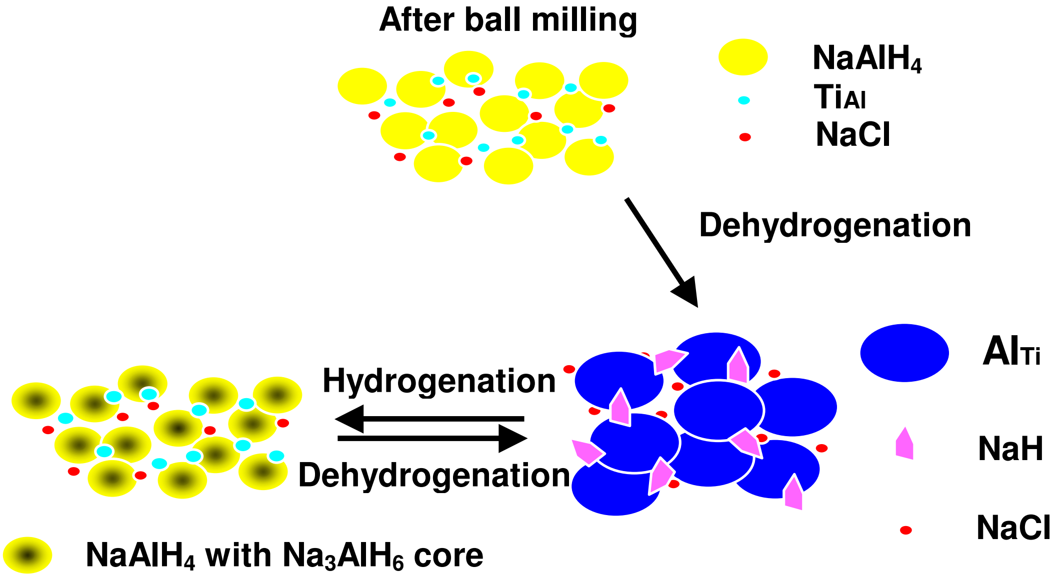


Figure 2. State of the system during cycling. The titanium is always present in a state resembling an aluminum/titanium alloy, either in high concentration in an aluminum matrix in the hydrogenated state or in low concentration in the dehydrogenated state.

Independent of the dopant the state of the titanium on the atomic scale is very similar in all cases. However, TEM combined with elemental analysis revealed that titanium reagents which are more efficient in accelerating the rehydrogenation lead to a more homogeneous distribution of the titanium over the sample on the scale of 10 to 100 nm which explains the better performance.

Ultimately, the theoretical capacity of 5.5 wt.% possible for $NaAlH_4$ is not sufficient for application of the material in cars on a large scale. Thus other hydrides have been explored with respect to their suitability as hydrogen storage compounds. Surprisingly, little is known on the synthesis or the thermodynamic properties of such compounds, so that it was necessary to develop synthesis protocols and to characterize the materials prepared. Different alanates were synthesized and characterized, such as $Mg(AlH_4)_2$, $Ca(AlH_4)_2$, $Zn(AlH_4)_2$. None of the materials turned out to be sufficiently stable for application as storage material. An encouraging result, however, was the acceleration of the decomposition process after doping with titanium in all cases, thus showing that titanium catalysis is a more general phenomenon, at least for the alanate materials.

Finally, it was attempted to improve the system performance by encapsulation of the alanate in highly porous matrices, such as carbon aerogels. This was expected to improve system kinetics due to the small particle sizes achieved in the porous matrices, and to improve the safety properties due to slower oxygen access. In both respects encouraging results have been obtained, but substantial optimization work is still required, since the matrix reduces the gravimetric storage capacity.

Publications resulting from this research area: 167, 168, 294, 310, 339, 424

External funding: Adam Opel AG; Powerfluid GmbH

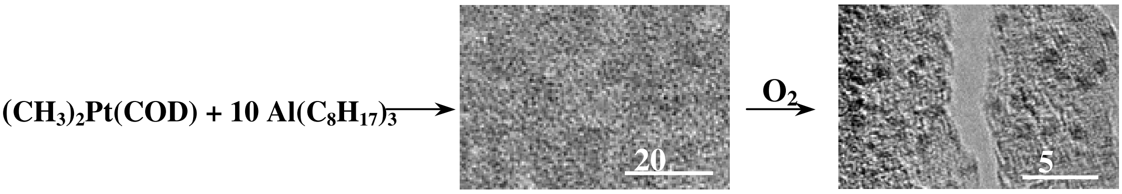
Cooperation: W. Grünert (Bochum, DE); B. Tesche (Mülheim/Ruhr, DE)

2.3.5 Research Area "Nanostructured Metal Colloids" (H. Bönnemann)

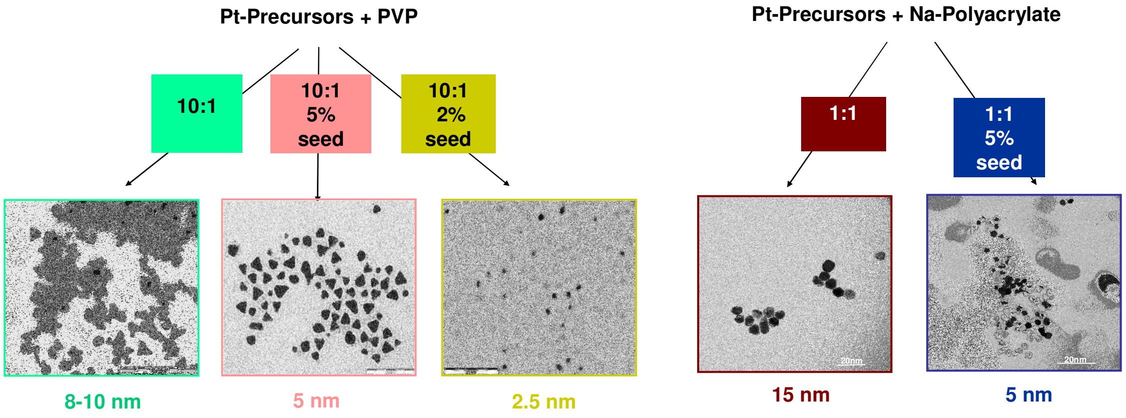
Involved: W. Brijoux, R. Brinkmann, H.-W. Hofstadt, S. Kinge, N. Matoussevitch, K. S. Nagabhushana, F. Wen

Objective: Development of nanostructured transition metal colloids as precursors for catalysts and new functional materials.

Results: Via the decomposition of dimethyl(1,5-cyclooctadiene)platinum (II) in the presence of trialkylaluminum the first example of a Pt_{13} cluster (size: 0.75 ± 0.1 nm) was obtained. The one-shell structure and the metallic state was confirmed by XPS and XANES.

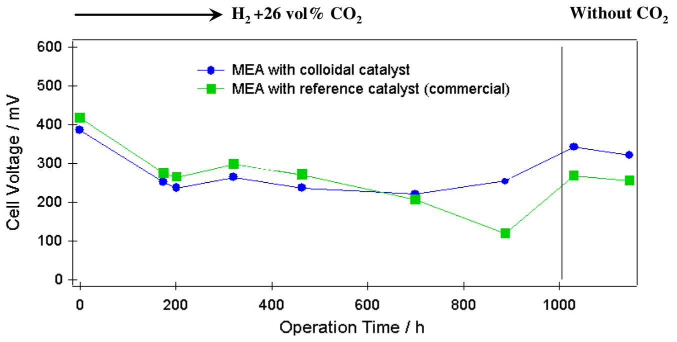


These Pt colloids were used as building blocks for 3-D nanoparticle-networks. When exposed to air the organoaluminum shell is transferred to an Al_2O_3 matrix where the Pt_{13} clusters are regularly dispersed. This is a promising precursor for solid catalysts. By reducing Pt salts (halides, acac) with hydrogen a "seed" is formed which may be used for the shape-selective synthesis of colloidal Pt particles. The particle size and shape can be controlled by the type of stabilizing surfactants. While PVP renders tetrahedral Pt nanoparticles, Na-polyacrylate causes formation of truncated octahedral particles. Further, by changing the concentration of the "seed" particles' size control can be achieved under diffusional growth conditions.



The "Precursor Method" offers the possibility of improving both the performance and the durability of fuel cell catalysts via a "modular design". Platinum based colloidal bi- and pluri-metallic precursors such as Pt/Ru/Co supported on carbon yield PEMFC and DMFC catalysts which surpass the commercial standard.

The precursors are supported on conductive carbon by "Dip Coating". Subsequently, the protecting shell is removed by reductive annealing ("Conditioning"). Metal loadings between 10 and 30 wt% with high dispersion and uniform distribution were obtained.



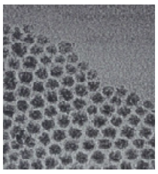
Test conditions: **j = 550 mA cm^{-2}**; $p_{anode} = p_{cathode}$ = 1 bar(abs),
T = 52 °C, l_{H2}= 1.3, l_{air}= 3.3 (recirculaton),
humidification: anode dry; cathode self-humidifying

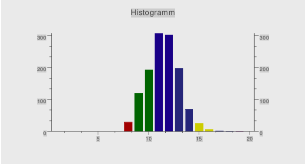
Comparison of colloidal catalyst and reference in a Durability Test

A novel, size selective preparation route leads to air stable "monodisperse" colloidal metallic and bi-metallic (Fe, Co, Fe/Co) nanoparticles (narrow size distribution) via the thermolysis of metal carbonyls in the presence of aluminum alkyls.

$$Co_2(CO)_8 + AlR_3 \xrightarrow[\text{2. smooth air oxidation (20°C, 6 - 10h)}]{\text{1. Thermolysis (Toluene, 110-140°C, 4 - 16h)}}$$

R = CH_3, C_2H_5, C_8H_{17}





IR spectroscopy has revealed that the aluminum alkyl acts as a catalyst in the thermal decomposition of the carbonyls. By varying the Al-alkyl chain length and the M : Al ratio the particle size may be adjusted between 3 and 10 nm. Subsequent smooth air oxidation of such particles yields long term air stable magnetic nanoparticles [according to X-ray Absorption Near Edge Structure (XANES) and other physical evidence].

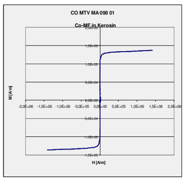
AlR_3	Co : Al	d [nm]
$Al(CH_3)_3$	10 : 1	3-4.5
$Al(C_2H_5)_3$	10 : 1	6.5 – 8.5
$Al(C_8H_{17})_3$	10 : 1	8.5 –10.5
$Al(C_8H_{17})_3$	1 : 2	5±1.1

Influence of Al-R and Ratio

The isolated particles can be used as dry powders or peptised with the help of surfactants to give remarkably stable magnetic fluids with high saturation magnetisation at low metal concentration. In kerosene a Co magnetic fluid with a saturation magnetization M_S of 140 kA/m (≈ 176 mT) was obtained (Fig. A). This is equivalent to a volume concentration of 9.6 %. A bimetallic Fe/Co magnetic fluid in kerosene (≈ 2.8 vol.-%) with a saturation magnetisation M_S of 67 kA/m (≈ 84 mT) showed no loss of magnetization after 20 days (Fig. B). Mößbauer investigations (Fig. C) of the magnetic Co/Fe fluid gave a spectrum which is the superimposition of the spectra of 2 components, i.e. a Fe/Co alloy (magnetic splitting: ≈ 30 T) and Fe^{3+} (magnetic splitting: 48 T). Mößbauer analysis also revealed that the particles consist of metallic cores probably protected by oxidic shells. From the Mößbauer spectra it can be derived that the main component in the fluid is Fe while Fe^{3+} is only a minor component (Fig. D).

Properties: Co-Fluid

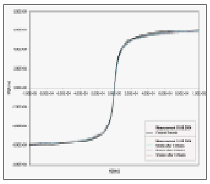
Magnetization



A

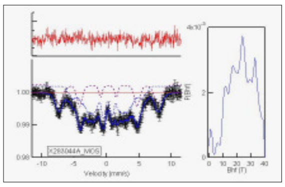
Properties: Co/Fe-Fluid

Magnetic Stability



B

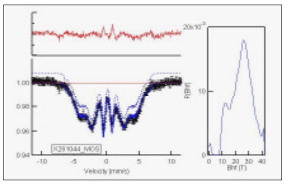
Mößbauer Spectra



C

Properties: Fe-Fluid

Mößbauer Spectra



D

Publications resulting from this research area: 3, 13, 14, 151, 164, 165, 166, 315, 318, 386, 393, 413

External funding: European Union; DFG

Cooperations: R. J. Behm (Ulm, DE); J. Hormes (Baton Rouge, USA); V. Kempter (Clausthal, DE); S. Neophytides (Patras, GR); J. Nørskov, (Lyngby, DK); S. Odenbach (Bremen, DE)

2.3.6 Research Area "Porous and Nanostructured Materials" (S. Kaskel)

Involved: K. Schlichte, H. Althues, R. Palkovits, A. Rumplecker, P. Krawiec, R. Panda

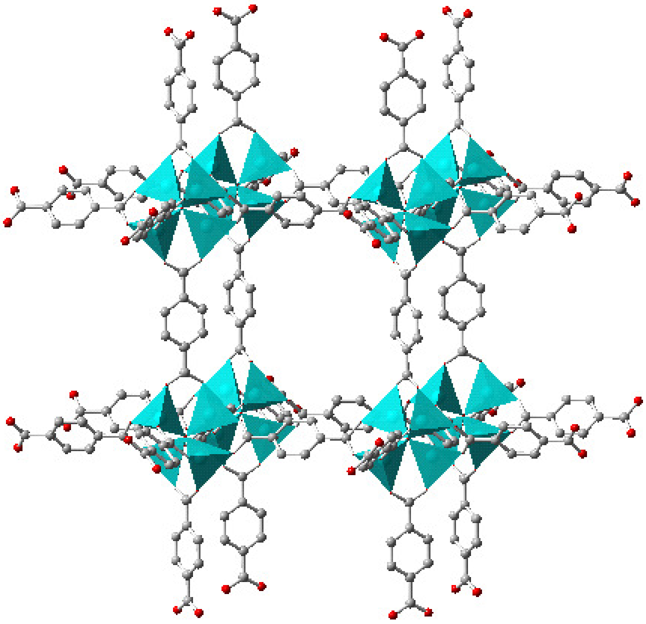
Objective: The functionality of inorganic solids can be tuned at the molecular or mesoscopic level. Such structured materials are crucial for the development of novel catalysts and functional materials. In the last two years, beyond the development of porous inorganic nitrides (2000-2004), the group started to study also other materials such as *Metal-Organic Frameworks* and *Hybridmaterials*.

The catalytic properties of Metal-Organic Frameworks are largely unexplored. They are also promising gas storage materials. Hybridmaterials profit from an inorganic functional module embedded in a polymer matrix and have applications in display and coating technology.

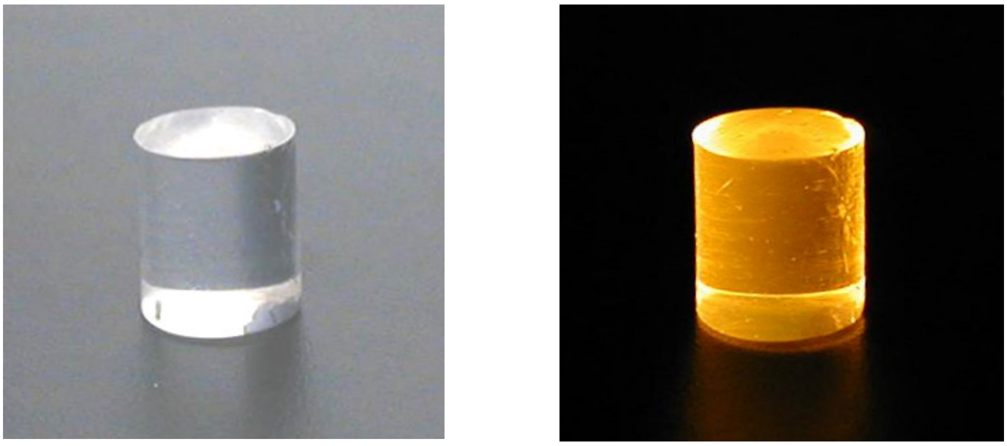
Results: New synthesis methods were developed for the production of porous gallium nitride materials and titanium nitride nanoparticles. Porous GaN is an orange luminescent material. The use of organometallic precursors and amines allows to adjust the pore size in the micropore regime.

However, the material is less stable as compared to porous silicon nitride developed earlier in our group and thus catalytic applications are rare. Titanium nitride was developed as a hydrogen storage catalyst and an active material for hydroalumination reactions.

Metal-Organic frameworks are promising materials for catalytic and gas storage applications. The framework Cu_3BTC_2 was shown to be an active catalyst in the cyanosilylation. In a cooperation with Ruhrgas (EON), Metal-Organic Frameworks are currently tested as methane and hydrogen storage materials.



Metal-Organic Framework (MOF-5)



Transparent luminescent nanocomposites (left: daylight, right: UV-irradiation)

In 2003 within the framework of the BMBF young scientist initiative, our expertise in small particle technology was directed towards the new class of hybrid materials. The ability to tailor the particle size was used to integrate new functions into transparent plastics without loss of transparency. Thus, transparent luminescent composites were synthesized using manganese-doped ZnS nanoparticles. Furthermore, a generic approach for the generation of transparent nanocomposites was developed. Whereas for catalytic applications, particle aggregation and agglomeration are not necessarily reducing the catalysts performance, in composite applications, dispersion stability is crucial to produce transparent composites.

Publications resulting from this research area: 2, 70, 71, 72, 87, 168, 177, 226, 227, 333, 334, 365, 366, 372, 416

External funding: DFG; BMBF; DAAD; FCI

Cooperations: B. Bogdanović (Mülheim/Ruhr, DE); J. S. Bradley (Hull, UK);
R. Fischer (Bochum, DE); F. Schüth (Mülheim/Ruhr, DE); G. Veser (Mülheim/Ruhr, DE); J. Weitkamp (Stuttgart, DE); U. Holle, D. F. Shantz (Texas, A&M, USA)

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

Involved: H. Bretinger, W. Dong, D. Konjhodzic, H. Li, J. Loerke, U. Wilczok

Objective: Ordered porous materials are highly interesting hosts for optically functional materials. Micro, meso, and macro pores have specific effects on guests and electromagnetic fields which 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. In addition, theoretical work is carried out in order to predict the physical properties of the materials.

Results: Three different directions have been pursued within this field of research: micro lasers, low-n materials, and photonic crystals.

Amplifying and lasing materials were designed with two different host systems, either by loading organic laser dyes into zeolite crystals or into ordered mesoporous oxides. Mesoporous hosts offer a high degree of flexibility for the incorporation of molecules and other optically functional units. Mesoporous silica fibers of an SBA-3-like synthesis have been loaded with Rhodamine dyes resulting in materials with a homogeneous distribution of the dye. If such fibers are irradiated with laser light exceeding a threshold energy, strong, gain-narrowed emission can be observed from the ends of the fibers. This shows that the fibers act as optical amplifiers with stimulated emission. To realize a laser the mesoporous silica fibers were coated with a reflective layer at the end faces. The emission band shows several sharp emission lines with a regular spacing dependent on the fiber dimensions. These sharp lines are the emission of a micro fiber laser.

Another important field of application of mesoporous substances are low-n materials. They are useful for all waveguide devices in which a high refractive index contrast between the waveguide core and the substrate or cladding is required. We have used mesoporous silica films as supports for 2-dimensional photonic crystals (Figure 1). By the mesoporous material, the confinement of the fields in the 2-dimensional photonic crystal structure was enhanced significantly. This lead to a reduction of optical leakage processes for

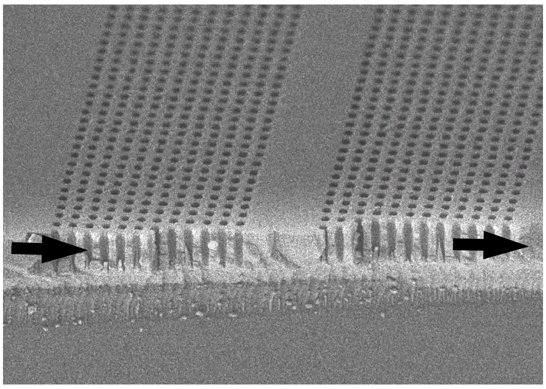


Figure 1. Waveguide structure consisting of two finite photonic crystals separated by a photonic “defect”. The defect can serve as a resonator. Optical transmission experiments indicated by the arrows have been carried out.

the modes, an enhancement of the transmission in the defect-resonance region, and in a good fitness of the resonator.

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 opals and inverse opals which are expected to show photonic band gaps. We have developed a new method for opal fabrication. This method exploits capillary forces and is much easier to handle than the known method. The method delivers large-area, homogeneous opal layers with a controllable crack structure. The cracks are a typical defect for opals which can likely not be avoided in layer systems.

The detailed structure of the inverse opals has been investigated by electron microscopy. Theoretical calculations showed that our photonic crystals have a modified photonic band structure. Optical measurements showed strong photonic effects.

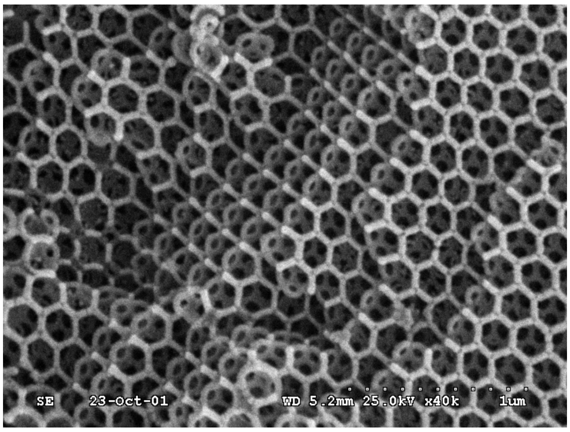


Figure 2. Macroporous titania skeleton structure. This type of photonic crystals can have a new photonic band gap. The lattice constant is comparable with the wavelength of light. Therefore, visible light is strongly diffracted by such a structure.

Publications resulting from this research area: 30, 88, 91, 117, 143, 188, 189, 219, 220, 224, 244, 253, 295

External funding: DFG SPP 1113 "Photonic Crystals"

Cooperations: M. Eich (TU Hamburg-Harburg, DE); S. Schröter (IPHT Jena, DE); F. Laeri (Darmstadt, DE); F. Schüth (Mülheim/Ruhr, DE); G. Stucky (Santa Barbara, USA); H. Winkler (Merck Darmstadt, DE)

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

Involved: H. Bretinger, D. Konjhodzic, 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.

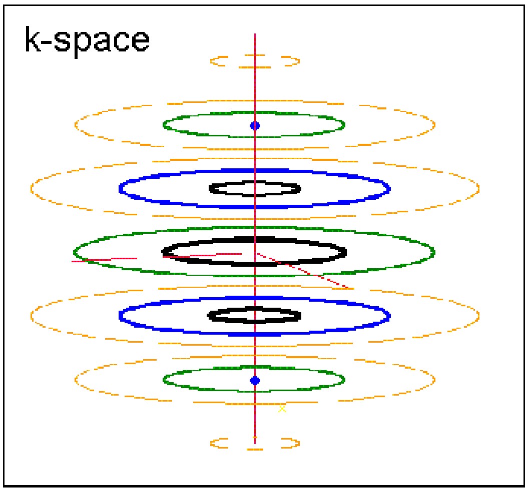


Figure 1. Reciprocal space of mesoporous fibers.

Results: The mesoporous fibers showed interestingly changed scattering properties relying on a novel structure of the reciprocal space of these solids. The reciprocal space does not consist of a reciprocal lattice as normal crystals but of a system of rings. This is the consequence of the novel real space structure. The pores in the fibers are arranged in circles or spirals normal to the fiber axis. This provides a very different kind of symmetry compared to the translational symmetry of crystals. Atomic ordering in solids occurs predominantly in crystal structures showing translational symmetry. Quasicrystals are one of the few exceptions: these are highly ordered but not translationally invariant. The observed circular structure is another example for a highly ordered, non-translationally invariant structure. It represents therefore a new type of solid state organization.

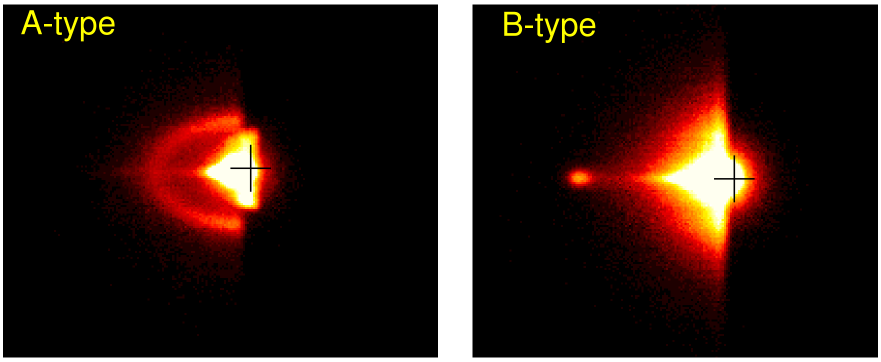


Figure 2. Two dimensional SAXS patterens of calcined A-type (left) and B-type (right) mesoporous silica films.

Also the mesoporous films have shown unexpected structural features. Depending on the fabrication conditions two types of films have been found. Whereas A-type films showed worm-like structures, the B-type films exhibited layer structures. Since the system can be calcined, a stable sustainer system must exist between the layers. The sustaining system is analyzed by AFM. We found a strong hint that the sustainers form an interconnected network.

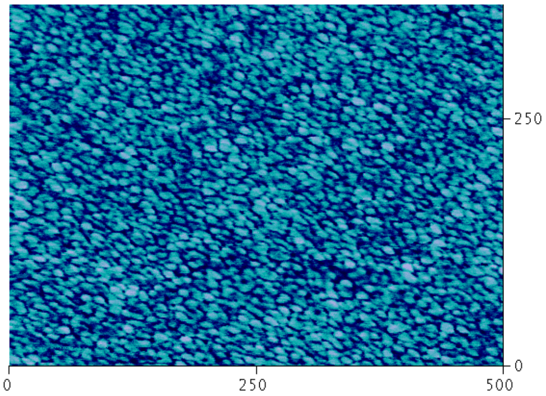


Figure 3. AFM phase picture of B-type films. The dark regions correspond to regions of large energy dissipation. They are assigned to sustainers below the surface of the film.

Publications resulting from this research area: 91, 244, 390, 417

External funding: DFG SPP 1113 "Photonic Crystals"; IMPRS "SurMat"

Cooperations: G. Stucky (Santa Barbara, USA); K. Thonke (Ulm, DE); M. Rohwerder (MPI für Eisenforschung, Düsseldorf, DE); F. Schüth (Mülheim/Ruhr, DE); C. Lehmann (Mülheim/Ruhr, DE); B. Tesche (Mülheim/Ruhr, DE)

2.4 Department of Organometallic Chemistry

Director:

Alois Fürstner (born 1962)
Publications: 35-49, 95, 148, 197-209, 254, 282, 344-349, 374, 375, 388, 389, 391, 392, 396, 414, 415, 425

Further group leader:

Frank Glorius (born 1972)
left the Institute in November 2004
Publications: 50, 150, 213, 308, 330, 350, 351

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

Special Activities

1997-	Member, Editorial Board of "Topics in Organometallic Chemistry"
2000-	Member, Advisory Board of "Advanced Synthesis & Catalysis"
2001-	Scientific Editor of "Chemical Communications"
2001-	Member, Board of Editors of "Organic Syntheses"
2002-	Member, Editorial Advisory Board of "Journal of Organic Chemistry"

2002-	Member of the Scientific Advisory Board (Wissenschaftlicher Beirat) of the Institut für Organische Katalyseforschung, Rostock
2002-	Member of the Selection Committee of the Alexander von Humboldt-Foundation (Feodor-Lynen-Program)
2004	Editor, Symposium-in-Print "Catalytic Tools Enabling Total Synthesis", (Tetrahedron Chair Issue)

Research in the Department of Organometallic Chemistry

The "Department of Organometallic Chemistry" in its present form exists since 1998 when Prof. Fürstner was appointed as Director at the Institute. Since then, the Department has undergone a phase of rapid growth, leading to its present size of ca. 40 coworkers. This number includes the group of Dr. Frank Glorius, who has joined the Institute in August 2001 (Liebig fellowship, Fonds der Chemischen Industrie). Dr. Glorius has rapidly assembled a sizeable team, allowing him to pursue his own scientific interests which fit excellently into the overall mission of the Department. Prior to finishing his "Habilitation", Dr. Glorius was offered a C3 professorship at the University of Marburg (effective December 2004). It is planned to replace him by a new group leader in 2005.

Prof. Fürstner's scientific interests focus on the use of organometallic reagents as tools for advanced organic synthesis. Thereby, special emphasis is given to catalysis in general as one of the most important and most rapidly growing areas amongst the chemical sciences. In this context, our long standing interest in alkene and alkyne metathesis deserves particular mentioning. Another long term project deals with "novel concepts" for catalysis, with the intention

(i) to replace established stoichiometric reactions by catalytic processes of equal or even higher efficiency
(ii) to increase the scope of existing methods by improved (ligand) design
(iii) to explore conceptually novel catalytic scenarios of potential relevance for organic synthesis.

As will be outlined in detail below, our investigations into cross coupling reactions (iron- rather than palladium-catalyzed; novel heterocyclic carbenes and carbene complexes etc.), platinum-catalyzed skeletal rearrangements, (*E*)-selective semi-reductions of alkynes, as well as the asymmetric hydrogenation of heterocycles (Glorius) fall into the realm of this research topic.

In parallel work, the organometallic reagents and catalysts studied and developed in Mülheim are put under scrutiny by applications to the total synthesis of bioactive natural products. The target molecules are chosen according to their structural complexity and biological significance. This line of research is pursued in the belief that the reach of synthesis to the *practical* construction of elaborate products lags far behind the seeming maturity of the discipline. Therefore it is important to find new reactions which have an impact on the fundamental logic of retrosynthetic planning. Further priority issues are (i) the "economy of steps" of the overall sequences, (ii) a significant increase in molecular complexity per step, (iii) a maximum mass transfer from the substrate to the products ("atom economy"), (iv) the valorization of bulk chemicals, and (v) the use of as many catalytic processes within a given sequence as possible. In this context it is worth mentioning that two total syntheses have been completed during the report period that are (almost) entirely catalysis based and employ almost exclusively methodology developed in our Department.

During the report period, our collaborations with biochemistry and biology experts outside the Institute have been significantly expanded and strengthened. This allows us to screen and evaluate all relevant products formed during our total synthesis campaigns in various enzymatic and cellular assays. Additional in vitro tests (e.g. DNA cleavage) are carried out in house. Particularly notable is the close collaboration with the Max-Planck-Institut für Molekulare Physiologie in Dortmund (Prof. Waldmann) which will become part of the "Chemical Genetics Center" of the Max-Planck-Society to be launched in 2005.

Finally, the significant overlap with research activities of other groups at the Institute should be pointed out. Pertinent examples are (i) the close collaboration with Dr. Glorius which led to the first implementation of the asymmetric pyridine-hydrogenation technology into an advanced total synthesis, (ii) a project with Prof. Thiel concerning the analysis of the stereochemical course of alkene metathesis reactions, and (iii) a fruitful exchange of information with Prof. Jonas in the new field of iron-catalyzed cross-coupling. Finally it should be mentioned that close ties to all analytical groups exist which are essential for success in the timely field of applied organometallic chemistry and catalysis research as carried out in this Department.

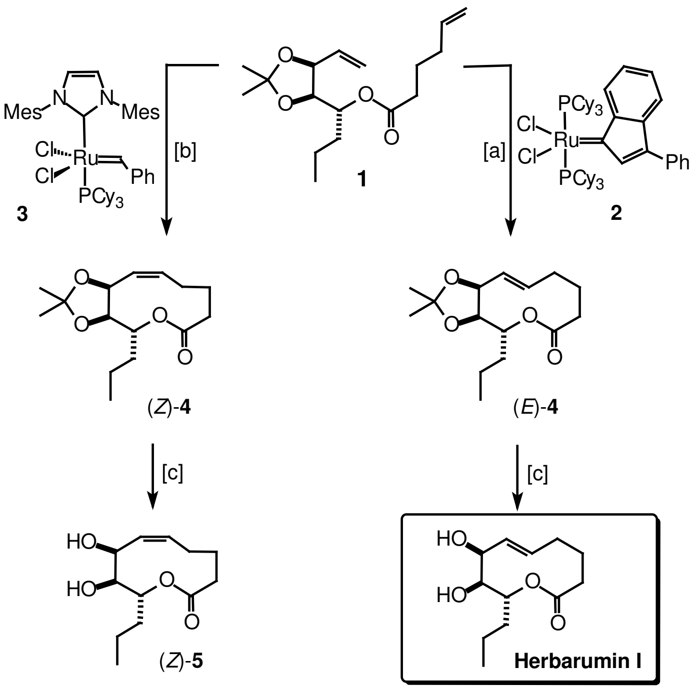
2.4.1 Research Area "Metathesis of Alkenes and Alkynes" (A. Fürstner)

Involved: C. Aissa, G. Blond, A.-S. Castanet, P. Davies, D. De Souza, F. Jeanjean, F. Lacombe, A. Leitner, L. Parra, S. Prühs, K. Radkowski, J. Ragot, P. Razon, R. Riveiros, B. Scheiper, F. Stelzer, M. Schlede, D. Song

Objective: Metathesis has revolutionized organic synthesis during the last decade. Our work in this highly competitive area intends (i) to demonstrate the strategic advantages associated with the use of this reaction by prototype applications to target oriented synthesis, (ii) to develop catalysts with even better performance, (iii) to control the stereochemical outcome of the reaction, and (iv) to improve its industrial application profile.

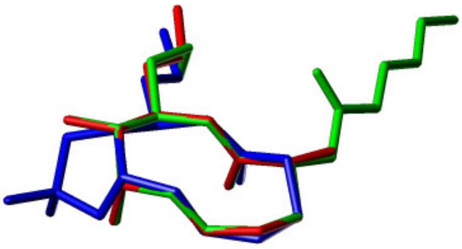
Results: As outlined in the last report, our work on ring closing alkene metathesis (RCM) started in 1995 when we were able to show that this reaction allows to form medium-sized and macrocyclic rings with exceptional efficiency, although such products were previously believed to be beyond its reach. Investigations into novel catalyst design (ruthenium allenylidenes, -indenylidenes, ruthenium-NHC complexes) as well as the first metathesis reactions in supercritical media followed shortly thereafter.

A major shortcoming of RCM as well as cross metathesis (CM), however, is the lack of control over the configuration of the newly formed double bond. A significant part of the work carried out during the report period has been dealing with this important problem. Thereby, several lines of investigations have been pursued:

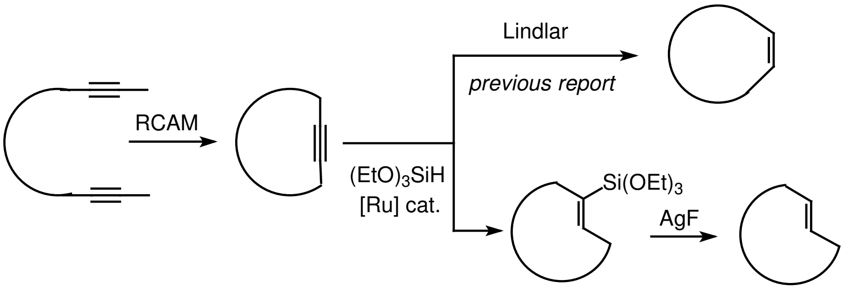


First, we have shown how to deal with this stereochemical issue by exerting thermodynamic versus kinetic control. This concept was implemented into the first total synthesis of the herbicidal lactone **herbarumin**.

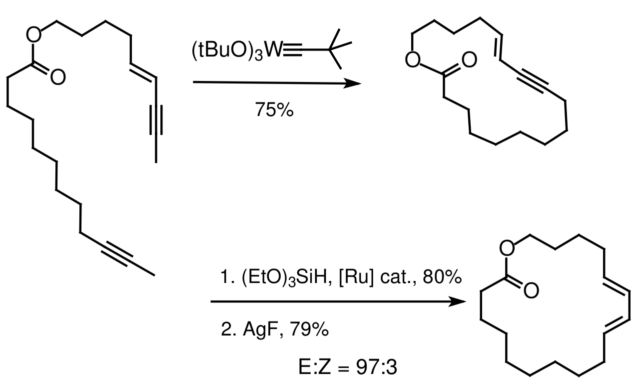
Specifically, semiempirical calculations for the corresponding isopropylidene acetal indicated that the (*Z*)-olefin (*Z*)-**4** is ca. 3.5 kcal mol^{-1} more stable than (*E*)-**4** due to the rigid bicyclic skeleton. This enthalpic difference translates into good stereoselectivity during ring closure. In fact, RCM of diene **1** using the ‘second generation’ ruthenium complex **3** resulted in the exclusive formation of the (*Z*)-alkene, likely because the chosen catalyst is able to equilibrate the products initially formed under the reaction conditions; this outcome is therefore deemed to reflect thermodynamic control. In contrast, the use of our indenylidene catalyst **2** bearing two phosphine ligands allowed to trap the kinetic (*E*)-isomer in excellent yield and purity. To the best of our knowledge, these transformations are the first example for the deliberate formation of either possible isomer of a given cycloalkene by stereocontrolled RCM. This concept was also successfully applied to the total syntheses of the marine natural product **ascidiatrienolide** and the herbicide **pinolidoxin**.



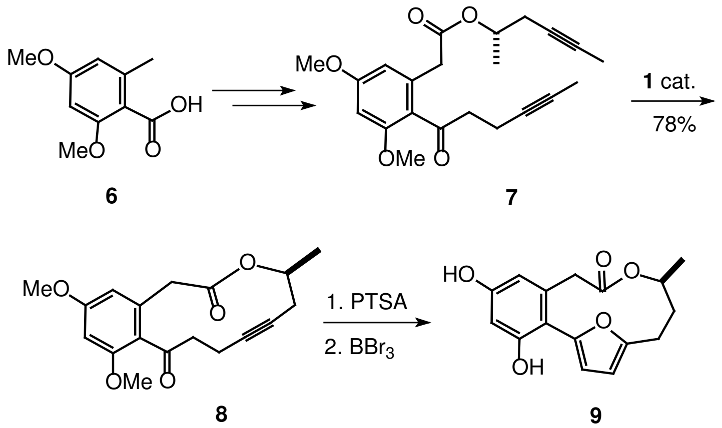
Overlap of the X-ray structures of **herbarumin** (red), **herbarumin** isopropylidene acetal (blue), and **pinolidoxin** (green) revealing the highly conserved conformation of their ten-membered lactone cores.



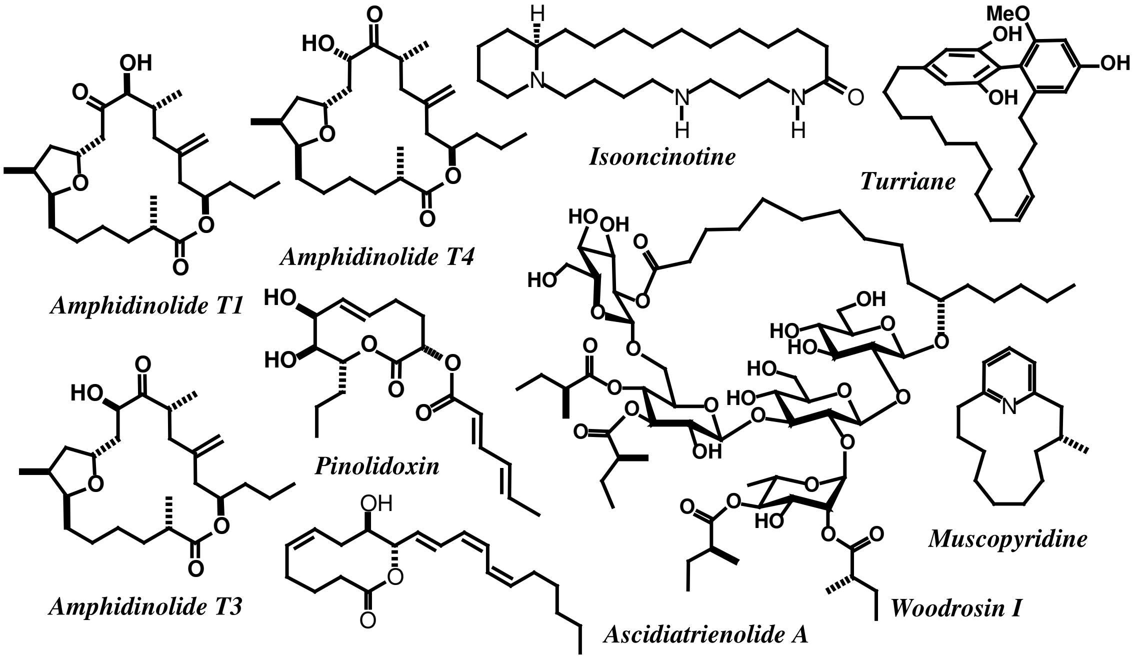
The third and so far most successful way to exert rigorous stereocontrol takes recourse to alkyne metathesis followed by semi-reduction. It had already been shown during the last report period that ring closing alkyne metathesis (RCAM) followed by Lindlar hydrogenation opens a reliable entry into macrocyclic (*Z*)-alkenes. Since the complementary methods for the conversion of alkynes to (*E*)-alkenes are limited in scope and rather unattractive, the full potential of RCAM could not be exploited. To fill this gap, a sequence of *trans*-selective hydrosilylation of the (cyclo)alkyne substrates followed by a protodesilylation of the resulting vinylsilanes was developed which opens an effective, mild and highly stereoselective entry into (*E*)-(cyclo)alkenes. [Cp*Ru(MeCN)$_3$]PF$_6$ turned out to be the catalyst of choice for the *trans*-hydrosilylation, while the protodesilylation is best achieved with either AgF or a combination of AgF cat./TBAF in aq. MeOH/THF.



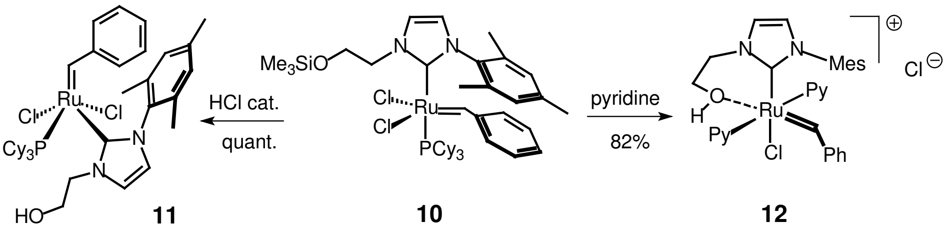
This concept was then extended to the preparation of stereodefined 1,3-dienes. Specifically, treatment of a suitable enyne-yne substrate with an alkyne metathesis catalyst engenders a high yielding formation of a cyclic enyne. *trans*-Selective hydrosilylation followed by protolytic cleavage of the C-Si bond affords the desired (*E,E*)-cycloalka-1,3-diene in good yield and excellent isomeric purity. This results is remarkable as it illustrates the fully chemoselective course of the alkyne metathesis as well as of the hydrosilylation reaction, both of which occur exclusively at the triple bond without affecting the adjacent alkene. It should be pointed out that conjugated dienes are most difficult to prepare by conventional alkene metathesis, because the established catalysts attack both double bonds with similar ease and therefore usually afford complex mixtures of various stereoisomers and ring-contracted products.



A conceptually different use of alkyne metathesis is featured in our synthesis of the tubulin binding compound **citreofuran** (**9**). The heterocyclic ring embedded into the macrocyclic skeleton of this compound was encoded by cycloalkyne **8** which derived from a high yielding RCAM reaction of the readily available diyne **7**. Treatment with acid renders the alkyne entity in **8** susceptible to nucleophilic attack by the adjacent ketone, thus forming the furan ring. RCAM can therefore serve heterocyclic chemistry as well.

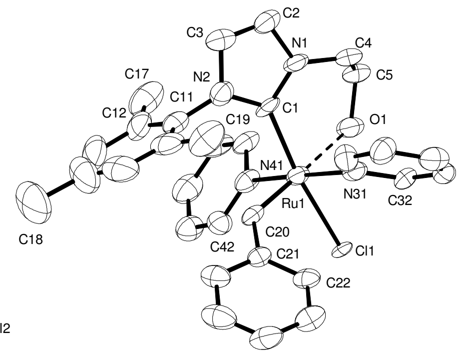


The scope of RCM and RCAM has been further illustrated by a host of applications to the total synthesis of various natural products. The most advanced examples are the complex glycolipid **woodrosin I**, and the entire family of the potent cytotoxic but very scarce marine macrolides of the **amphidinolide T** series. The **turrianes** were prepared both by an alkene- and by an alkyne metathesis route, thus allowing for a direct comparison of these methods. While the standard ruthenium catalysts for alkene metathesis are easy to use, it is only the alkyne metathesis approach which enables a fully stereoselective and hence practical synthesis. Although structurally less complex, the spermidine alkaloid **isooncinotine** and the olfactory alkaloid **muscopyridine** also deserve mentioning, because their syntheses rely (almost) exclusively on metal catalyzed reactions developed in our laboratory (see below).



11 **10** **12**

Finally, two unusual and unprecedented rearrangements of Grubbs-type ruthenium carbene complexes have been discovered during our work on the immobilization of functionalized derivatives such as **10**. Cleavage of the lateral silyl group with ethereal HCl spontaneously affords complex **11** in which the NHC- and the phosphine ligand are *cis*- rather than *trans*-disposed. Even more strikingly, treatment of the same complex with pyridine engenders an ionization by loss of one of the chlorides with formation of the octahedral complex **12**. It is particularly surprising that the hydroxyl group on the alkyl side chain in **12** merely serves as a Lewis base rather than as an alkoxide ligand to the Ru center. The structure of this very unusual complex has been secured by X-ray analysis.



Publications resulting from this research area: 36, 38, 44, 45, 46, 48, 49, 95, 148, 198, 201, 202, 204, 205, 206, 282, 374, 396, 415

External funding: DFG (Leibniz program); Fonds der Chemischen Industrie; Merck Research Council; Boehringer-Ingelheim

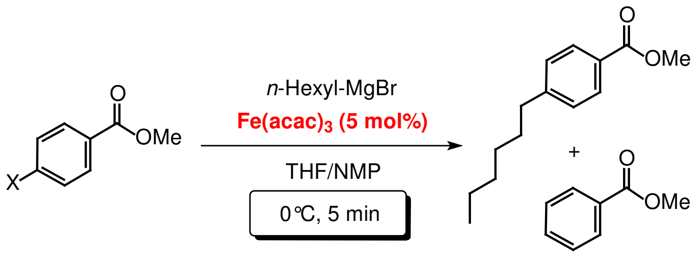
Cooperation: W. Thiel (Mülheim/Ruhr, DE)

2.4.2 Research Area "Iron Catalyzed Cross Coupling Reactions" (A. Fürstner)

Involved: M. Bonnekessel, E. Kattnig, H. Krause, D. Laurich, A. Leitner, O. Lepage, R. Martin, M. Méndez, B. Scheiper, G. Seidel

Objective: Cross coupling reactions using palladium (or nickel) catalysts constitute one of the most important developments in preparative chemistry during the last 40 years; they are widely practiced in academia as well as in industry. We intend to explore conceptually novel alternatives to these classical C-C-bond forming reactions, employing catalysts that are cheap, efficient, benign and non-toxic.

Results: Reminiscent of a pioneering study of Kochi et al. published as early as 1971 on the use of iron salts for the cross coupling of *vinyl* halides with organometallic reagents (a reaction which found surprisingly few applications during the following decades), a program was launched with the aim to investigate the potential of iron catalysis in more detail. Thereby our investigations were guided by the mechanistic hypothesis that the reaction of iron salts with e.g. Grignard reagents might lead to highly reduced clusters containing iron centers of the formal oxidation state –II (as suggested by previous studies of Prof. Bogdanović) as the catalytically competent species. Based on this, we were able to show that cheap, non-toxic, air-stable, non-hygroscopic, and environmentally benign $Fe(acac)_3$ and related pre-catalysts effect the cross coupling of *alkyl*magnesium halides with (hetero)aryl halides and –sulfonates with truly remarkable efficiency. The most notable features of this process can be summarized as follows:



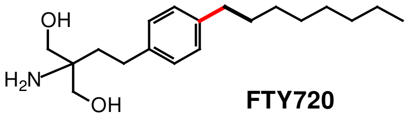
X	Coupling	Reduction
I	27%	46%
Br	38%	50%
Cl	> 95%	
OTf	> 95%	
OTs	> 95%	

(i) Aryl chlorides, -triflates and even –tosylates are better substrates than the corresponding aryl bromides or –iodides which prevail in palladium-catalyzed reactions. In view of the lower price and better availability of aryl chlorides, this reactivity profile constitutes a major advantage in practical terms.

(ii) The reactions proceed with unprecedented rates at or even below ambient temperature, reflecting the exceptional capacity of the iron catalyst formed in situ for C-Cl bond activation.

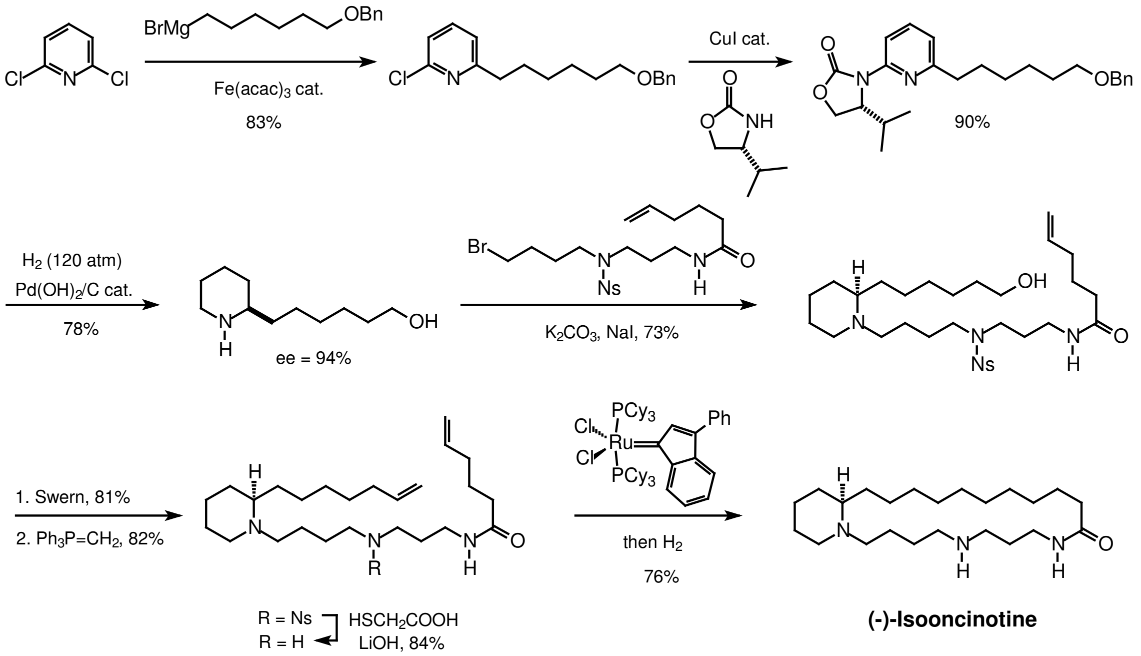
(iii) This remarkable rate of cross coupling translates into an attractive chemoselectivity profile, tolerating functional groups that usually react with Grignard reagents (esters, nitriles, sulfonates etc.)

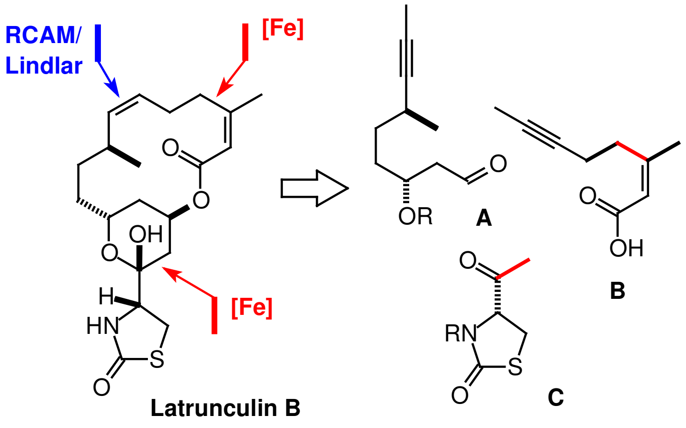
(iv) The reactions can be easily performed on multigram scale, as shown by the synthesis of **FTY720**, a promising immunomodulatory drug candidate presently in clinical phase III studies.



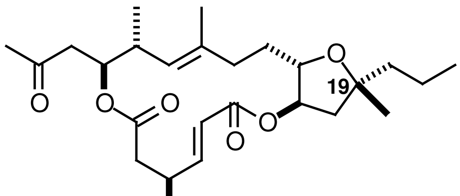
FTY720

(v) The method also allows for consecutive cross coupling reactions in one pot, as exemplified by a highly integrated synthesis of the musk-odored alkaloid **muscopyridine**. This synthesis is entirely catalysis based and employs only procedures developed in our laboratory. Similarly, the iron-catalyzed method constitutes a key transformation en route to the spermidine alkaloid **isooncinotine**, which also features the power of the asymmetric pyridine hydrogenation technology developed by Dr. Glorius, as well as the ease of macrocyclization via RCM employing our ruthenium indenylidene catalyst.

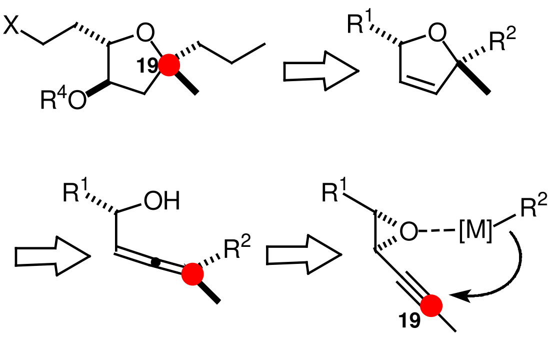




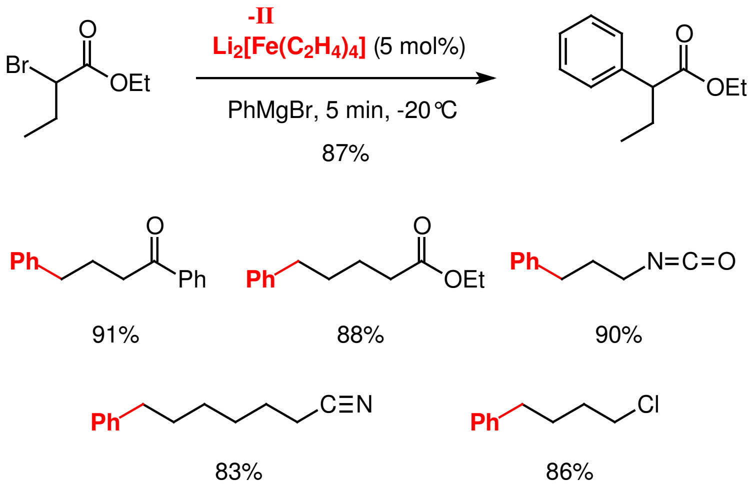
In addition to (hetero)aryl chlorides and –sulfonates, iron catalysis also applies to alkenyl triflates as well as to acid chlorides as the electrophiles. Since various functional groups are again tolerated, this method provides access to e.g. functionalized ketones that are difficult to prepare otherwise. The formation of the building blocks **B** and **C** required for the total synthesis of the highly potent actin-binding macrolide **latrunculin B** illustrate this aspect. Taking recourse to the alkyne metathesis/Lindlar strategy for the construction of macrocyclic (*Z*)-alkenes, we were able to accomplish a concise and highly flexible total synthesis of this bioactive target as well as of a library of analogues (cf. Chapter "Catalysis Based Syntheses and Evaluation of Bioactive Natural Products").



Amphidinolide X



Propargyl epoxides represent yet another class of electrophiles that were found to react with Grignard reagents in the presence of catalytic amounts of Fe(acac)$_3$. Under these conditions, they convert into allene derivatives with complete transfer of the central chirality of the epoxide to the axial chirality of the emerging product. Since the major allene isomer formed is *syn*- rather than *anti*-configured, this new iron-catalyzed method nicely complements the (mainly stoichiometric) copper-based procedures previously described in the literature. This stereochemical outcome is tentatively explained by a directed delivery of the nucleophile. This novel transformation served as a key step of the first total synthesis of the cytotoxic marine natural product **amphidinolide X** recently completed in our laboratory. In our approach, the quarternary center C-19 is relayed to a readily available propargyl epoxide via a chiral allene intermediate.



Low-valent iron catalysts induce an even more unusual transformation. While palladium- and nickel catalyzed cross coupling reactions of *alkyl* halides are notoriously difficult and have been possible only recently using rather sophisticated and highly optimized ligand systems, we found that bare iron centers effect such reactions with exceptional ease and efficiency. Although "in situ" systems can be used for this purpose, best results were obtained with the well defined complex $[(\mathrm{tmeda})\mathrm{Li}]_2[\mathrm{Fe}(\mathrm{C_2H_4})_4]$ originally developed by Prof. Jonas. Under these conditions, chemoselective cross coupling reactions of secondary bromides, primary iodides and all kinds of allylic halides with *aryl*-Grignard reagents can be accomplished even in the presence of other electrophilic sites such as ketones, esters, nitriles, or isocyanates. The fact that the Jonas ate-complex containing an Fe(–II) center leads to an exceptionally active catalyst system supports the notion that highly reduced metal centers may play a decisive role in such catalytic processes. Mechanistic investigations aiming at a better understanding of this aspect are presently underway.

Publications resulting from this research area: 40, 41, 202, 206, 208, 375, 391, 414, 425

External funding: DFG (Leibniz program); Fonds der Chemischen Industrie (Kékule stipends for B. Scheiper and M. Bonnekessel); Alexander von-Humboldt-Foundation (stipends for O. Lepage, R. Martin, and M. Méndez); Deutsch-Israelische Projekt-kooperation (DIP)

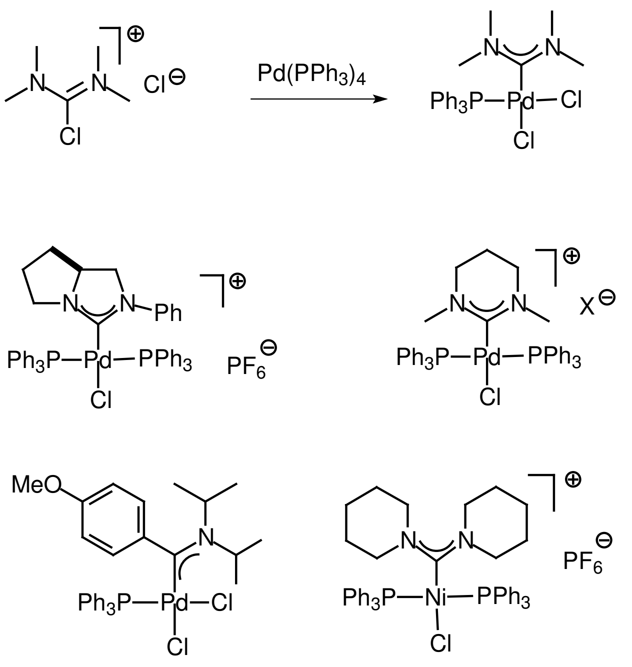
Cooperations: K. Jonas (Mülheim/Ruhr, DE); F. Glorius (Mülheim/Ruhr, DE)

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

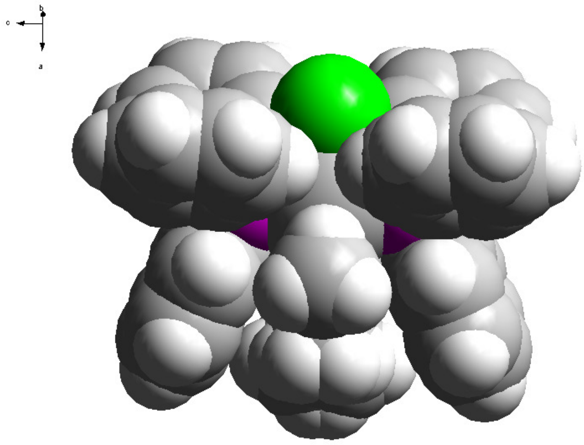
Involved: T. Gress, P. Hannen, H. Krause, D. Kremzow, V. Mamane, G. Seidel

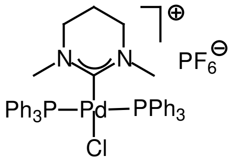
Objectives: A long term goal consists in the development of novel catalytic scenarios for advanced organic synthesis. Particular emphasis is given to transformations that result in a significant increase in molecular complexity. Moreover, we intend to develop alternative routes to established catalyst- and ligand systems of proven relevance.

Results: Transition metal complexes with N-heterocyclic carbene (NHC) ligands show considerable potential as catalysts for organic synthesis and fine chemical production. They are usually prepared by ligand exchange or salt metathesis on treatment of a suitable metal precursor with the appropriate carbene formed as a discrete or a transient species. In none of these established procedures does the metal template change its oxidation state. As part of our program aiming at the design of novel metal-NHC catalysts and their applications to advanced organic synthesis, we considered that oxidative insertion of a low-valent metal into a 2-chloro-1,3-disubstituted imidazolinium salt may open an alternative entry into this important class of compounds. In fact, reaction of either $Pd(PPh_3)_4$ or $[Ni(cod)_2]/PPh_3$ with various 2-chloroimidazolinium- or –amidinium salts affords metal-diaminocarbene complexes in good to excellent yields. This procedure allows to incorporate (acyclic or ring expanded) carbene fragments that are very difficult to access otherwise. Moreover, a variety of enantiomerically pure, chiral metal-NHC complexes have been prepared by this novel route. Furthermore it was shown that oxidative insertion also paves a way to prototype Fischer carbenes of Pd(II). Since the required starting materials are readily available from urea- or thiourea derivatives, this approach allows for substantial structural variations of the ligand backbone. The catalytic performance of the resulting library of nickel- and palladium-carbene complexes has been evaluated by applications to



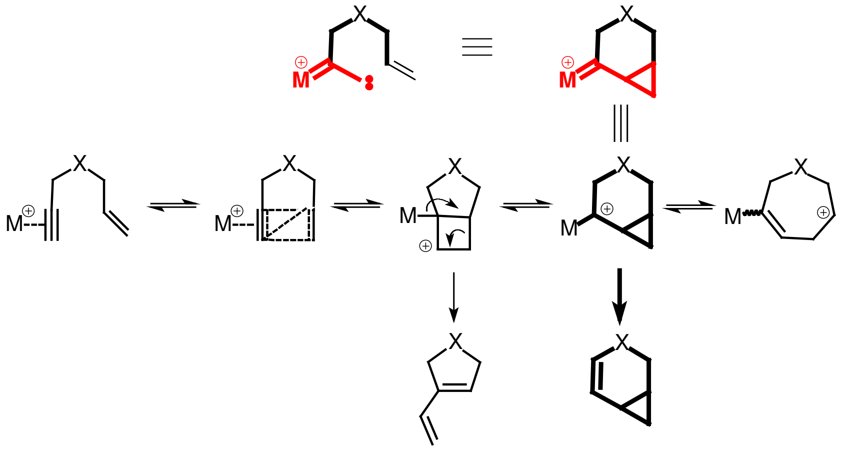
prototype Suzuki-, Heck-, and Kumada-Corriu cross coupling reactions as well as Buchwald-Hartwig aminations. It was found that even Fischer carbenes show appreciable catalytic activity. Moreover, representative examples of all types of neutral and cationic metal carbene complexes formed in this study were characterized by X-ray crystallography.

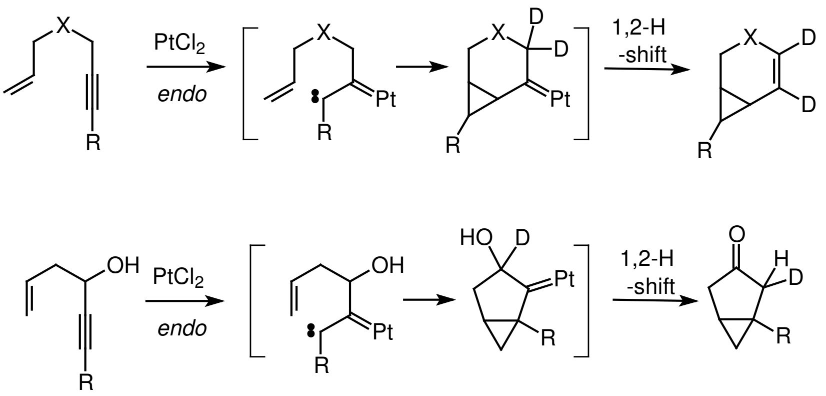




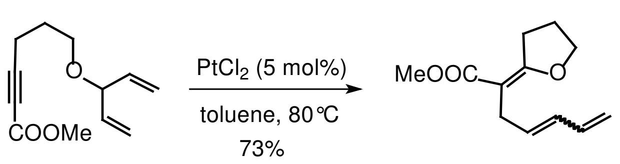
Space filling representation of the cationic carbene complex shown in the insert. The 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2-ylidene ligand is sandwiched between two phenyl rings. The chlorine (green) in *trans* position to the carbene is readily accessible.

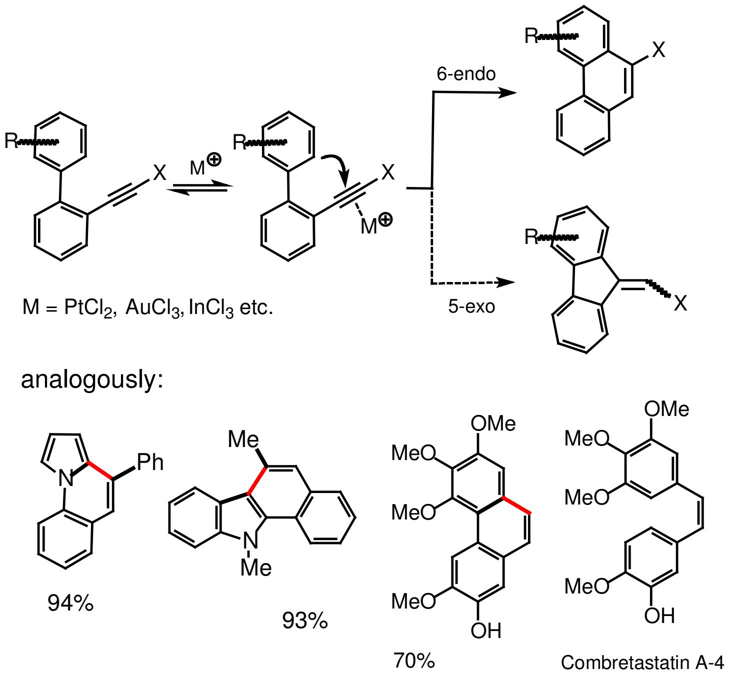
Another major line of research is dealing with skeletal rearrangements effected by catalysts with high affinity to π-systems. In previous work we had suggested that alkynes coordinated to suitable π-acids are susceptible to attack by tethered nucleophiles, engendering a host of cycloisomerization reactions. Depending on the nature of the chosen catalyst, the reactive intermediates are best viewed as "non-classical" carbocations (M^+ = proton) or as a cyclopropylcarbene species (M^+ = Pt, Au, In etc.). Since the cyclopropyl ring of the latter itself formally derives from attack of a carbene onto the double bond of the substrate, the original alkyne complex represents a *vic*-dicarbene synthon; such species are elusive in conventional chemistry. We have been able to demonstrate the "carbenoid" character of the reactive intermediates by labeling experiments and have exploited these complexity inducing reactions for various preparative purposes.



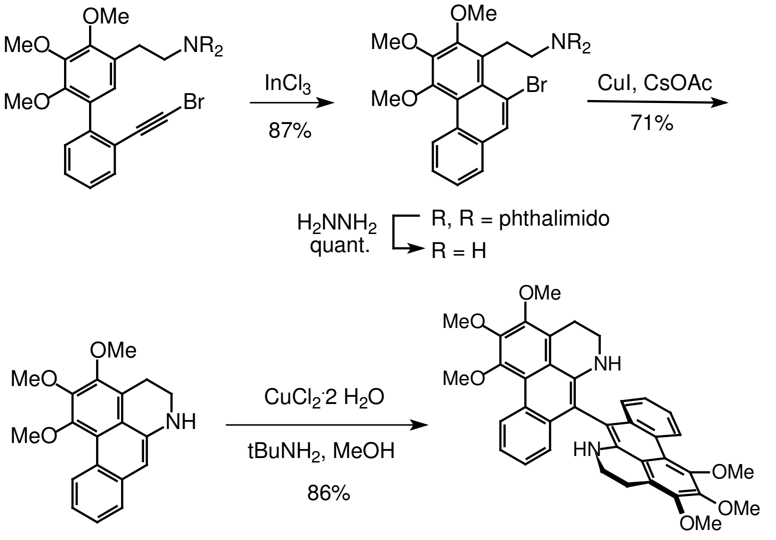


Specifically, they allow to form bicyclo[3.1.0]-hexane skeletons from readily accessible homoallylic alcohols. A concise total synthesis of the terpene derivatives sabinol and sabinone illustrates this aspect. If the homoallylic alcohols used as the substrates are enantiomerically pure, excellent levels of chirality transfer can be secured.





Furthermore, it was possible to extend this concept beyond alkenes as the tethered nucleophilic reaction partners. Thus, the use of allyl ethers results in an unprecedented O→C allyl transfer process which also takes a highly stereoselective course. Even more useful in preparative terms are closely related skeletal reorganizations of alkynes attached to suitable biaryl residues. They open access to phenanthrenes as well as to various types of polycyclic heteroarenes. The mild reaction conditions and the compatibility of the late transition metal catalysts with various functional groups enabled the first total synthesis of an **aporphine alkaloid** derived from *Polyalthia bullata* as well as the total synthesis of a series of naturally occurring phenanthrenes that are closely related to the cytotoxic agent **combretastatin A4** which is presently undergoing phase II clinical studies for the treatment of solid tumors.



isolated from *Polyalthia bullata*

Publications resulting from this research area: 42, 47, 207, 209, 254, 346, 388, 389

External funding: DFG (Leibniz program); Fonds der Chemischen Industrie; Merck Research Council; Deutsch-Israelische Projektkooperation (DIP)

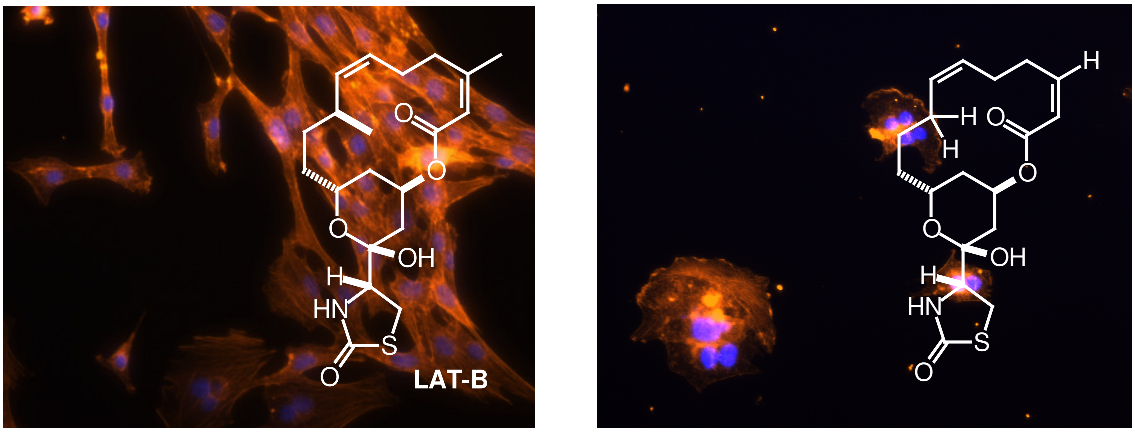
Cooperation: none

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

Involved: M. Albert, M. Fenster, F. Feyen, H. Krause, D. Kirk, M. Matheu, J. Mlynarski, H. Peters, K. Radkowski, J. Ruiz-Caro, F. Stelzer, D. De Souza, L. Turet

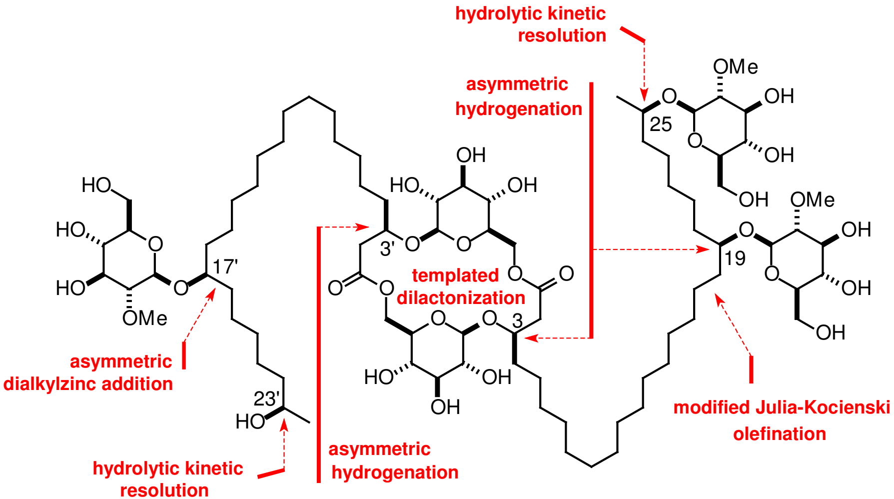
Objectives: We intend to prepare complex natural products, preferably those which are hardly available from their natural sources, and to validate their biochemical and biological properties. Special emphasis is given to the design of synthesis routes that are largely catalysis based, economic in the overall number of steps, and highly flexible. Where appropriate, focused libraries of analogues are prepared for structure/activity relationship studies.

Results: Actin as one of the two major components of the cytoskeleton determines the shape and mechanical properties of eukaryotic cells and is responsible for cell motility processes as fundamental as exo- and endocytosis. Our present knowledge about the many biological roles of actin derives to a large extent from a "chemical genetics" approach using probe molecules able to dissect this highly sophisticated and inherently dynamic microfilament structure. Among them, the **latrunculins** gained particular importance because of their striking selectivity and the rapid onset of action. They form 1:1 complexes with actin monomers which are incapable of polymerizing to the intact protein filament network. Surprisingly though, very little is known about the structural elements responsible for actin binding.



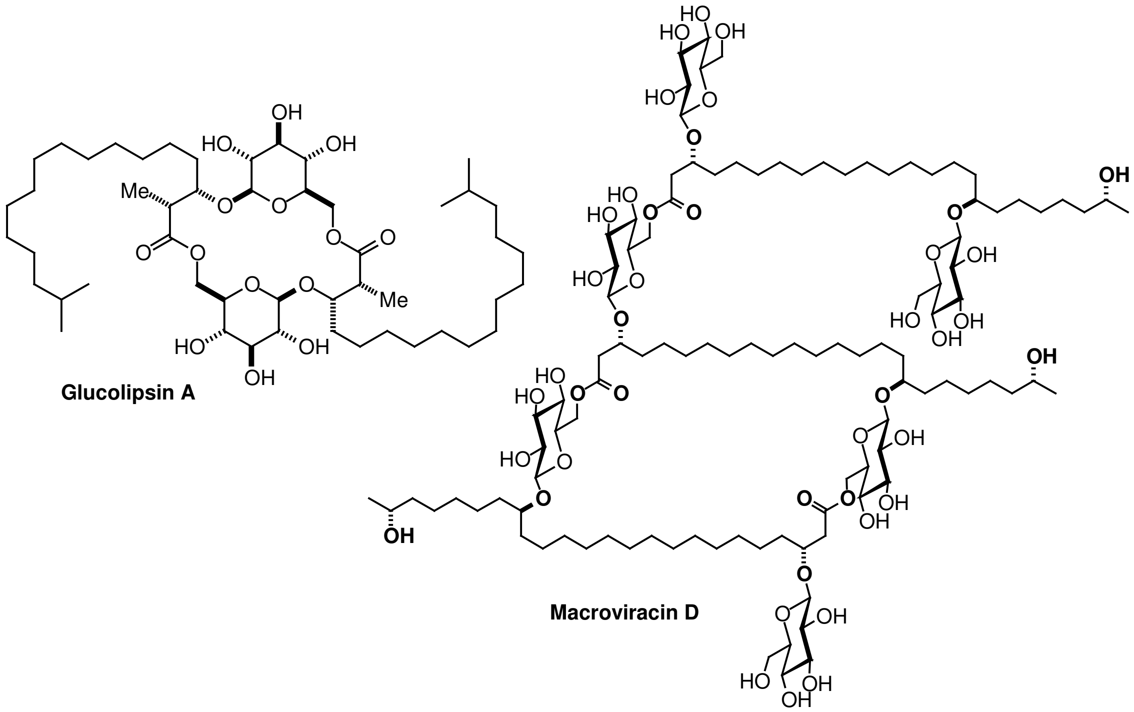
Stained cell line incubated with latrunculin B (left) or a structurally simplified latrunculin B analogue (right) which turned out to be significantly more potent.

Since our group has been able to develop a highly efficient total synthesis of the marine natural product **latrunculin B** using catalytic methodology developed in the laboratory (see above), it seemed lucrative to divert this synthesis to the preparation of a focused library of fully synthetic analogues which enabled us to investigate this aspect. Gratifyingly, this synthesis campaign resulted in a simplified analogue which is 1-2 orders of magnitude more potent in actin binding than the natural product itself as shown by a cell-based assay.



Cycloviracin B$_1$

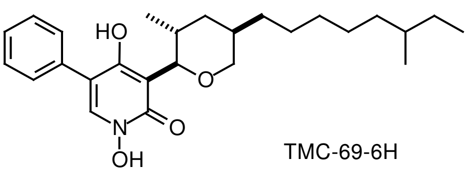
A major effort during the research period concerned the structure elucidation and total synthesis of the antivirally active glycoconjugate **cycloviracin B$_1$** (briefly mentioned in the previous report). While its constitution was known at the outset of our investigations, no information on the absolute stereochemistry of the glycosylated, secondary –OH functions residing on the fatty acid residues was available. In view of these uncertainties and the size of the target, only a very flexible and convergent synthesis plan might allow to reach these goals. Our approach was based on the hidden symmetry of this glycolipid and pursued a two-directional synthesis strategy. The key design element made use of the supposed ionophoric character of the lactide core, which was forged by a highly productive, template-directed macrodilactonization reaction. The different lateral side chains were then attached to this core by a modified Julia-Kocienski olefination and a titanium-catalyzed, asymmetric addition of a functionalized diorganozinc derivative to the aldehyde at C-17’. This strategy allowed us to unambiguously establish the absolute stereochemistry of the 6 chiral centers on the lipidic chains as (3*R*,19*S*,25*R*,3’*R*,17’*S*,23’*R*) and to complete the first total synthesis of this challenging compound. Along similar lines, the related lactide **glucolipsin A** and the even larger glycoconjugate **macroviracin D** have also been conquered by total syntheses, which rigorously established the previously unknown absolute stereochemistry of these glycolipids as shown. In collaboration with external partners, the antiviral acitivity of these natural products has been mapped (cycloviracin turned out to be most active against a *Herpes simplex* virus strain that is resistant to acyclovir). Moreover, it was found that glucolipsin is an effective inhibitor of the phosphatases Cdc25A and PTP1B, two key regulatory enzymes of the cell cycle.



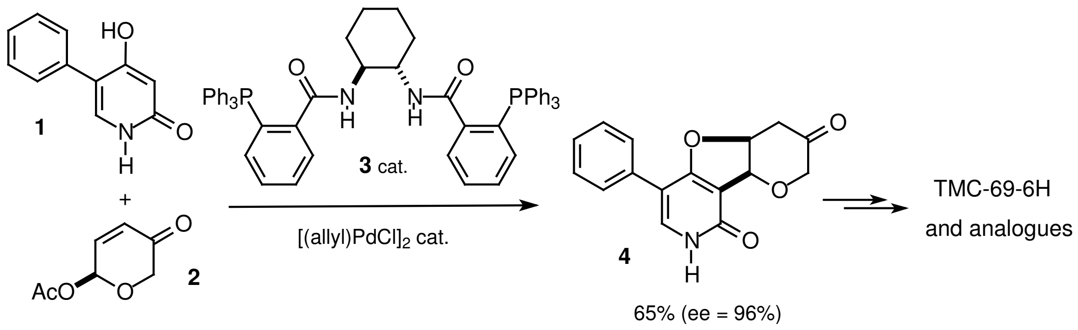
Glucolipsin A

Macroviracin D

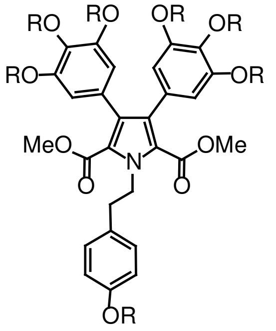
The eminent importance of phosphatases in cell cycle control drew our attention to the cytotoxic agent **TMC-69-6H** recently isolated by an industrial group in Japan. This heterocyclic compound has already proven effective *in vivo* for the treatment of murine leukemia and B16 melanoma in nude mice. The first total synthesis was achieved using a palladium catalyzed C-heteroarylation reaction between pyridone **1** and the enantiomerically enriched 6-acetoxy-pyran-3-one **2** as the key step; this transformation is accompanied by a spontaneous 1,4-addition of the phenolic –OH to the enone of the emerging product. The optically active tricyclic compound **4** thus obtained served as a convenient platform not only for the total synthesis program itself, but also for the preparation of a sizeable library of analogues for biological profiling. The most striking result of these investigation is the finding that TMC-69-6H – in contrast to the claims in the literature – turned out to be only a rather weak inhibitor of the Cdc25A phosphatase, whereas it shows very promising activities against the tyrosine protein phosphatase PTP1B, the dual specific phosphatase VHR, and the serine/theronine phosphatase PP1.



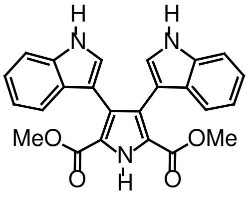
TMC-69-6H



Our long-term project on the synthesis and biological evaluation of pyrrole alkaloids has also been successfully continued. Specifically, palladium-catalyzed cross coupling reactions were used to prepare the core structure of **storniamide A**, a marine natural product able to re-sensitize multidrug resistant tumor cell lines. Moreover, we have shown that this compound is capable to oxidatively cleave DNA, provided that the peripheral –OR groups are unprotected (R = H). Along similar lines, a short synthesis of **lycogalic acid** dimethyl ester has been accomplished.



Storniamide core



Lycogalic acid dimethyl ester

Publications resulting from this research area: 36, 37, 38, 39, 43, 45, 46, 48, 148, 199, 200, 201, 202, 203, 204, 205, 344, 345, 348, 349, 375, 392, 415

External funding: DFG (Leibniz program); Fonds der Chemischen Industrie; Alexander von Humboldt-Foundation (stipends for M. Fenster and J. Mlynarski); Merck Research Council

Cooperations: E. DeClercq (University of Gent, BE; antiviral assays);
H. Waldmann, H. Prinz, O. Müller (MPI Dortmund, DE; phosphatase inhibition and actin binding assays)

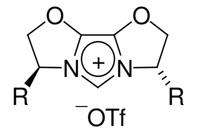
2.4.5 Research Area "New Concepts for Catalysis" (F. Glorius)

Involved: G. Altenhoff, C. Burstein, S. Holle

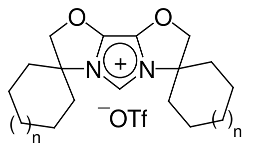
Objective: The purpose of our research program is to significantly facilitate organic synthesis by the implementation of new concepts for catalysis. We focus on the development of new transformations and on increasing the selectivity and efficiency of chemical processes.

1. New N-heterocyclic carbenes (NHCs) as ligands for transition metal catalysis

Since their first application in transition metal catalysis in 1995, NHC have become indispensable ligands for many different applications like cross-coupling or metathesis reactions. NHC are strong σ-donors with negligible π-acceptor properties and as a result are very strong electron donor ligands. Often, they form chemically and thermally robust and nevertheless extraordinarily active complexes. We have developed a new class of bioxazoline derived NHC ligands (IBiox). These ligands are electronically (less electronrich than "normal" NHC) and sterically (rigid backbone) unique. The latter property allows the synthesis of rigid chiral ligands (**1**,**3**) as well as of achiral ligands with flexible steric bulk (**2**). We have successfully employed these ligands in the enantioselective α-arylation of amides and in the Suzuki cross-coupling of sterically hindered substrates.



1



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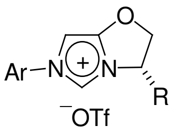
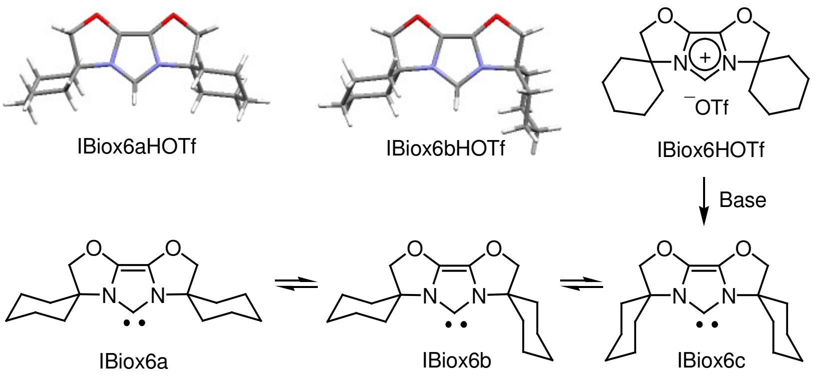
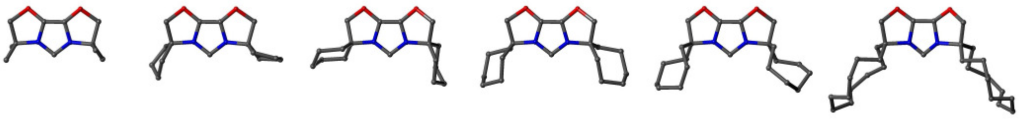


3

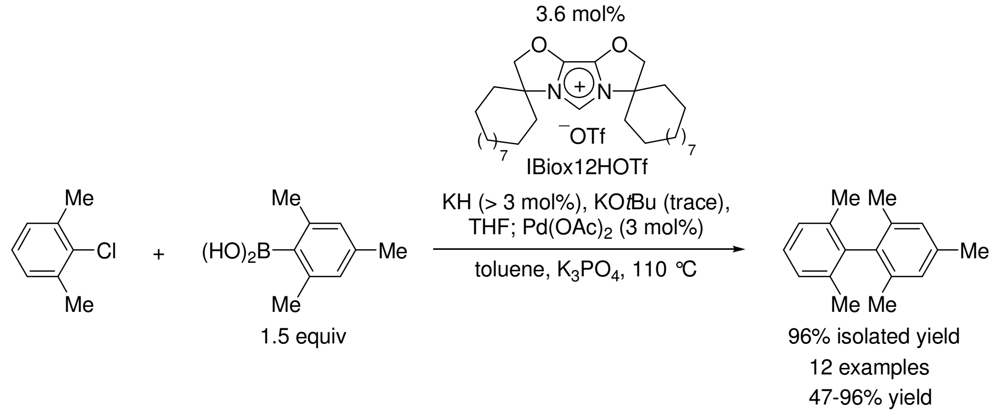
NMR- and X-ray structural analysis showed that IBiox6·HOTf (**2**, n = 1) exists in form of at least two different conformers which rapidly interconvert at room temperature. We reasoned that the flexible steric bulk caused by chair flipping of the cyclohexyl rings proves beneficial in the catalytic cycle of the Suzuki-Miyaura coupling reaction and that the sterically more demanding conformations would favor the formation of a catalytically active monoligated Pd(IBiox6)$_1$ species. However, while IBiox6·HOTf was successfully employed for the synthesis of many different ortho-substituted biaryls, the challenging formation of tetraortho-substituted biaryls remained out of reach. We have synthesized a series of structurally related imidazolium salts with cycloalkyl rings of varying ring size (cyclopentyl to cyclododecyl, Scheme 1). The electronic properties of these IBiox ligands are very similar whereas the steric demand gradually



increases within the series. These characteristics render these ligands valuable for the optimization of the catalyst system for a particular application. For the first time, these ligands allow the transformation of arylchlorides into tetra-ortho-substituted biaryls via palladium catalyzed Suzuki cross-coupling. IBiox12, the ligand containing two cyclododecyl rings, was best suited for this reaction, generally giving the highest yields of biaryl product.



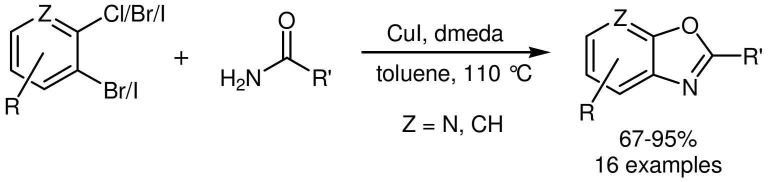
Scheme 1. X-Ray structures of the imidazolium salts (hydrogen atoms and triflate counterion are omitted for clarity).



2. Innovative C-C- and C-heteroatom-bond forming reactions

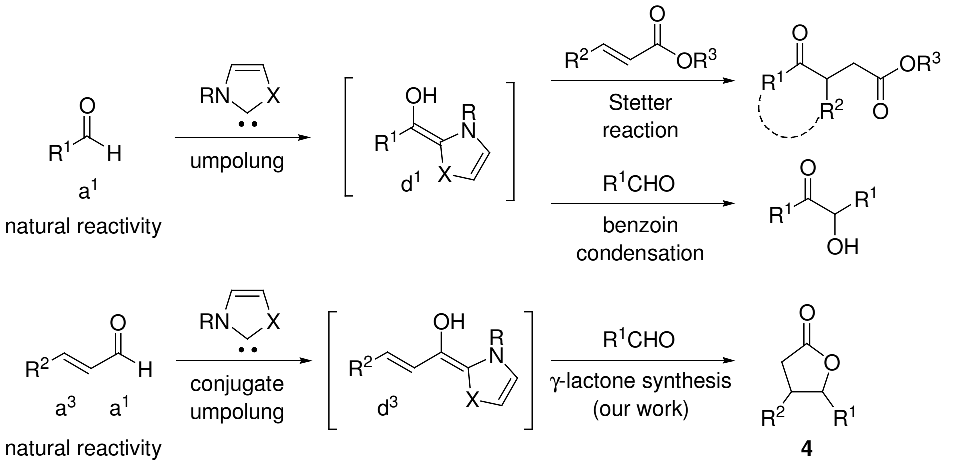
C-C- and C-heteroatom bond forming reactions are at the heart of organic chemistry. In the common Heck reaction aryl halides (C-sp^2-centers) are used as coupling partners. In stark contrast, we have developed a Heck reaction in which chloroacetamides (C-sp^3-centers) react with different olefines significantly expanding the scope of the Heck reaction.

Furthermore we have developed a novel copper catalyzed domino-C-N-/C-O-bond formation. This allows the one step synthesis of benzoxazoles starting from o-dihalobenzenes and primary amides. Different strategic bonds are formed following traditional syntheses of benzoxazoles, which employ 2-aminophenols and carboxylic acid derivatives as starting materials. Our method provides ready access to this versatile class of heterocycles.



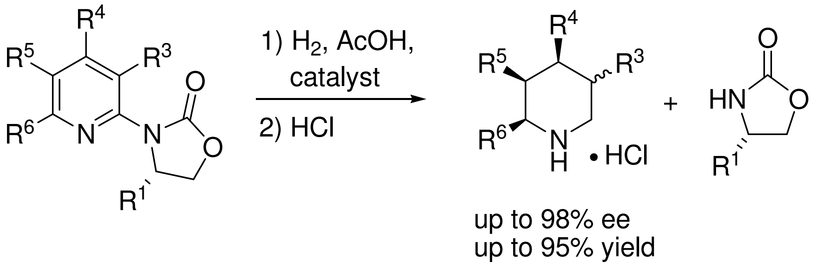
3. Conjugate Umpolung for the synthesis of γ-butyrolactones

Most transformations of organic synthesis are polar and can be described as the reaction of a nucleophile (donor d) with an electrophile (acceptor a). The umpolung of the "natural" reactivity of a functional group opens up an avenue to a new set of reactions. It has been known for a long time that the umpolung of electrophilic aldehydes can be achieved by using catalysts like cyanide or thiazolium derived carbenes. The resulting d^1-nucleophiles can react with aromatic aldehydes (benzoin condensation) or with electron poor, polarized olefins (Stetter reaction). However, for selectivity reasons these reactions are generally limited in scope. The benzoin condensation is mostly run as a self-condensation, whereas the Stetter reaction is generally conducted in an intramolecular fashion. However, some enzymes are intriguingly selective catalysts and enable the crossed and asymmetric benzoin condensation. In contrast to the a^1-to-d^1-umpolung described above, we use the term "conjugate" umpolung to describe the transformation of α,β-unsaturated aldehydes into d^3-nucleophiles (homoenolate equivalents) by attack of a nucleophilic catalyst onto the aldehyde function. We have discovered this new type of umpolung and have utilized it for the synthesis of substituted γ-butyrolactones, the *cis*-isomer being predominantly formed. The reaction is very sensitive to the choice of catalyst. Many well known umpolungs catalysts fail to provide any of the desired product **4**. Intriguingly, using IMes as the catalyst under optimized conditions γ-butyrolactones result in good yields, while the possible benzoin condensation and Stetter reaction products are hardly formed. We have shown that variation of the cinnamaldehyde and benzaldehyde component is tolerated, so that differently substituted butyrolactones are accessible. Fortunately, even ketones can be used as electrophiles. In contrast to the classical aldehyde umpolung reactions the conjugate umpolung has the advantage that it cross-couples two different aldehydes in an intermolecular fashion, giving products with two new stereocenters.



4. Asymmetric hydrogenation of pyridines

The asymmetric hydrogenation of aromatic compounds is a powerful transformation since numerous aromatic substrates exist and multiple stereocenters can be created simultaneously. Three highly enantioselective partial hydrogenations of annulated heterocycles (chinolines, indoles, pyrazines) have been reported, leading to the formation of only one chiral center. In these hydrogenations, the annulated benzene ring is required for increasing reactivity and selectivity, albeit severly limiting the substrate scope. Highly selective and general methods for the complete hydrogenation of aromatic substrates have not been developed. We have developed a conceptually novel, practical and efficient synthesis of optically active piperidines, an important substructure of many biologically active compounds. This process is distinguished by the fact that piperidines with multiple stereocenters can be formed in very good yields and excellent optical purities. For the first time, this transformation allows highly selective chirality transfer and nondestructive and traceless cleavage of the chiral auxiliary in one reaction. In addition, the piperidinium hydrochloride and the auxiliary can be easily separated by extraction and the auxiliary recycled. In collaboration with Professor Fürstner, this methodology was applied in the total synthesis of isooncinotine.



Publications resulting from this research area: 50, 150, 213, 308, 330, 351, 415

External funding: Fonds der Chemischen Industrie; BMBF (Liebig fellowship to F. Glorius); DFG

Cooperation: A. Fürstner (Mülheim/Ruhr, DE)

2.5 Department of Theory

Director:

Walter Thiel (born 1949)
Publications: 4, 18, 58, 59, 64-66, 84, 85, 115, 120, 136, 137, 141, 161, 170, 174, 178-184, 186, 210, 223, 237, 279, 283, 286, 289, 303, 311, 320-322, 329, 335, 336, 354, 358, 359, 363, 364, 377, 382, 418, 419, 428, 432

Further group leaders:

Klaus Angermund (born 1958)
Publications: 3, 80, 93, 151, 187, 432

Michael Bühl (born 1962)
Publications: 3, 20-25, 60, 61, 130, 131, 139, 141, 151, 161, 171, 172, 222, 234, 323-329, 342, 357, 427

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

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-	Reviewer (Fachgutachter) of the Deutsche Forschungsgemeinschaft
2000-	Member of the Board (Lenkungsausschuss) of the Bavarian Supercomputer Center (Höchstleistungsrechenzentrum Bayern)
2001-	Chairman of "Arbeitsgemeinschaft Theoretische Chemie"
2004-	Member of "Ständiger Ausschuss der Bunsengesellschaft"
2004-	Member of the Beirat of the "Lise Meitner Minerva Center for Quantum Chemistry", Jerusalem/Haifa, Israel

Research in the Department of Theory

The Department of Theory comprises the research groups of Prof. W. Thiel and PD Dr. M. Bühl (Heisenberg fellow), and integrates the modeling activities that had previously been pursued at the Institute (PD Dr. K. Angermund). Dr. V.R. Jensen, a long-term member of the modeling team, has accepted the position of Associate Professor at the University of Bergen (Norway) in 2003.

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) properties of fullerenes, nanotubes, and other nanosystems,
(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 the simulation of temperature and solvent effects on NMR chemical shifts, and on the reactivity of transition metal compounds, particularly in the area of homogeneous catalysis.

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

More detailed information on the research areas of the Department is available in the following six individual reports and in the 80 scientific papers published in 2002-2004. 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. New activities have started or intensified in several areas, including the accurate variational treatment of nuclear motion in ab initio vibration-rotation spectroscopy, the development of better approximate methods for electronically excited states and of improved QM/MM techniques, and the study of dynamic events. Interactions with the local experimental groups have also triggered new projects, for example in the fields of directed evolution and organocatalysis. For the future, we expect that the theoretical groups will continue to complement each other in their work in areas (a-e). We anticipate that the focus on large complex systems will become even more prominent in the future research of the Department, both with regard to methodological developments and chemical applications.

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

Involved: J. Breidung, H. Lin, F. Mariotti, S. N. Yurchenko, J. Zheng

Objective: High-level ab initio methods with large basis sets are used to compute the structures, stabilities, and vibration-rotation spectra of small molecules. The theoretical predictions need to be reliable enough to guide the spectroscopic identification of short-lived molecules and to assist in the analysis of their high-resolution vibration-rotation spectra both in the fundamental and overtone regions. They are required to be accurate also for molecules with large amplitude motions.

Results: Our ab initio studies are carried out in close cooperation with external experimental groups. Employing standard ab initio notation, we normally calculate geometries, energies, and harmonic force fields at the CCSD(T)/cc-pVQZ level, and anharmonic force fields at the MP2/cc-pVTZ or CCSD(T)/cc-pVTZ level. In our experience, theoretical results at these levels are generally adequate to provide useful guidance for our experimental partners. If highest accuracy is needed, we use even more extended basis sets and extrapolations to the complete basis set (CBS) limit. Our work in this area has been reviewed recently [428].

Bismuthine BiH_3, the heaviest of the ammonia-type hydrides XH_3, is a textbook molecule which has been synthesized in 1961, but has remained poorly characterized because of its instability and difficulties in repeating its preparation. Using a combined experimental and theoretical approach, BiH_3 has been detected in the gas phase by high resolution infrared and millimeter-wave spectroscopy [65]. The ab initio predictions are in good agreement with the observed spectra [65,322,363]. In order to achieve high accuracy for the vibrational frequencies, it is necessary to include spin-orbit effects by an appropriate configuration interaction treatment, in spite of the fact that BiH_3 is a closed-shell molecule [322]. Accurate equilibrium geometries and spectroscopic parameters are now available for BiH_3 [322,363].

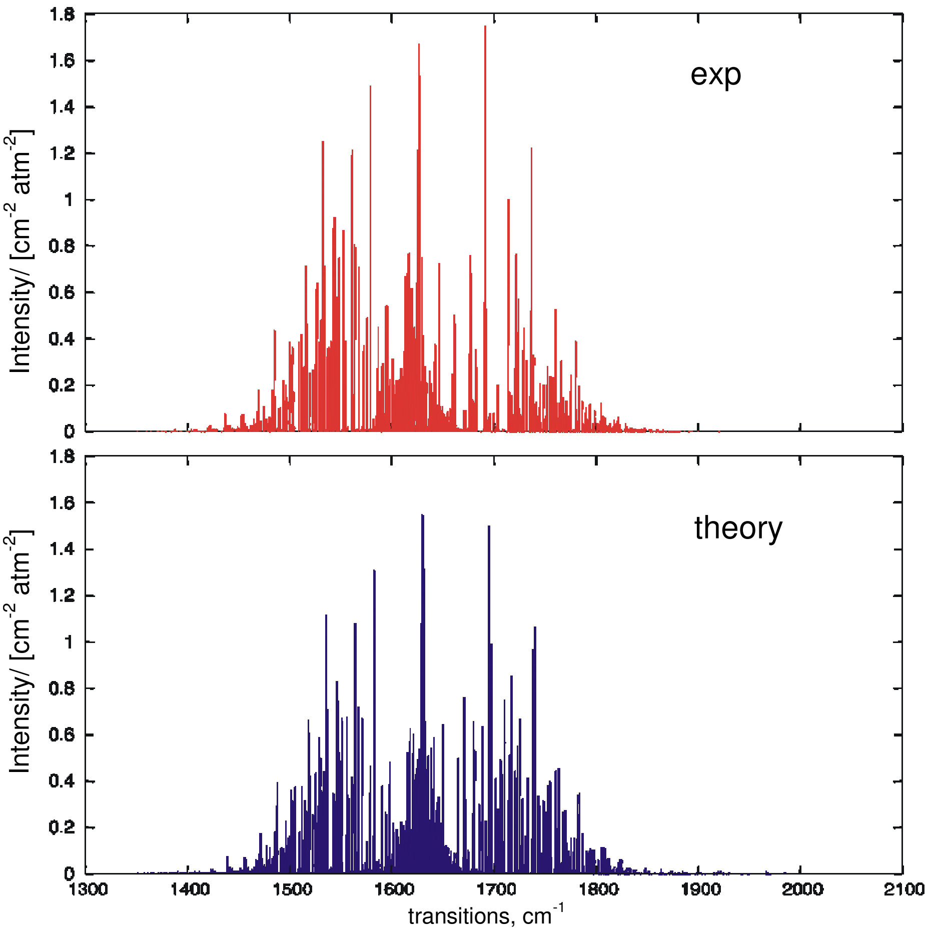
Xenon compounds with a formal Xe-C bond are quite rare and unstable. Following up on our earlier work on $XeCCF_2$, the complex XeCC has been studied [18]. The molecule has a linear structure and a considerable dipole moment due to charge transfer from xenon to dicarbon. The calculations recover most of the observed red shift in the CC stretching frequency upon complexation and thus support the reported identification of XeCC in a xenon matrix. The electronic structures of XeCC and $XeCCF_2$ are similar [18].

The fluorocarboxyl radical FCO_2 plays an important role in atmospheric chemistry. This short-lived species has been generated by low-pressure pyrolysis of the peroxide dimer in the gas phase and detected by high resolution spectroscopy [303]. Observation and identification of its millimeter-wave spectrum have relied on accurate ab initio predictions at the open-shell coupled cluster level [303]. The excellent agreement between experiment and theory confirms the structure of the FCO_2 radical whose ground-state parameters are now well established [303].

Vanadium hexacarbonyl $V(CO)_6$ is the only homoleptic transition-metal carbonyl that exists near room temperature as a free radical. It is expected to undergo Jahn-Teller distortion from octahedral to lower symmetry, but numerous previous investigations had not reached a consensus on the nature of the distortion. Open-shell coupled cluster calculations, and static and dynamic density functional computations, combined with new experimental vibrational spectra and a reinterpretation of published ESR data, show unambiguously that at temperatures below 20 K, $V(CO)_6$ isolated in inert matrices exhibits a static Jahn-Teller distortion to a D_{3d} structure [161], ruling out the previously suggested D_{4h} distortion. At room temperature, the molecule is highly fluxional with an average octahedral structure [161].

The preceding studies, as well as those on F_2BOH [321], CHF_3 [320], and NF_3 [170], are based on the calculation of anharmonic force fields followed by a second-order perturbation treatment of nuclear motion. This standard approach for semirigid molecules is no longer suitable for vibrationally excited polyatomic molecules with high vibrational energy and for floppy molecules with large amplitude motion. In such cases, it is necessary to resort to a variational treatment.

We have tackled this task in a case study on ammonia, the prototype of a molecule with large amplitude inversion motion, and attempted to compute its complete vibration-rotation-inversion spectrum as accurately as possible. This involves the calculation of six-dimensional (6D) potential energy surfaces at the CCSD(T) level with CBS extrapolation and corrections for core-valence correlation and relativistic effects [85], the fitting of such surfaces to a suitable analytical form, the development of an appropriate 6D variational treatment of nuclear motion, and the actual variational computations with construction and diagonalization of the corresponding Hamiltonian matrices. The adopted variational model is based on the Hougen-Bunker-Johns approach with an Eckart-frame kinetic energy operator. The published results for the vibrational energies [85] show overall rms deviations of around 13 cm^{-1} in the range up to 15000 cm^{-1}, but less than 5 cm^{-1} for the fundamental modes, and around 1 cm^{-1} for inversion splittings. In subsequent unpublished work, we have further improved the potential energy surfaces (more points), their fitting (to higher order), and technical aspects of the variational calculations (with regard to convergence) which has reduced the overall rms deviations from around 13 to 5 cm^{-1}. Furthermore, the theoretical treatment has been extended to rotational excitations and to the evaluation of rovibrational line intensities on the basis of ab initio 6D dipole moment surfaces. To illustrate the present status of the development, the computed and observed spectra for the $\nu_4/2\nu_2$ band system of ammonia are shown in the Figure. It is obvious that the first-principles calculation reproduces the experimental spectrum remarkably well.



Intensities of the $\nu_4/2\nu_2$ bands in ammonia: Ab initio theory vs. experiment

Publications resulting from this research area: 18, 59, 65, 85, 161, 170, 303, 320, 321, 322, 428

External funding: European Research Training Network SPHERS (HPRN-CT-2000-00022)

Cooperations: M. Bogey (Lille, FR), H. Bürger (Wuppertal, DE), J. Demaison (Lille, FR), L. Fusina (Bologna, IT), L. Halonen (Helsinki, FI), P. Jensen (Wuppertal, DE), H. Stoll (Stuttgart, DE) and H. Willner (Duisburg, DE); other SPHERS partners include A. Campargue (Grenoble, FR), J.-M. Flaud (Paris, FR), M. Herman (Brussels, BE), T. Rizzo (Lausanne, CH) and J. Tennyson (London, UK)

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

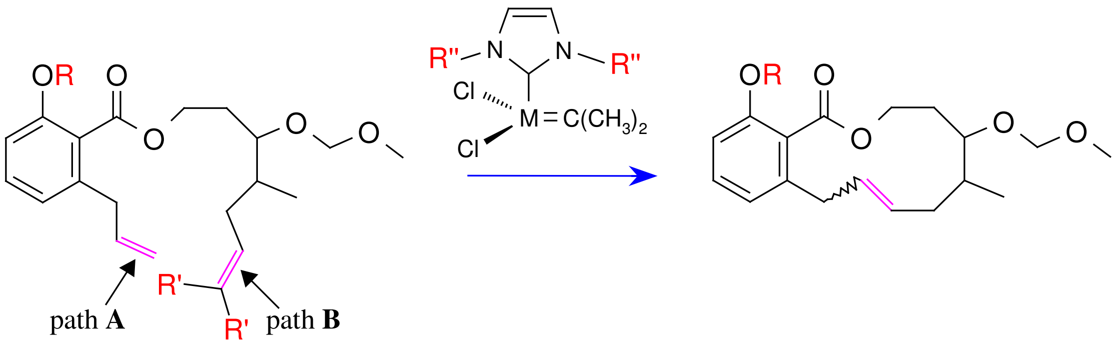
Involved: K. Angermund, M. Bühl, Z. Chen, A. Fu, M. Graf, H. Hermann, M. N. Jagadeesh, V. R. Jensen, D. Koley, S. F. Vyboishchikov

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. Further targets of our investigations are fullerenes and nanotubes.

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

Previous joint studies with the Fink group on propene polymerization have 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. More recent DFT calculations indicate that the larger deviations at higher temperatures are due to the onset of epimerization (back-skip) processes not included in the original model, while the activation of other internal motions does not play a significant role according to Car-Parrinello molecular dynamics (CPMD) simulations. A systematic DFT investigation of zirconocene-catalyzed norbornene oligomerization has revealed qualitative differences compared with ethylene (e.g., with regard to the resting state and the relative energies of the relevant agostic conformers), and has given quantitative measures for stereochemical endo/exo and syn/anti preferences. In the course of this work, it has become apparent that σ-bond metathesis reactions are feasible in norbornene oligomers, with a computed free energy barrier of 12 kcal/mol in the dinorbornyl chain, which rationalizes the experimentally (X-ray) observed C7 linkage in such systems [364].

In a collaborative project with the Fürstner group, we have studied olefin metathesis reactions catalyzed by Ru-based carbene complexes. For the parent system $Ru(CH_2)(PH_3)(X)Cl_2$ with $X=PH_3$ or $X=C_3N_2H_4$ (Arduengo carbene ligand), the DFT calculations show [141] that the dissociative pathway is favored and that the incoming olefin coordinates trans to X (without a barrier) before inserting in the rate-determining step to form the intermediate metallacycle. In an attempt to understand the stereochemistry observed in the Fürstner group during the synthesis of salicylihalamid and related model compounds (Z/E preferences) we have investigated the mechanism for the ring-closing metathesis (RCM) reaction of large sterically hindered α,ω-olefins considering four substrates, two catalysts, and two possible pathways (see Figure). We find that the stereochemistry is always determined in the second metathesis reaction, but the rate-determining step may be different for different substrates, catalysts, and pathways. Good agreement with the experimentally observed stereochemistry is only achieved when using the real catalysts and substrates in the DFT calculations. The comparison with simpler models provides insight into the role of the mesityl substituents in the catalyst and other factors that influence the stereochemistry .



Survey of RCM reactions studied computationally: Substrates I (R=R'=H), II (R=CH_3, R'=H), III (R=H, R'=CH_3), IV (R=R'=CH_3); model catalyst with R"=H, real catalyst with R"=mesityl.

A cooperation with the Gooßen group addresses palladium-catalyzed cross coupling reactions. The oxidative addition of aryl halides to a Pd(0) complex is the initiating step in these reactions. According to mechanistic studies by Amatore and Jutand, three-coordinate Pd(0) complexes with a counteranion ligand are present initially, and it has therefore been proposed and commonly accepted that the oxidative addition yields five-coordinate Pd(II) intermediates. Our DFT calculations suggest a different mechanism, with the aryl halide coordinating to Pd via the halide atom to form a four-coordinate complex, that subsequently rearranges to the desired addition product without ever forming a five-coordinate intermediate [354]. This work has been triggered by analogous findings in extensive DFT studies on Pd-catalyzed cross coupling reactions between phenylboronic acid and acetic anhydride where the complete catalytic cycle (including oxidative addition, transmetalation, isomerization, and reductive elimination) has been computed in four variants in order to gain mechanistic insight.

Further collaborative DFT work within the Institute concerns the enantioselectivity of Rh-catalyzed hydrogenation of functionalized olefins (Reetz group, see also section 2.5.5), the properties of the proton sponge 4,9-dichloroquino[7,8-*h*]quinoline and its catalytically active palladium complexes (Schüth group), and the enantioselectivity of proline- and 2-methylproline-catalyzed α-alkylation of aldehydes (List group).

Several DFT studies have been carried out without involvement of experimental groups from the Institute, for example on the binding of dinitrogen to the FeFe cofactor in Fe-only nitrogenase [174] and on valence trapping in a mixed-valent dimanganese complex [329] (see also section 2.5.6). The initial activation of Pt-based precatalysts for hydrosilylation has been elucidated in an external cooperation with an industrial partner [64]. Finally, DFT calculations have been used in combination with ab initio and semiempirical calculations to investigate fullerenes and nanotubes; topics include the properties of C_{20} [335] and C_{50} [382], the NMR spectra of fullerene anions [283], heterofullerenes [66,179,223,358], the structure and stability of Si_{60} and Ge_{60} cages analogous to C_{60} [181], and the structure and reactivity of nanotubes [184,336].

Publications resulting from this research area: 64, 66, 136, 141, 174, 178-182, 223, 283, 329, 335, 336, 354, 358, 364, 382, 432

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

Cooperations: R. Blom (SINTEF, Oslo, NO); M. S. Brookhart (Chapel Hill, USA); Z. Cao (Xiamen, CN); F. Diederich (Zürich, CH); G. Fink (Mülheim/Ruhr, DE); A. Fürstner (Mülheim/Ruhr, DE); L. Gooßen (Mülheim/Ruhr, DE); A. Hirsch (Erlangen, DE); S. Nagase (Okazaki, JP); M. Rabinovitz (Jerusalem, IL); 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: Z. Chen, R. Kevorkiants, D. Khoroshun, A. Koslowski, 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. Applications are usually motivated by requests from experimental partners or by topical chemical problems, but they also serve to explore the limits of new methods and codes.

Results: Over the past years, we have worked on semiempirical methods that go beyond the standard MNDO model by including orthogonalization corrections at the NDDO level. This has led to two new approaches labelled OM1 and OM2 (orthogonalization models 1 and 2) which offer significant improvements over established MNDO-type methods in several areas, including conformational properties, hydrogen bonds, reaction barriers, and electronically excited states. In the reporting period, the parameterization of the OM3 variant has been completed, which neglects certain of the less important OM2 terms. OM3 is somewhat faster than OM2 and has similar overall accuracy. Parameters for the elements H, C, N, O and F are now available for OM1, OM2 and OM3.

The improved description of electronically excited states in OMx methods will facilitate realistic studies of photochemical reactions in larger organic molecules. For this purpose, we have implemented the GUGACI method in a semiempirical context [237] such that general CI expansions can be treated efficiently in a relatively small active space. This in-core code is quite flexible and allows for CI calculations with up to about 100000 configurations, for all excitation classes up to full CI. It incorporates an analytic GUGACI gradient. Analytic integral derivatives have been programmed up to now only for MNDO-type methods, but not for OMx methods. For the latter, we have written a semi-analytic GUGACI gradient code which handles all the expensive steps analytically and evaluates only the integral derivatives numerically, leading to the same scaling behaviour as the fully analytic implementation.

Using the GUGACI code we have extended previous validations of OMx-CI methods for electronically excited states. In the case of vertical excitation energies, comparisons with CASPT2 reference data for 332 singlet-singlet and 103 singlet-triplet transitions indicate typical OMx deviations of 0.4 eV overall, and of 0.3 eV for the lower valence transitions, whereas MNDO-type methods systematically underestimate the excitation energies by more than 1 eV. Further validation studies for excited-state geometries and other properties are in progress. An independent validation of OM2-CI has been done in joint work with the Elstner group (Paderborn) who find excellent agreement with high-level ab initio CI results for models of retinal proteins.

In a collaboration with the Engels group (Würzburg) we have worked on a semiempirical parameterization for excited states and chiroptic properties at the OM2-CI level using ab initio reference data. The parameter sets derived in Würzburg show significant improvements in the excited-state target properties, but at the expense of larger discrepancies for ground-state properties, and they will thus only be of limited utility. We have therefore decided to go for a second OM2-CI parameterization that aims at a balanced treatment of ground and excited states. We are currently in the process of generating the needed high-level ab initio reference data.

A number of other methodological projects have been completed in the reporting period. These include the implementation of linear scaling techniques in our semiempirical program (using the conjugate gradient density matrix search as a replacement for diagonalization), the generation of derivative code by automatic differentiation of Fortran77 programs (using the ADIFOR software), and the development of improved parameterization tools (using a combination of systematic searching, genetic algorithms, and local nonlinear least-squares minimizations).

Further methodological advances have been pursued in three external cooperations. A state specific transfer Hamiltonian has been defined and parameterized for selected reactions with regard to CCSD reference data, for use in large-scale molecular dynamics simulations (Bartlett group). An interface to the Xiamen valence-bond (VB) program has been written to explore the merits and limitations of semiempirical VB calculations (work with Wei Wu during his visit as guest professor). A smooth solvation model SCOSMO has been developed in the context of semiempirical methods with an spd-basis, which provides smooth energies and gradients by overcoming discretization errors and will therefore allow numerically more stable geometry optimizations and molecular dynamics simulations in solution (cooperation with the York group).

Concerning applications, the performance of semiempirical MNDO-type methods in fullerene chemistry has been validated by extensive comparisons with B3LYP/6-31G* results for relative energies and nucleus-independent chemical shifts [183]. This provides additional justification for employing these methods in some of our recent work on fullerenes and nanotubes [184,336,382]. In a collaboration with the Suhm group (Göttingen), we have studied large N_2O clusters containing up to 177 molecules at the AM1 level. The simulated spectra at different cluster sizes show excellent agreement with the observed spectra, and the calculations thus help to shed light on the microscopic structure of these nanosystems [359].

Publications resulting from this research area: 183, 184, 237, 286, 289, 336, 359, 382

External funding: Fonds der Chemischen Industrie

Cooperations: R. J. Bartlett (Gainesville, USA); B. Engels (Würzburg, DE); M. Elstner (Paderborn, DE); S. Patchkovskii (Ottawa, CA); M. A. Suhm (Göttingen, DE); W. Wu (Xiamen, CN); D. M. York (Minneapolis, USA)

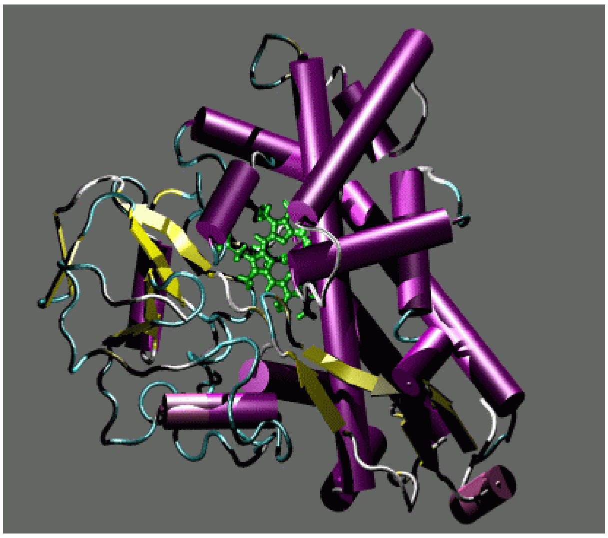
2.5.4 Research area "Combined Quantum Mechanical/Molecular Mechanical Methods" (W. Thiel)

Involved: A. Altun, I. Antes, S. R. Billeter, M. Bocola, J. Kästner, H. Lin, N. Otte, N. Reuter, J. C. Schöneboom, H. M. Senn, F. Terstegen, 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: The European QUASI project (Quantum Simulations in Industry, 1998-2001) has led to the development of a flexible and general QM/MM environment with an open-ended design that allows the integration of many QM and MM codes in a modular manner. The resulting ChemShell software has been described along with the underlying theory and some illustrative applications [279]. In the reporting period, we have extended this software according to our needs. The modules for geometry optimization have been enhanced by introducing improved microiterative techniques in general, and three-layer optimizations for transition state searches in particular. In the module for molecular dynamics (MD) simulations, a number of features have been added that provide new functionality (friction dynamics, Nose-Hoover chain thermostat with corresponding integrator, additional SHAKE constraints, etc.) and better control (error estimates, convergence of thermodynamic integration, etc.). A new interface has been written for the MOLPRO code from the Werner group (Stuttgart) to access high-level ab initio QM methods within ChemShell, including local correlation approaches that are expected to be essential for large QM regions. The existing interface to the GROMOS code from the van Gunsteren group (Zürich) has been upgraded to conform to the present GROMOS version and to handle the recently proposed polarizable force fields in GROMOS. The performance of the latter in QM/MM approaches is currently evaluated in a joint project.

Our most extensive QM/MM application during the past three years has addressed the catalytic cycle of cytochrome P450cam at the B3LYP/CHARMM level (B3LYP hybrid density functional, CHARMM force field), in close collaboration with the Shaik group (Jerusalem). Several intermediates have been characterized including the resting state [419], the pentacoordinated ferric and ferrous complexes, the last experimentally accessible intermediate Cpd 0, the yet unobserved reactive species Cpd I [120], and the product-enzyme complex [377]. Moreover, some key reaction steps have been investigated, in particular the stereospecific camphor hydroxylation by Cpd I [418] and the proton transfers leading from Cpd 0 to Cpd I. 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 40-130 atoms) allows us to assess the role of the protein environment in P450cam. In the following, we summarize a few selected results. The QM/MM calculations correctly give a low-spin resting state and high-spin pentacoordinated complexes, and they reproduce the known experimental geometries and spectroscopic parameters of these species quite well. The protein environment causes a notable differential stabilization of the high-spin states in the resting state, and it inverts the relative energies of two close-lying quintet electromers of the pentacoordinated ferrous complex. The experimentally yet unknown Compound I has almost degenerate doublet and quartet states, with the doublet slightly more stable. It adapts its electronic structure to the environment: when going from the gas phase to the enzyme, the spin density distribution changes from a predominantly sulfur-based radical to a porphyrin-based radical, due to the stabilization of electron density at sulfur by hydrogen bonding interactions with nearby residues. Camphor hydroxylation by Cpd I follows a rebound mechanism with two-state reactivity: the initial hydrogen abstraction involves a sizable barrier in both spin states (slightly lower in the doublet), whereas the subsequent radical recombination (rebound) has essentially no barrier in the doublet and a small but finite barrier in the quartet, for analogous reasons as in the gas phase (orbital correlations). The protein environment does not change the basic mechanism of hydroxylation, but it does modulate the electronic structure and the relative energies along the reaction pathway. Our QM/MM calculations do not support the recent proposal that spin density at heme side chain carboxylates is essential for catalytic activity by Cpd I. Three local minima are found in QM/MM optimizations of the product-enzyme complex which is consistent with EPR observations of three distinct species. Finally, reasonable agreement between computed and observed spectroscopic constants is obtained for heme model compounds, the resting state, and some known intermediates so that the corresponding theoretical predictions for Compound I may be helpful in future attempts to detect it by EPR or Mössbauer spectroscopy.



Cytochrome P450cam (heme in green)

Another enzyme project involves a collaboration with the Reetz group on directed evolution in lipases, where we employ classical MD and QM/MM calculations in an attempt to understand the enantioselectivity in the lipase-catalyzed ester hydrolysis and its optimization through successive mutagenesis. In the first stage of this project, we have performed 1 ns CHARMM-MD simulations of the relevant tetrahedral intermediates in 20 enzyme/substrate combinations, with the *R* and *S* enantiomers of α-methyldecanoic acid ester serving as substrates for the wild-type lipase from *Pseudomonas aeruginosa* and for nine selected mutants [311]. The resulting geometric and energetic changes during these MD runs allow an interpretation of some experimentally observed effects of mutations, particularly with regard to the "hot spots" at residues 155 and 162, in terms of a steric relay or the creation of a new binding pocket [311], thereby providing insight into remote and cooperative effects of mutations. In the second stage of the project, we have located the relevant stationary points for the rate-determining step (Michaelis complex, transition state, and tetrahedral intermediate) through BLYP/CHARMM geometry optimizations and evaluated the electrostatic influence of individual residues on the reaction barrier by single-point QM/MM calculations with zero MM side chain charges on the corresponding residue. In the case of *Bacillis subtilis* lipase A, this prescreening identifies His76 as a potential "hot spot" which has been confirmed experimentally. These two examples indicate that theoretical modeling can rationalize and predict "hot spots" in directed evolution.

A number of other biomolecular systems have been studied at the QM/MM level during the reporting period. An extensive QM/MM calibration study on the conversion of dihydroxyacetone phosphate into glycerinaldehyde 3-phosphate by triosephosphate isomerase (TIM) has been completed and published [84] which supports a four-step proton transfer via an enediol, with involvement of neutral His95 acting as a proton donor. In p-hydroxybenzoate hydroxylase (PHBH), the rate-determining OH transfer from the hydroperoxide of the cofactor (flavin adenine dinucleotide) to the substrate (p-hydroxybenzoate) has been investigated at the AM1/GROMOS level; the free energy barriers from thermodynamic integration do not differ much from the average energy barriers obtained in a series of separate optimizations for different snapshots, which implies that entropic effects are not overly important in this case. In preparation of planned QM/MM studies on electronically excited states of green fluorescent protein (GFP) and photoactive yellow protein (PYP) we have derived the necessary MM parameters for the GFP chromophore and carried out exploratory classical MD simulations for GFP and PYP in the ground state [4,115]. Finally three new QM/MM projects have been started recently in the framework of external cooperations, which involve mechanistic studies on 4-oxalocrotonate tautomerase and some synthetic analogues (with E. Keinan, Haifa), on the Bergman cyclization of dynemicin A in a DNA environment (with D. Cremer, Göteborg), and on enzymatic C-F bond formation by a fluorination enzyme (with D. O'Hagan, St. Andrews).

Publications resulting from this research area: 4, 84, 115, 120, 137, 186, 210, 279, 311, 377, 418, 419

External funding: German-Israeli Foundation for Scientific Research and Development (GIF project I-626-44.5); Deutsch-Israelische Projektkooperation (project DIP-F.6.2)

Cooperations: C. R. A. Catlow (London, UK); D. Cremer (Göteborg, SE); K.-E. Jaeger (Jülich, DE); E. Keinan (Haifa, IL); F. Neese (Mülheim/Ruhr, DE); D. O'Hagan (St. Andrews, UK); M. T. Reetz (Mülheim/Ruhr, DE); A. Schäfer (BASF, Ludwigshafen, DE); S. Shaik (Jerusalem, IL); P. Sherwood (Daresbury Laboratory, UK); W. F. van Gunsteren (Zürich, CH); H.-J. Werner (Stuttgart, DE)

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

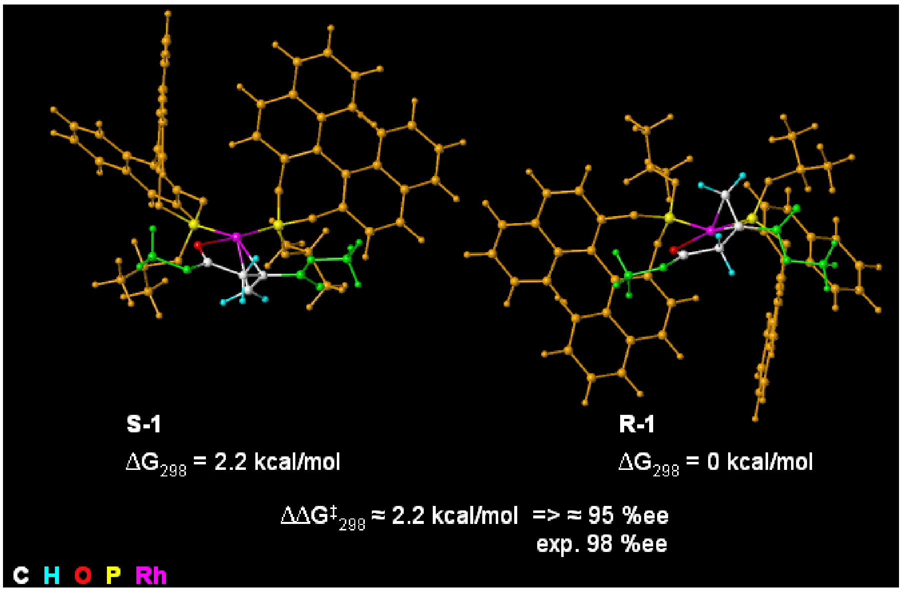
Involved: M. Graf, H. Hermann

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:

1. Ziegler-Natta polymerization of norbornene: Based on our previous work on the stereospecificity of the polymerization of propene using zirconocene catalyst models of the transition states of all possible insertion steps of the ethane norbornene copolymerization were calculated. Their relative energies can be correlated to the microstructure of the co-polymer (for further details see Thiel 2.5.2). Based on a crystal structure of the pentamer and NMR data of the pentamer and heptamer a model for polynorbornene was derived which explains the insolubility of the homopolymer (for further details see Fink 2.1.6).

2. Enantioselective Rh-catalyzed hydrogenation of functionalized olefins: Experiments with monodentate phosphorus compounds as ligands in the Rh-catalyzed hydrogenation of functionalized olefins show high enantioselectivity (see Reetz 2.1.1 for further details). To investigate the cause of this enantioselectivity DFT calculations of four different low-energy reaction pathways have been undertaken. The results of the still ongoing research suggest 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) for these non-



chelating phosphorus ligands the formation of the more stable, "major" adduct (R1) determines the enantiomeric outcome of the reaction.

Publication resulting from this research area: 432

External funding: none

Cooperations: G. Fink (Mülheim/Ruhr, 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: S. Grigoleit, P. Imhof, F. T. Mauschick, M. Repisky, R. Schurhammer

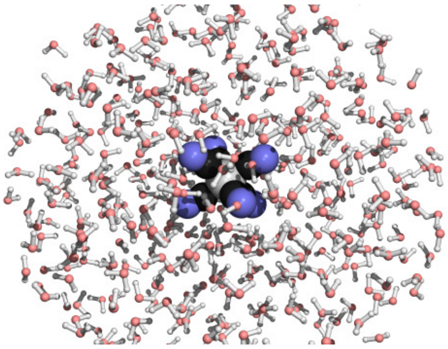
Objective: Our research focuses on the application of modern quantum-mechanical methods to obtain information on structural, spectroscopic, and energetic properties of transition-metal compounds. Special attention is called to the simulation of temperature and solvent effects on the properties of interest,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

Results:

1. NMR chemical shifts of transition-metal compounds: Multinuclear NMR spectroscopy is a prime source of information for transition metal complexes, and chemical shifts, including those of the metal nuclei, can be well described with the modern tools of density-functional theory. Using static equilibrium geometries, for instance, trends in experimental $\delta(^{55}Mn)$ and $\delta(^{49}Ti)$ values have been reproduced reasonably well. In collaboration with experimental groups, computed chemical shifts have facilitated the interpretation of ^{1}H and ^{13}C resonances in organopalladium and -platinum complexes.

Molecular dynamics (MD) simulations, a popular means of going beyond such static computations, have been used to model the effects of finite temperature on the NMR properties by averaging them over the trajectories. This methodology, based on Car-Parrinello MD for pristine complexes, has been applied to numerous Ti-, V-, Mn- and Fe-complexes. Despite no systematic increase in accuracy, the accord between theoretical shifts with experiment is improved in many cases upon thermal averaging.

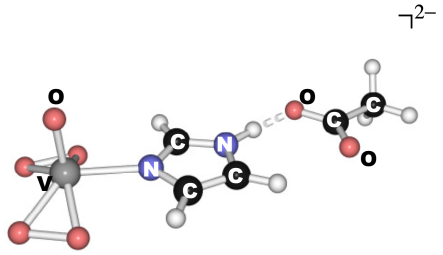
This MD-based approach can be extended to include the solvent explicitly. Simulations of aqueous vanadate and permanganate have revealed only small solvation effects on $\delta(^{51}V)$ and $\delta(^{55}Mn)$. In contrast, $\delta(^{57}Fe)$ of $Fe(CN)_6^{4-}$ is more sensitive to thermal and solvent effects, and errors exceeding 1000 ppm can occur if the latter are neglected. For this system, a new MD approach based on a mixed quantum-mechanical/molecular-mechanical description of the solute/solvent system has been successfully validated, thus extending the toolbox for the computation of chemical shifts in solution.



Snapshot from a QM/MM simulation of aqueous $Fe(CN)_6^{4-}$.

A perturbational approach to evaluate quantum mechanical zero-point effects, which are not accounted for in the MD simulations, has been adapted and tested for its application to transition-metal chemical shifts. These zero-point corrections turn out to be qualitatively similar to the MD-based classical thermal effects, but are smaller in magnitude than the latter. Thermal averaging of the chemical shifts can be rationalized in terms of the elongation of the metal-ligand bonds from their equilibrium values.

2. Mechanistic Studies in Homogeneous Catalysis: Theoretical computations of key intermediates and transition states are valuable complements for the elucidation of reaction mechanisms and catalytic cycles. Contributions have been made to unravel the mechanism of olefin metathesis with Ru-carbene complexes. A strategy towards computational design of new catalysts, namely selection of catalytic systems with low or moderate activity, identification of the rate-determining barrier in the cycle, and prediction of substituent effects on this barrier, has been applied to a number of systems. Using this approach, specific predictions have been made how to increase the activities of Ti-β-diketonates in ethylene polymerization, of Fe-cyclopentadienyl complexes in silane alcoholysis, and of peroxovanadium(V) species in olefin epoxidation. In the latter study, the key role of a specific hydrogen bond has been highlighted, which has implications for the further design of biomimetic catalysts.

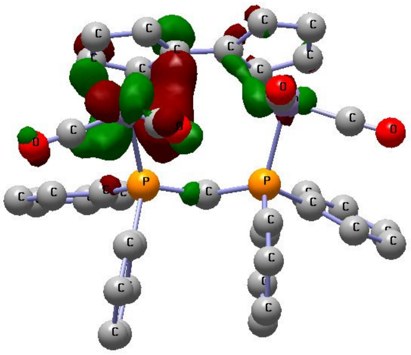


A strong hydrogen bond to the imidazole moiety significantly reduces the rate-limiting barrier in catalytic olefin epoxidation.

In collaboration with K. Pörschke, intramolecular rearrangement pathways of Ni-allyl complexes have been computed, which account for the observed dynamical processes.

3. Open-shell species: MD simulations have been performed for $V(CO)_6$, in order to study the dynamical aspects of the distortions in this prototypical Jahn-Teller system. At cryogenic temperatures, the system stays within the potential well of a D_{3d}-symmetric minimum. At room temperature, the fluctuations are so large that the averaged structure is essentially O_h-symmetric. After a reinterpretation of the low-temperature EPR spectrum, effected in the group of Prof. Willner, the observed hyperfine coupling constants agree well with those computed for the static D_{3d} form.

The electronic structure of a dinuclear mixed-valent manganese complex, linked by a fulvalene bridge and a bidentate phosphine, can depend sensitively on the density functional used in the calculation. Only when the odd electron is essentially localized on



The SOMO of a mixed-valent dimanganese complex is largely localized on one Mn center.

one of the metal centers, as with the popular B3LYP functional, are observed IR vibrational frequencies reproduced computationally. The delocalized, symmetrical transition state is only a few kJ/mol higher in energy, indicative of a highly fluxional character, and consistent with the findings that the localized structure can only be detected with the fastest spectroscopical methods.

Publications resulting from this research area: 3, 20, 21, 22, 23, 24, 61, 131, 141, 151, 161, 171, 172, 323, 324, 326, 327, 328, 329, 357, 427

External funding: DFG (Heisenberg-fellowship for M. B., Post-doc positions for P. I. and S. G.); Humboldt Foundation (Research Fellowship for R. S.); DAAD

Cooperations: S. Bienz (Zürich, CH); H. Bönnemann (Mülheim/Ruhr); C. J. Elsevier (Amsterdam, NL); H. Fleischer (Mainz); J. F. Hartwig (Yale, New Haven, USA); D. Hnyk (Prague, CZ); M. Kaupp (Würzburg); K. Pörschke (Mülheim/Ruhr, DE); W. Thiel (Mülheim/Ruhr, DE); G. Wipff (Strasbourg, FR); K. Jonas (Mülheim/Ruhr, DE); B. Wrackmeyer (Bayreuth, DE)

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 are being developed for online monitoring, for high-throughput screening systems, and for characterization of very sensitive or transient species, 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, H. Bruns, G. Lüder, P. Walkamp, L. Winkel, K. Mehler

The "Technikum" of the Max-Planck-Institut für Kohlenforschung includes the central high pressure laboratories, large scale synthesis facilities, central solvent purification and drying distillation apparatus, the central treatment of waste chemicals and a glove box for shared access. The involved co-workers are specifically skilled for the execution of the associated tasks. One chemical engineer (A. Brinkmann) and one laboratory assistant (L. Winkel, successor of G. Lüder who retired in June 2004) are mainly concerned with the provided service who are partially supported by our current trainees (H. Bruns and P. Walkamp).

The high pressure laboratories provide equipment and support to carry out chemical reactions under elevated pressure to all groups of the institute. High pressure stainless steel reactors of various designs are available from 50-5000 ml volume for batch wise synthesis and exploratory studies. These central facilities were intensively used in the reporting period as the utilisation ratio was 100% for the larger boxes (No. 1-5) and between 60% and 100% for the medium size (No 6-13) and small boxes (14-27). According to the legal regulations concerning pressure vessels, large-scale reactors and pressure cylinder were regularly controlled by the external Technical Inspection Agency (TÜV) whereas small ones (which don't fall in the legal regulations) are checked by especially trained co-workers of the Institute's mechanical workshop (K. Gräfenstein and W. Kersten) in clear defined operation agreements.

Facilities for large scale synthesis include various glass reactors of up to 200 l reaction volume, some of which can be operated under an inert atmosphere. As a part of a research cooperation with Aluminal GmbH, 53 kg of a Al/Mg-electrolyte were synthesized (co-operation F. Schüth group/Technikum). In addition 6.5 kg of magnesium-anthracene were prepared which is used as a drying agent for tetrahydrofuran. Further centrally purified, dried, and deoxygenated solvents (about 1800 l per year) are dichloromethane (since January 2004), diethylether, n-pentane and toluene. The water content of these solvents is steadily controlled by coulometric Karl Fischer titration before handing out to the individual scientific groups (since October 2003). Moreover about 1800 l ethyl acetate and 4600 l *iso*-hexane were purified by simple distillation and about 1100 l n-pentane were rectified annually. Every year about 20000 l of non-halogenated solvents, 1800 l of halogenated solvents and 1000 kg of solid special waste are accepted and applied to an appropriate and environmental benign waste disposal.

3.2 Chromatography and Separation Science (D. Belder)

The chromatography group serves as central facility for the analysis and isolation of compounds in chemical mixtures. A section of the group is also engaged in independent research projects in electrophoresis and microfluidics. 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 decentral facilities.

Multidimensional Large Scale Gas Chromatography (Prep.-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

Objective: We aim on the development of techniques and instrumental configurations to realise integrated micromachined devices for fast analyses and multiplexed high throughput screening. We mainly focus on microchip-electrophoresis (MCE), which is currently the most successful microfluidic "lab-on-a-chip" technique.

Results: Microfluidic channels of glass chips have been coated with poly(vinyl alcohol) (PVA) which resulted in an improved separation performance in MCE. This could be demonstrated by video microscopy of electrophoretic separations of fluorescently labelled amines, as shown in figure 1. While a distorted sample zone was injected using uncoated chips the use of PVA-coated devices resulted in improved peak shapes and reduced band broadening enabling sub-second separations utilizing separation length of only 650 µm.

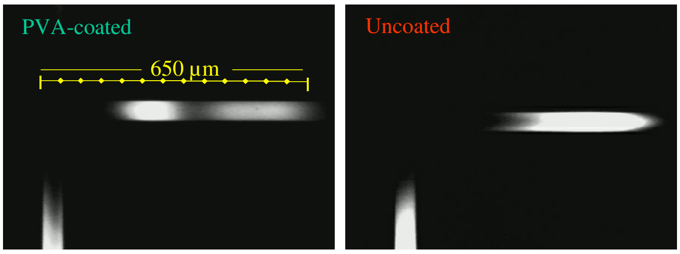


Figure 1. Improved separation performance using PVA coated chips in MCE visualized by video microscopy

PVA-coatings could also be applied to microfluidic devices manufactured by powder blasting, which is a new economic alternative to classical wet chemical etching. Powder-blasted chips have, however, rarely been used in MCE as the rough channel surfaces hamper high resolution electrophoretic separations. We could show that internal coatings can greatly improve the separation performance of powder-blasted channels which makes them now applicable to high performance microchip-electrophoresis.

An important application of these developed techniques was the realisation of fast chiral separations on microfluidic devices applying very high field strengths on a special homebuilt system. The fastest chiral separation could be obtained in 720 ms, which is currently the fastest chiral separation reported, see figure 2. This demonstrates the potential of MCE for the realisation of integrated systems for chiral high throughput screening.

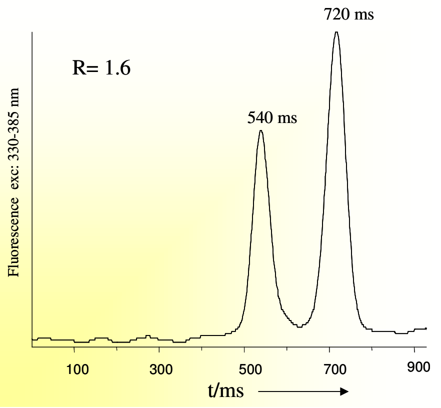


Figure 2. Sub-second chiral separation of DNS-tryptophan

In order to widen the applicability of this technique we recently developed an instrument enabling native fluorescence detection utilising a deep UV-laser. This enabled for the first time on-chip fluorescence detection of unlabelled small aromatic compounds and proteins. This new detection technique is currently applied in a joint project with M.T. Reetz to realise an integrated chip based device for high throughput screening of enantioselective catalysts.

Publications resulting from these research areas: 6, 7, 156, 157, 158, 250, 251, 395, 429

External funding: DFG: BE 1922/1-1; BE 1922/1-3; BE 1922/3-1;
Egyptian Government scholarship (stipend to K.M. Tolba)

Cooperations: M. T. Reetz (Mülheim/Ruhr, DE); M. L. Riekkola (Helsinki, FI)

3.3 Mass Spectrometry (W. Schrader)

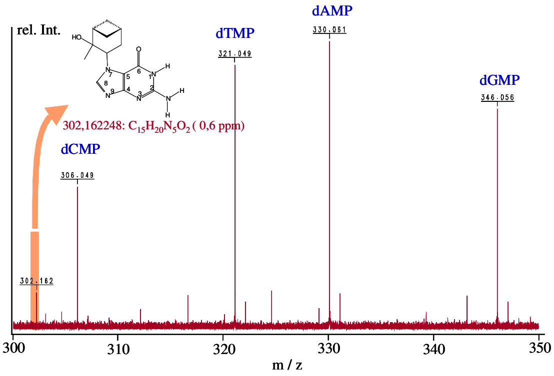
The mass spectrometry group is a service and research group for both MPI institutes (Kohlenforschung and Bioanorganische Chemie) for the analysis of a wide variety of samples. The very diverse nature of problems makes it necessary to use a wide range of ionization techniques and instruments with a high quality of measurements. A rapid completion is a strong priority, that allows the synthetic chemists to obtain the results and implement them into their work. This service includes the interpretation of the obtained data for immediate use for the chemists. An important part of the interpretation is the maintenance of the spectra databases, which allow a faster and more detailed interpretation and includes the software package MassLib that was developed at the institute for this purpose. The number of analyses measured varies between 6000-8000 samples annually, resulting in more than 12000 identified compounds.

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

Special measurements: The purchase of a new Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR MS) has allowed to be more flexible with the analyses and it also enabled to analyze a larger variety of samples that was not possible before. The machine was installed in 2002 and the staff was trained on it afterwards. Since then the instrument is fully involved in all kinds of measurements. FTICR MS allows faster and highly resolved analysis of the samples, giving also accurate mass data. Other special measurements of mixtures with impurities, low volatile compounds, and accurate mass measurements are still offered.

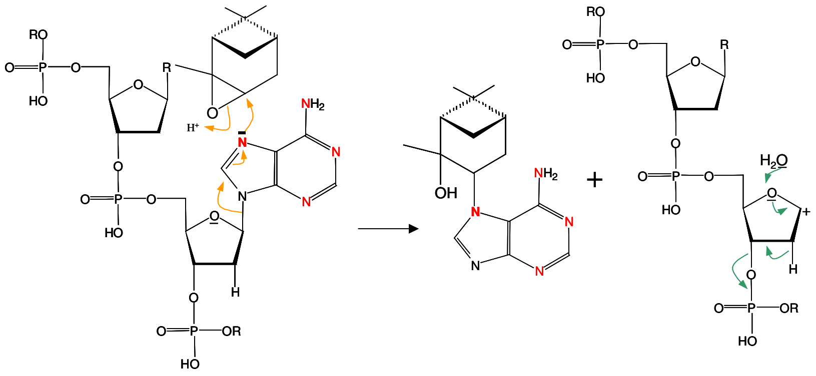
The main theme of the **research interest** is the development and utilization of analytical instrumentation to investigate complex reactions. In this regard some cooperations developed and include two projects with groups in the Institute and two cooperations outside of the Institute. The project of investigating nucleation in solution with the group of Prof. Schüth continued. Here, it was possible to construct and built three different reactors to measure the time-dependent formation of silicate species in solution. While other analytical methods allow to either study the precursor molecules or the resulting solids, the nucleation process is still in question. Although the nature of the components makes a detailed study difficult, it was possible to determine the formed species along the time axis of the reaction, and study optimized conditions up to the crystallization point.

Another project involves the investigation of organocatalytic reactions to develop leads for a better understanding of mechanisms and the catalytic cycle. This project just started in cooperation with the List group.



MS spectrum of digested DNA, showing mononucleotides and the N7-guanin adduct

One project included the investigation of the gas phase reaction of monoterpenes with ozone to form an organic aerosol in the atmosphere and the influence of the formed terpenoids on organisms. Here it was shown that terpenoids, especially compounds with an epoxide group, like α-pinene oxide, can react with DNA to form adducts. DNA adducts are markers that allow to observe the influence of xenobiotic compounds on organisms, which in theory can lead to a tumor development. Two different enzymatic approaches were used to study the reaction of terpenoids with DNA: first, the use of nuclease P1 and, second, a combination of the enzymes benzonuclease with an alkaline phosphatase. While nuclease P1 digests DNA to form mononucleotides the benzonuclease produces a number of oligonucleotides of different chain length, which leads to oligonucleotides of the form n-nucleoside-(n-1)-phosphate.



Proposed mechanism leading to formation of N7-guanine adduct and subsequent hydrolytic cleavage

The results indicate a reaction between α-pinene oxide and DNA. A total of 10 different adducts have been characterized using MS and MS/MS studies and accurate mass determinations. Additionally, a possible mechanism was proposed that illustrates the effect of DNA alkylation by leading to a strand break after hydrolytic cleavage.

Publications resulting from these research areas: 121, 421

External funding: none

Cooperations: F. Schüth, (Mülheim/Ruhr, DE); B. List (Mülheim/Ruhr, DE);M. T. Reetz (Mülheim/Ruhr, DE); T. Hoffmann (Mainz, DE); J. T. Andersson (Münster, DE)

3.4 Nuclear Magnetic Resonance (R. Mynott)

The NMR Department is equipped with five high resolution NMR spectrometers with magnetic field strengths from 7.05 to 14.1 Tesla (^{1}H resonance frequencies of 300 to 600 MHz) and two spectrometers with magnetic field strengths of 7.05 and 11.7 Tesla (^{1}H: 300 and 500 MHz, respectively) for solid state studies. It provides the following services:

Fully automatic measurements (open access): Two NMR spectrometers with proton frequencies of 400 and 300 MHz, respectively, are available to the scientific and technical staff round the clock. The NMR data are acquired, processed and plotted fully automatically. 2D NMR spectra (proton COSY and ^{1}H,^{13}C correlated spectra) can be run on the 400 MHz spectrometer. In 2003, more than 27700 spectra (^{1}H, 54%; ^{13}C, 37%; and ^{31}P, 8%) were measured in automatic mode.

To ensure that waiting times are kept as short as possible, both instruments have been set up with a selection of standard experiments for which the measurement parameters are predefined and cannot be altered by the users.

Routine measurements. Samples can be submitted for routine measurements by our operators on two further 300 and 400 MHz spectrometers. Such measurements are required, for example, if the standard parameters must be altered to optimize the spectra, low temperature measurements are needed, reactions followed in the NMR tube, or other cases where special treatment is required.

Special Studies are carried out in close cooperation with the chemical research groups. A much more flexible approach is possible to the analytical challenges presented by each molecule and a much greater choice of NMR techniques is available than is practicable for automatic or routine analyses. The NMR group selects and carries out the NMR experiments on our 600 and 400 MHz NMR spectrometers and interprets the results in detail. Methods for determining connectivities include diverse variants of HSQC or HMQC, HMBC, TOCSY and inverse TOCSY, and proton-detected 2D-INADEQUATE for carbon frameworks. In nitrogen-containing compounds, ^{15}N NMR is a valuable tool for determining connectivities. ^{13}C NMR, NOESY and coupling constant data are used for stereochemical analyses, while structural dynamics are investigated using line shape analysis and 2D exchange spectroscopy.

The main emphasis of our current work is the characterization of organic and organometallic compounds using a wide range of 1D and 2D NMR techniques:

- Determination of the structure, stereochemistry and conformations of organic and organometallic compounds from various groups in the Institute, in particular from the groups of A. Fürstner, B. List, M. Haenel, and M. T. Reetz.

- The characterization of pentalene complexes of the transition metals, particularly the determination of the structures of complexes with alkyl substituted pentalene ligands and the study of their molecular dynamics (cooperation with K. Jonas).
- Monitoring reactions by NMR, including the initial stages of reactions leading to the formation of nano-scaled metal colloids (cooperation with H. Bönnemann).
- Continuation of detailed NMR analyses of partially deuterated organic compounds to study reaction mechanisms (AK Leitner).
- Characterization of oligomers of norbornene prepared catalytically in hydrogen or deuterium atmospheres up to and including of the heptamer ($C_{49}H_{86}$ and $C_{49}H_{84}D_2$). A full assignment of the ^{13}C NMR spectra of was achieved using 2D INEPT-INADEQUATE and ^{13}C,^{1}H correlated spectra, supported by COSY spectra. Together with stereochemical information from the ^{1}H NMR spectrum derived from ^{1}H,^{1}H coupling constants and NOESY spectra, it was established that a σ-metathesis occurs after the third, fifth and seventh insertions. This study, part of a cooperation with AK Fink and the Department of Theory (K. Angermund), also provided the basis for the simulation of the solid state ^{13}C NMR spectrum.

Solid State NMR finds wide application in the characterization of new materials synthesized in the Department for Heterogeneous Catalysis (B. Zibrowius). This work has focussed on monitoring the various steps in the preparation of surface-functionalized mesoporous silicas and on processes occurring during the dehydrogenation/rehydrogeneration of potential hydrogen storage materials such as alkali and alkaline earth aluminium hydrides. Other work includes:

- Studies of the structures and structural dynamics of organometallic compounds, in particular five-coordinate Ni-allyl complexes (A. Rufińska).
- ^{13}C CP/MAS studies led to the discovery of new structures of polynorbornenes produced by metallocene catalysts (A. Rufińska). This led directly to the studies of the norbornene oligomers in solution (outlined above) to determine their microstructures.

External Data Processing: The NMR data from automatic and routine measurements can be downloaded by the chemists and processed further on PCs using software installed on the NMR central computer. In 2004, new processing software (Bruker, *TopSpin*) was installed on a new Linux workstation and the users in the Institute instructed on its use in internal workshops given by members of the group. The NMR Department is responsible for the installation, maintenance and administration of these programs and provides the users with technical support.

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. These research activities include methodological developments as well as high resolution electron density studies.

Service Activities: The service activities currently comprise a number of diffraction techniques like single crystal structure analysis, powder diffraction analysis, 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.

Single crystal structure analysis makes use of state-of-the-art technology based on three area detector systems positioned in front of two rotating anode X-ray generators. A broad variety of samples, ranging from inorganic via organometallic and organic to macromolecular protein crystals comprise the approximately 500 data sets collected each year. This includes an increasing number of twinned structures and the determination of the absolute configuration of crystal structures containing light atoms using Cu-K_α radiation. Statistical methods ascertain the correct assignment for products with 90% *ee*, where one in ten crystals is of the opposite hand. Hardware and software have been installed enabling the elucidation of protein crystal structures. This has been demonstrated with the known structures of lysozyme (14 kDa), streptavidin (53 kDa), and thaumatin with a molecular weight of 22 kDa (R. Goddard).

The micro-diffraction facility allows the investigation of samples with a spatial resolution better than 100 µm and to collect small angle diffraction data up to 200 Å instrumental resolution. In collaboration with F. Marlow thin film studies have been carried out.

For the routine phase identification of other polycrystalline materials three powder diffractometers are available. In-situ X-ray diffraction studies of phase transformation both at low and high temperatures are carried out in order to study the formation of metastable phases, sintering effects, segregation or decomposition reactions. Further activities in this area include structure solution of organic polycrystalline samples using direct space methods and Rietveld refinement, which has been added to the scope of methods.

Research Projects:

Electron Density Studies (E. Duman): Recently electron density studies of push-pull chromophores used in photo refractive and non-linear optic materials have commenced. This work is carried out in collaboration with Prof. Würthner (Würzburg) and will become part of a DFG priority program starting in 2005. The one electron properties of these push-pull chromophores show a strong dependence on the surrounding molecular environment, either embedded in high concentration in a polymer matrix or as part of a crystal and its field. Hence calculations based on isolated molecules or measurements in diluted solutions have a limited value for explaining and predicting the material properties. For the photo refractive material ATOP-10 we have obtained an experimental in crystal dipole moment of 25 D, which is considerably higher than the dipole moment of 15 D measured in solution.

Hydrogen Storage Project (C. Weidenthaler, F. Schüth, M. Felderhoff): Metal doped sodium alanate ($NaAlH_4$) is at present one of the most promising materials for hydrogen storage. Investigations of phase transformation processes of Ti-doped $NaAlH_4$ during de- and rehydrogenation were performed by means of powder diffraction methods. The combination of quantitative phase analysis by the Rietveld method and solid state NMR techniques enables to follow every step of de- and rehydrogenation qualitatively and quantitatively. The function of the catalyst is of fundamental interest to understand the process, but in the past little was known about the state of the catalyst. XAFS studies, in-situ high temperature powder diffraction investigations and photoelectron spectroscopy (XPS) analysis provided new insights into the state of the catalyst during the hydrogen storage and release processes.

Ion exchange of low silica zeolites. (C. Weidenthaler, W. Schmidt): Transition metal (Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}) exchanged low silica zeolites A, X, and Y were analyzed in terms of their different ion-exchange behavior, structural changes and their potential use as precursors for the generation of high surface area materials. As an example the maximum iron loading of the different zeolites was determined by repeated exchanges and the fate of the ferrous cations and their oxidation into ferric iron in different environments was investigated. The behavior of the iron cations in the bulk zeolites was monitored by Mössbauer spectroscopy, the chemistry on the surface of the zeolites by XPS spectroscopy, and the changes to the zeolite host were traced by MAS NMR spectroscopy and by XRD experiments.

Publications resulting from this research areas: 142, 177, 293, 294, 339, 351

External funding: Two year exchange program with Argentina (DAAD/PROALAR)

Cooperations: F. Würthner (Würzburg, DE); G. Punte (La Plata, AR); H. Willner (Wuppertal, DE); J.-F. Carpentier (Rennes, FR)

3.6 Electron Microscopy (B. Tesche)

In collaboration with different Departments of the Institute the activities of the group have continued, concentrated on analytical studies based on EDX and structure research through HRTEM, SEM and SPM of isolated and supported colloids, porous materials and supported catalysts for gas-phase polymerization processes. Cooperation among the various Departments with extended interaction between various research groups has become more pronounced, confirming the hopes that such inter-departmental "give and take" would lead to impact new methodical developments. The success of this line of thinking can be seen in the list of scientific publications.

Selected research project: "Development and characterization of supported catalysts for fuel cell applications"

Introduction: A great deal of recent research has centered around the preparation of nanosized transition metal colloids in the zero-valent state for fuel cells. Less is known concerning the respective metal oxides in the form of nanosized particles.

Results: The Reetz group showed that the synthesis of carbon supported nanosized platinum oxide and platinum alloys is possible without stabilizing surfactants if the hydrolysis is carried out in presence of carbon black (instant-method). A number of such materials were prepared, including PtO_2/C which was reduced to Pt/C. A potential field of application is electrocatalysis in direct methanol fuel cells (DMFCs) and polymer electrolyte membrane fuel cells (PEMFCs). In PEMFCs carbon supported platinum catalysts are used as catalysts for oxygen reduction. For that application it is desirable to possess Pt/C or Pt-alloy/C catalysts with high metal loadings and small particle sizes so that high current densities and low platinum costs for the fuel cells can be achieved. Traditionally, Vulcan XC72 is used as the carbon black. Since the Electron Microscopy Department has a long-standing interest in studying the morphology of different types of carbon blacks, these supports were provided to the Reetz group. Following immobilization using the instant method, the materials were tested as electrocatalysts (see Reetz report). The electrocatalyst derived from Printex XE2 turned out to be exceptionally active. Detailed HRTEM studies showed that the unloaded supports are very different, Vulcan XC72 has a smooth surface, while Printex XE2 is characterized by a rough surface. Moreover, under operating conditions the Pt-nanoparticles agglomerate significantly more in the case of Vulcan XC72, in contrast to the electrocatalyst derived from Printex XE2. Thus, rough surfaces prevent extensive undesired Pt-particle growth.

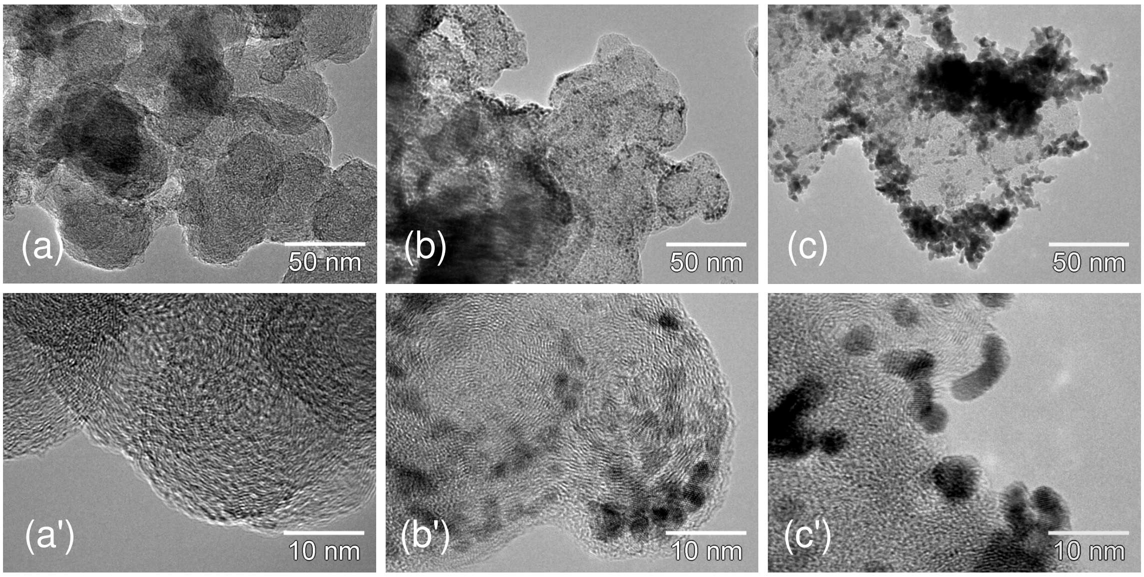


Figure 1. HRTEM images of Vulcan XC72-based materials: Unloaded carbon support in an overview (a) and high resolution (a'); PtO_x-loaded carbon support in an overview (b) and high resolution (b'); Pt/C following electrochemical reduction in an overview (c) and high resolution (c').

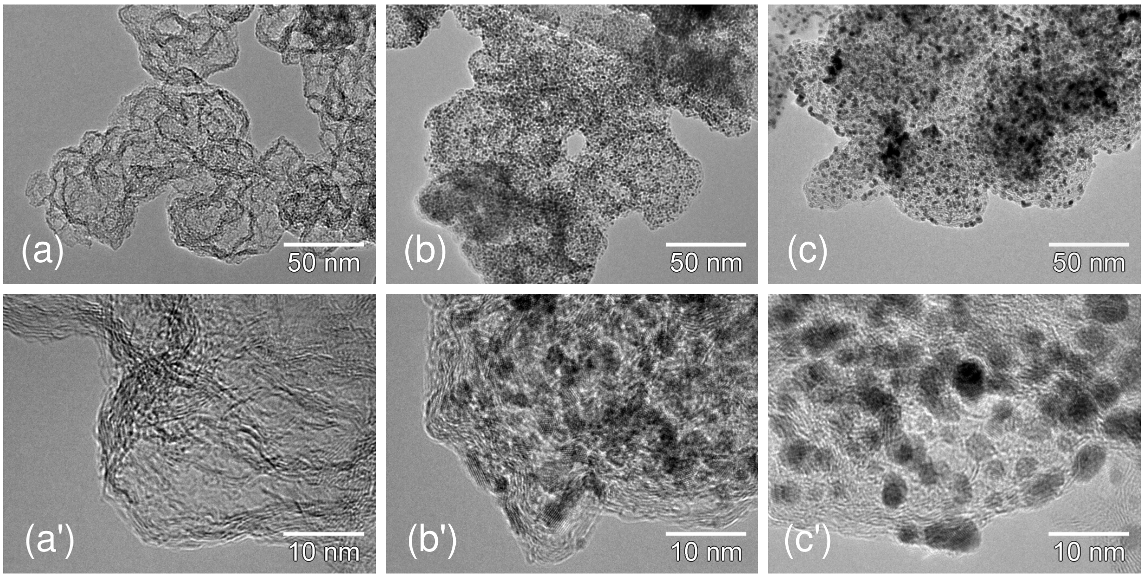


Figure 2. HRTEM images of Printex XE2-based materials: Unloaded carbon support in an overview (a) and high resolution (a'); PtO_x-loaded carbon support in an overview (b) and high resolution (b'); Pt/C following electrochemical reduction in an overview (c) and high resolution (c').

Conclusion: Our studies show that variation in the type of carbon black used in the immobilization of Pt-nanoparticles has a profound influence on the ease of Pt-loading and on the respective electrocatalytic properties.

Publication resulting from this research area: 409
External funding: none
Cooperations: G. Fink (Mülheim/Ruhr, DE); M. T. Reetz (Mülheim/Ruhr, DE);
F. Schüth (Mülheim/Ruhr, DE); Degussa (Hanau, DE)

3.7 Library and Information Management (W. Richter)

The increasing accessibility of chemical journals via the Internet also has a major impact on our library. Many journals we had traditionally subscribed to are now part of the so-called "Grundversorgung" that makes journals available on-line to every person within the Max-Planck Society. These contracts include major publishing groups like Elsevier, Springer, and Wiley. Consequently, a range of print-journals is no longer subscribed, for print-editions of Wiley journals we pay a deep discount price (10%). As all our Elsevier-subscriptions are discontinued the number of shelved journals is drastically reduced; the merger of other traditional journals adds to the decline of some 30 % of our holdings. On the other hand, many less used journals are now electronically available to us through the "Grundversorgung".

Apart from the "Grundversorgung" the library arranged licence agreements with the most important chemical publishers American Chemical Society and the Royal Society of Chemistry to achieve on-line access to the majority of their journals, with the ACS in particular to their whole archive collection.

Publications, which cannot be accessed by our on-line routes, are quickly ordered via the on-line SUBITO service – and at a low price. The inclusion of the ETH and Vienna University has increased the efficiency of the system.

Our scientists browsing or retrieving the chemical literature mainly use two routes: The "Web of Science" provided by the MPG which allows bibliographic and science citation searches and the Chemical Abstract Service which consists of the largest bibliographic and chemical structure files. Whereas the WoS (now embedded into the "Web of Knowledge") is designed by ISI as an end-user tool, the Chemical Abstracts apart from "CA on CD" was not. After long bargaining between CAS and the MPG their new end-user tool SciFinder was introduced at the end of 2004 in the MPG. This will enable every chemist to run a (sub-)structure search from his desk-top. Special tasks, in particular patent information, are performed in the library using STN Express. The library also serves as a support centre for related data banks and electronic sources.

Our library has successfully replaced its old library system DOCSYS by the powerful ALEPH library management system, which is shared by some 40 institutes within the MPG. Our ~17 000 books and monographs are now well-presented in the Internet. ALEPH also enables book searches across many MPG library catalogues. It also allows extension to other public library systems. The ALEPH portal also includes a link to our journal holdings and to those of other Max-Planck-Institutes.

3.8 Computer Group (E. Ziegler, A. Koslowski)

In December 2003 A. Koslowski took charge of the computer group. Its responsibilities have remained the same since the last evaluation. It supports both Max-Planck-Institutes in Mülheim 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.

Local Area Network: The computers in both institutes are connected via a common hierarchically structured LAN. Its center is a Cisco router to which four network lines are connected: The common network of all buildings of both institutes, the SAP network of the administration, the newly created so-called demilitarized zone which allows Wireless LAN connections and video conferencing, and the link to the German science network (WiN) which has been extended from 2 to 34 Mbit/s. The buildings are connected among each other by Gigabit fiber technology, the compute servers and the central RAID storage of the Department of Theory (located in the central computer room of the Kohlenforschung) by Gigabit copper technology. The other computers of the Kohlenforschung are linked by 100 Mbit/s copper technology, and in the Bioanorganische Chemie 100 Mbit/s fiber technology is used to prevent interference of electromagnetic radiation with the sensitive experiments. For security reasons, only three central UNIX servers have internet addresses which can be reached from outside the institutes. All other network devices have internal addresses.

Server computers: The Computer Group operates the central UNIX servers, the compute and storage servers of the Department of Theory, and manages and/or provides support for PC servers and application servers (e.g. for mass spectrometry, chromatography, electron microscopy). The central UNIX servers include the internal login server which is a quad-CPU AlphaServer ES40, the server for external logins and mail dispatch and receipt which has been upgraded to a dual-CPU AlphaServer DS20E, a single-CPU AlphaServer DS10 for the demilitarized zone, and the central backup server which is a dual-CPU AlphaServer 1200. Other central services (web pages, WWW cache, name service etc.) are also distributed among these servers. The backup system currently in use is based on a 60-slot IBM Scalar 100 tape library with one remaining LTO1 drive. Since its capacity of 6 TB (uncompressed data) and its speed do no longer meet current demands, a new system with ca. 120 TB (uncompressed data) and three drives has been acquired at the end of 2004. The highly redundant RAID storage system of the Department of Theory has been upgraded to a capacity of 1356 GB, which corresponds to almost three times the original amount of disk space. Linux clusters with a total of 57 dual-Xeon nodes, 20 dual-Opteron nodes and 17 quad-Opteron nodes have been acquired as compute servers for the Department of Theory. All machines in the computer room of the Kohlenforschung and most workstations and PCs in the Department of Theory and the Computer Group are connected to an uninterruptible power system.

Workstations and PCs: PCs represent the largest number of work place computers. There are ca. 300 in the Kohlenforschung and ca. 200 in the Bioanorganische Chemie. Most of them run Windows 2000 or Windows XP. In the Department of Theory, in several service groups of the Kohlenforschung and work groups of the Bioanorganische Chemie UNIX-based workstations are used for more demanding applications (mostly Alpha and, for the visualization of chemical structures, Silicon graphics). Some VMS workstations are also in use.

Computerization of experiments: From the real-time data acquisition systems which have been designed and implemented by the Computer 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: The mass spectrometry software MassLib, which has been developed in the Computer group and which is licensed to more than 100 laboratories in the chemical industry and in universities, is under constant development due to customer requests. Safety data sheets on all chemical compounds used in our laboratories can now 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 now be done electronically for gas chromatography, X-ray crystallography and soon also for mass spectrometry. An elaborate book-keeping system for the samples in gas chromatography has been designed and implemented and is being maintained. Raw data and reports from mass spectrometry are being archived, and archival of gas chromatography data is currently under development. These systems will be integrated into an electronic laboratory journal system which is being planned. The Computer Group provides support to the libraries of both institutes concerning the Aleph 500 integrated library system. It also supports the Beilstein and Gmelin data bases which are about to be replaced by SciFinder.

Research projects: Software development (B. Weimann) for the projects "Olefin polymerization with silica supported metallocene/MAO catalysts" (G. Fink) and a radiation chemistry project (F.-W. Grevels) was continued. An important new development is the determination of enzyme activity by quantitative mass spectrometry for a project by L.-W. Wang and M. T. Reetz. For this purpose the numeric integration of individual peaks in the mass spectrum was implemented into MassLib (B. Weimann). A general multi-reference configuration interaction module for the semiempirical quantum chemistry program MNDO has been developed (A. Koslowski) and is being maintained. The self-consistent field module of the program has been parallelized for SMP systems using OpenMP (W. Angenendt). The entire MNDO program is kept up to date concerning new developments of operating system 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**, **post-docs**) an important task. Their number has risen from around 60 before 1988 to about 100 today (cf Fig. 1 – The ratio of funding by the Institute's standard research budget and third party funds depends upon their relative contributions).

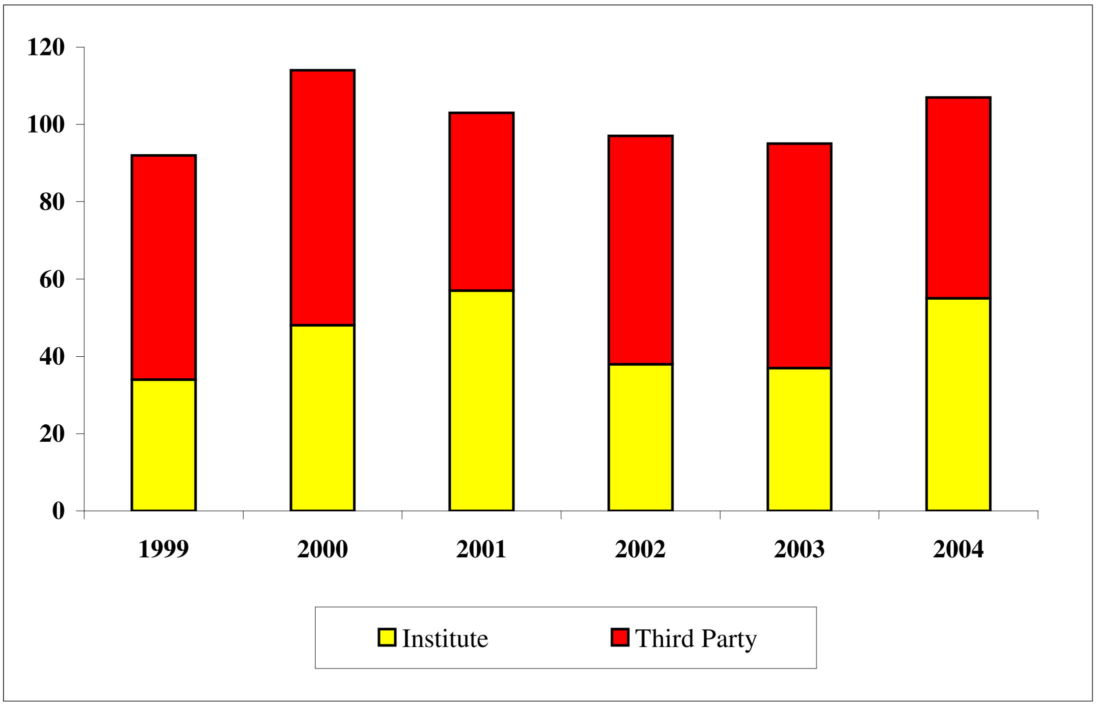


Figure 1. Support for young scientists

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. The latter category includes 11 scholarship awardees (1 Heisenberg, 4 Kekulé, 2 Liebig, and 3 Alexander von Humboldt, 1 Studienstiftung des Deutschen Volkes, and in addition 4 similar awards from abroad, 31 December 2003).

Table 1 Young Scientists

Status 31.12.2002	Total	Institute	Third Party Funds	national (n) internat. (i)	female (f) male (m)
Diploma students	0				
PhD students	68	27	41	46 n 22 i	15 f 53 m
Post-docs	29	11	18	5 n 27 i	12 f 17 m
Status 31.12.2003					
Diploma students	1	1		1 n	1 m
PhD students	58	18	40	38 n 20 i	16 f 42 m
Post-docs	36	18	18	2 n 34 i	6 f 30 m
Status 31.12.2004					
Diploma students	2	2		1 n 1 i	1 f 1 m
PhD students	53	24	29	29 n 21 i	14 f 36 m
Post-docs	52	29	23	51 i	6 f 45 m

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, Bochum, Dortmund, Duisburg/Essen, Düsseldorf, Köln, Münster, Siegen, and Wuppertal. The training of the young scientists is supplemented by regular seminars within their department or group and by the interdisciplinary colloquia held on Fridays. The latter are open to the whole Institute and the vast majority of them are held by the young scientists themselves.

The doctoral students themselves organize an internal program of lectures on catalysis to which all the groups 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 post-docs of the Institute took place, covering homogeneous and heterogeneous catalysis, biocatalysis, aspects of chemical engineering and theory. In spring 2003 a repetition of this lecture cycle was started. Lecturers, students and post-docs 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. A survey of the diploma and doctoral theses completed in the period of this report is summarized in Table 2.

Students finishing their doctoral studies in 2002 and 2004 had, on average, received financial support for 3 years and were awarded their doctorates at the age of 29.2 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 nineteen by students from the MPI für Kohlenforschung. In the period covered by this report one young scientist received the Otto Hahn Medal.

Table 2 Completed Habilitations, Dissertations and Diploma Theses in 2002, 2003 and 2004

Habilitations 2002 - 2004

Belder, D.: Oberflächen- und Elektrolytchemie in miniaturisierten elektrophoretischen Trennverfahren. Wuppertal 2003.

Gooßen, L. J.: Neue übergangsmetallkatalysierte Reaktionen für die organische Synthese. Bochum 2003.

Kaskel, S.: Nanostructured Inorganic Nitrides. Bochum 2003.

Dissertations 2002 - 2004

Eipper, A.: Neue Methoden für die Gerichtete Evolution von Enzymen. Bochum 2002.

Hoffmann, C.: Entwicklung von Methoden für die parallelisierte Herstellung und Ausprüfung von Festoffkatalysatoren. Bochum 2002.

Johann, T.: Neue Detektionsmethoden für den Einsatz in der Hochdurchsatz-Katalysatorforschung basierend auf dem photoakustischen Effekt. Bochum 2002.

Kleitz, F.: Ordered Mesoporous Materials: Template Removal, Frameworks and Morphology. Bochum 2002.

Korber, F.: Reaktionskalorimetrische Untersuchungen der stereospezifischen Propylen-Polymerisation in Suspension und Masse mit Metallocen/MAO/SiO_2-Katalysatoren. Düsseldorf 2002.

Krein, M.: Herstellung und Anwendung von nanostrukturierten Metalloxid-Kolloiden. Bochum 2002.

Sell, T.: Monodentate P-Liganden für die homogene asymmetrische Hydrierung. Bochum 2002.

Stelzer, F.: A. Totalsynthese von Turrianen – Anwendung und Vergleich von RCM und RCAM. B. Metallkatalysierte Cycloisomerisierungen von Eninen. Dortmund 2002.

Tielmann, P.: Neue Methoden für die Optimierung von Biokatalysatoren in der organischen Synthese. Bochum 2002.

Waldöfner, N.: Aluminiumorganisch stabilisierte Übergangsmetallkolloide. Synthese, Bildungsmechanismus und Aufbau von organisierten Strukturen. Aachen 2002.

Busch, O. M.: Hochdurchsatzmethoden für die Austestung von Feststoff-Katalysatoren. Bochum 2003.

Dierkes, T.: Totalsynthese von (-)-Salicylihalamid und Studien zur Totalsynthese von Nakadomarin A. Dortmund 2003.

Kevorkiants, R.: Linear scaling conjugate gradient density matrix search: Implementation, validation, and application with semiempirical molecular orbital methods. Düsseldorf 2003.

Leitner, A.: Neue übergangsmetallkatalysierte Kreuzkupplungsreaktionen von Arylchloriden und –sulfonaten. Dortmund 2003.

Mauschick, F. T.: Dichtefunktionalstudien zu katalytischen Aktivitäten und NMR-chemischen Verschiebungen von Titan- und Eisen-Komplexen. Wuppertal 2003.

Meiswinkel, A.: Chirale Monophosphite als effiziente Liganden für die asymmetrische Hydrierung. Bochum 2003.

Mörtel, R.: Anodenkatalysatoren für PEM-Brennstoffzellen aus kolloidalen Vorstufen. Aachen 2003.

Peters, H.: Neue metallorganische Synthesen von Heterocyclen und ihre Anwendung in der Naturstoffsynthese. Dortmund 2003.

Prühs, S.: Darstellung und Immobilisierung von neuartigen Rutheniumcarbenkomplexen. Dortmund 2003.

Rosskamp, E.: 1,8-Diaminoanthracene und 4,5-Diaminoacridine als Liganden für Übergangsmetalle. Düsseldorf 2003.

Schneider, M. A.: Iridium- und Rhodiumhydrido-Komplexe mit 1,8-Bis(diorganylphosphino)anthracen-Liganden als thermostabile homogene Katalysatoren für die Dehydrierung von Alkanen. Düsseldorf 2003.

Schöneboom, J. C. C.: Combined Quantum Mechanical / Molecular Mechanical Calculations on Cytochrome $P450_{cam}$. Düsseldorf 2003.

Scholten, M.: Semiempirische Verfahren mit Orthogonalisierungskorrekturen: Die OM3 Methode. Düsseldorf 2003.

Sommer, K.: Neue LEWIS-Säuren für die Homogene Katalyse. Bochum 2003.

Song, D.: Studien zur Totalsynthese von makrocyclischen Pyron-Metaboliten. Dortmund 2003.

Steiger Kohler, R.: Quantenchemische Programmentwicklung: Automatische Erzeugung von Ableitungen und Parametrisierung semiempirischer Methoden. Zürich 2003.

Theyssen, N.: Selektive Oxidationsreaktionen mit molekularem Sauerstoff in komprimiertem Kohlendioxid. Aachen 2003.

Torre, C.: Untersuchungen zur gerichteten Evolution einer Epoxidhydrolase aus *Aspergillus niger.* Bochum 2003.

Urschey, J.: Kombinatorische und konventionelle Entwicklung von Mischoxiden für die oxidative Dehydrierung von n-Butan und die einstufige Phenolsynthese aus Benzol. Saarbrücken 2003.

Weiß, Ö.: Neue Lasermaterialien auf Basis von Molekularsieb-Laserfarbstoff-Kompositen. Bochum 2003.

Alberti, D.E.G.: Neue Nickel- und Palladium-Allyl-Komplexe. Düsseldorf 2004.

Babik, S. T.: Mechanismus der Olefinpolymerisation mit Metallkatalysatoren der 8. Gruppe. Düsseldorf 2004.

Bocionek, D.: Herstellung von Kern-Schale-Verbundpolymeren mit einem Kern aus ultrahochmolekularem Polyethylen und einer Schale aus Hd-Polyethylen. Düsseldorf 2004.

Brunner, B.: Directed Evolution as a Method to Create Enantioselective Cyclohexanone Monooxygenases. Graz 2004.

Feyen, F.: Totalsynthese von TMC-69-Derivaten und deren Eigenschaften als Phosphatase-Inhibitoren. Dortmund 2004.

Freitag, K.: Darstellung und Charakterisierung metallbeladener Nafion®/Silikat-Verbundwerkstoffe. Bochum 2004.

Ilhan, Y.: Synthesis and catalytic applications of crosslinked colloidal zeolite catalysts. Instanbul 2004.

Karafilidis, C.: Norbornen-Homopolymerisation und Copolymerisation mit Ethen und CO mit homogenen Übergangsmetall-Katalysatoren sowie Untersuchung der Polymermikrostrukturen. Düsseldorf 2004.

Kestenbaum, H.: Zur Synthese von Ethenoxid in einem Mikroreaktionssystem. Frankfurt/Main 2004.

Kiener, C.: Verwendung von Hochdurchsatz-Methoden zur Untersuchung starker Metall-Träger-Wechselwirkungen bei Cu/ZnO-Katalysatoren für die Methanolsynthese. Bochum 2004.

Klanner, C.: Evaluation of Descriptors for Solids. Bochum 2004.

Knoke, S.: Video- und elektronenmikroskopische Untersuchungen der Olefinpolymerisation mit trägerfixierten Katalysatorsystemen. Düsseldorf (2004).

Kremzow, D.: Synthese von Pd- und Ni-Carben-Komplexen durch oxidative Addition. Dortmund 2004.

Krumm, H.: Beiträge zur gerichteten Evolution von Hydrolasen. Bochum 2004.

Lacombe, F.: Synthesis of (E)-cycloalkanes and (E,E)-cycloalkadienes by ring closing diyne or enyne-yne metathesis. Dortmund 2004.

Ludwig, M.: Schnelle chirale Trennungen in mikrofluidischen Strukturen. Siegen (2004).

Paetzold, J.: Carbonsäuren als Startmaterialien in der Übergangsmetallkatalyse. Bochum 2004

Pletsch, A.: Untersuchungen zur Gerichteten Evolution von Übergangsmetallkatalysatoren. Bochum 2004.

Prühs, S.: Darstellung und Immobilisierung von neuartigen Rutheniumcarbenkomplexen. Dortmund 2004.

Wiesenhöfer, W.: Neue Methoden zur Anwendung von Lipasen in der organischen Synthese. Bochum 2004.

Diploma Theses 2002 - 2004

Bilge, A.: Ethen-Cycloolefin-Copolymerisation mit Metallocen-Katalysatoren. Düsseldorf 2002.

Grininger, M.: Studien zur Totalsynthese von Crocacin D. Graz 2002.

Krawiec, P.: Synthesis and Infiltration of Mesoporous Silica Materials with Silicon Carbide. Cracow/FHS Münster 2002.

Olejnik, S.: Aufbau eines Hochdurchsatz-Reaktors für die Wasserstoffherstellung. Dortmund 2003.

Palkovits, R.: Herstellung von Nanokompositen durch Integration von SiO_2 und ZrO_2 in PMMA. Dortmund 2003.

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 benzene 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 independance 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 a long time ago.

The objects of Studiengesellschaft Kohle are

- patent prosecution for inventions based on the research results
- licensing of the technology to industrial partners
- enforcement of intellectual property rights
- negotiating research cooperations with industrial partners.

8 new patent applications in 2002, 8 in 2003 and 6 in 2004 were filed. For 37 applications from earlier years patents were issued in 2002/04 in Europa, USA, Canada.

License contracts exist for the production of immobilized lipases, the electrochemical coating with aluminum and with aluminum/magnesium-alloys, the production of coated chromatographic columns, process for the production of monodispersible magnetic nanocolloides, chiral monodentate phosphorus ligands as well as ferrocene-based diphosphonites for asymmetrical catalysis and the contract for the distribution of software (MS) developed in the Institute has been extended.

Over the period 2002/2004 there were 21 direct cooperations with industrial partners. 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.
Furthermore, there were cooperations with industrial and university partners supported by BMBF and cooperations without financial obligations, e.g., with hte AG, Messer Griesheim, CNRS and ANSTO.

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. The second Geschäftsführer, Professor Dr. Engelbert Ziegler, retired in 2003. His operational functions were taken over 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.

CHAPTER 6

Special Events and Activities

6 Special Events and Activities

Three special events took place during the reporting period: The Institute opened the doors to the general public for an open house, the 60th birthday of Manfred T. Reetz was celebrated with a scientific symposium, and the government of the state of Nordrhein-Westfalen visited the Institute.

6.1 Open House

The Institute opened for the public on May 24rd 2003, after about ten years since the last open house of the Institute. A Saturday was chosen for this event in order to allow as many people as possible to visit. All the research groups, the analytical departments, and the work shops had prepared demonstrations of their work, and performed interesting experiments which were easy to comprehend and thus transported information on the mission of the Institute. These included the IR camera, which is normally used to analyze the performance of catalysts in parallel, to image the faces of the visitors, molecular mechanics simulations of enzymes and working catalysts, oscillating catalytic reactions on a platinum wire, an automobile exhaust catalyst, a "smell-bar", where complex natural products synthesized in the Institute could be identified by their smell, which also conveyed information about chirality, possibilities to analyze jewelry items by elemental analysis, demonstrations of the scanning electron microscope and many others. In addition, the workshop employees demonstrated their skills. For instance, the glass blowers gave examples of their work by blowing small vases and other pieces, or the machine shop had the robot set to produce pen holders with the Institutes name engraved into them. One of the most popular demonstrations, however, was the production of various flavors of ice-cream using liquid nitrogen for refrigeration which indeed produced a very creamy type of ice-cream.

Altogether about 4000 people, relatives and friends of the employees, Mülheim citizens, but also visitors interested in the science coming from further away, were on the grounds over the six hours the Institute was open. Those visitors who gave us feedback were fascinated by the wide variety of topics covered by the research of the Institute and the way it was presented. All Institute employees participating were highly motivated and did their best to make the day memorable to our guests.

Impressions from the open house on May 24th 2003. Clockwise from upper left: magnetic fluids attracted by electromagnet; Prof. Pörschke's Ice Cream Parlor; smell bar; on the gallery in the laboratory building.

On the 22nd, two days before the open house, a selected group of about 30 decision makers from politics and business, as well as chemistry teachers from local high schools had been invited. This provided the opportunity to establish closer contacts, which were especially fruitful with the teachers, because these contacts helped to further intensify the links to the schools and made them more aware of the possibilities for cooperation with the Institute.

6.2 60th Birthday of Manfred T. Reetz

On a more scientific note, the Institute celebrated the 60th birthday of Professor Manfred T. Reetz with a scientific symposium and a reception on 14th of October 2003. About 300 guests, members of the Institute, former students, colleagues and friends, were present in the Stadthalle in Mülheim. Helmut Schwarz from the Technische Universität

Berlin presented the laudation, followed by two scientific lectures by Steven Ley and Willem Stemmer which were related to the scientific oeuvre of Manfred. This celebration was a perfect opportunity for the Institute to thank Manfred for everything he has done for the Institute in the difficult times during the restructuring and the reestablishment of a firm financial basis in the 1990s, and is of course continuing to do as one of the directors.

6.3 Visit of the Cabinet of the State Government

Finally, on the 22nd of June 2004, most members of the government of the state of Nordrhein-Westfalen visited the Institute and the neighboring Max-Planck-Institute for Bioinorganic Chemistry on the occasion of a cabinet meeting which occasionally takes place outside of Düsseldorf, the seat of the government. This allowed the Institute to present the scientific achievements in form of a guided tour to some of the politicians who are relevant in deciding on the funding of the Max Planck Society. Also one of the vice-presidents of the Society took this opportunity to convey the perspectives of the presidium of the Max Planck Society on the state of fundamental research, the funding situation and other issues concerning science policy.

All these events and several more were covered by the local and regional newspapers, so that the Institute is a lively and visible part of the city of Mülheim and its vicinity.

6.4 Other Events and Activities

Karl-Ziegler-Lectureship 2002

Workshop on Reaktionen an Oberflächen: Vom Atomaren zum Komplexen

18-20 November 2002*;* Main Lecture 20 November 2002

Professor G. Ertl

Fritz-Haber-Institut, Berlin, DE

Karl-Ziegler-Lectureship 2003

Workshop on Structure-based reaction discovery

24-27 February 2003*;* Main Lecture 26 February 2003

Professor David A. Evans

Harvard University, Cambridge, USA

Karl-Ziegler-Lectureship 2004

Workshop on hybrid heterogeneous catalysts: Elements in toolbox for fine chemical heterogeneous catalysis

25-26 November 2004; Main Lecture 25 November 2004

Professor P. A. Jacobs

K. U. Leuven, BE

Liebig Lectureship 2002

Workshop on Chemical approaches to modulating cell surface architecture

14 May 2002

Frau Professor C. Bertozzi

UC Berkeley, USA

Liebig Lectureship 2003

Workshop on Memory and amnesia in asymmetric allylations

24 June 2003

Professor G. Lloyd-Jones

Bristol, UK

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. Manfred Bochmann

Professor of Inorganic Chemistry - Wolfson Materials and Catalysis Centre - School of Chemical Sciences and Pharmacy - University of East Anglia, GB, European Research Training Network: New Polyolefin Materials via Metal Catalyzed Copolymerizations (HPRN-CT-2000-00004), 10-18 March 2004
Host: G. Fink

Visiting Scientist Professor Dr. Margaret M. Kayser

Department of Chemistry, University of New Brunswick, Saint John, CA
2-9 May 2003 and 23-30 April 2004
Host: M. T. Reetz

Visiting Scientists Professors Dr. Zexing Cao and Wei Wu

State Key Laboratory of Physical Chemistry of Solid Surfaces,
Department of Chemistry, Xiamen University, Xiamen, CN,
partly funded by the Alexander-von-Humboldt Foundation,
9 January - 30 March 2003 (Cao) and 21 June - 13 August 2004 (Wu)
Host: W. Thiel

Lecture course on catalysis, a four-semester program, 2002-2004

F. Schüth	*Basic Heterogeneous Catalysis* (16 weeks)
A. Fürstner	*Basic Homogeneous Catalysis* (16 weeks)
M. T. Reetz	*Basic Biocatalysis* (6 weeks)
W. Thiel	*Theoretical Approaches in Catalysis* (8 weeks)
G. Veser	*Introduction to Catalytic Reactor Engineering* (10 weeks)

Workshop on Magnetic Fluids

5. Deutscher Ferrofluid Workshop
25-27 June 2003, 76 participants from 3 countries
Chairman: H. Bönnemann

German-Chinese Bilateral Symposium on Organometallic Catalysts and Olefin Polymerization
14-18 September 2003
Chairmen: G. Fink, W. Kaminsky (Hamburg), W. J. Richter

Meeting of the Regional Section "Ruhr" of the German Society for Petroleum and Coal Science and Technology (DGMK)
20 November 2003
M. W. Haenel, F. Schüth

61st Meeting of the Working Group "Coal Processing" of the German Society for Petroleum and Coal Science and Technology (DGMK)
11-12 November 2004
M. W. Haenel

Organocatalysis in Germany
Initiated nation-wide DFG Priority Program (SPP1179) "Organocatalysis",
sponsored by the German Research Foundation
16 January 2004
Conference Organization: B. List

Symposium "Computational Modelling of Catalysis"
16-18 July 2003, 105 participants from 19 countries
Chairman: W. Thiel

COST Workshop
Theoretical Modelling of Oligomerization and Polymerization Reactions
13-14 November 2003
Host: W. Thiel

CHAPTER 7

Appendices

7.1 List of Publications 2002 - 2004

2002

1. *Agren, P., S. Thomson, Y. Ilhan, B. Zibrowius, W. Schmidt and F. Schüth:* Chemical linking of MFI-type colloidal zeolite crystals. Stud. Surf. Sci. Catal. **142**, 159-166 (2002).
2. *Althues, H. and S. Kaskel:* Sulfated Zirconia Nanoparticles Synthesized in Reverse Microemulsions – Preparation and Catalytic Properties. Langmuir **18**, 7428-7435 (2002).
3. *Angermund, K., M. Bühl, E. Dinjus, U. Endruschat, F. Gassner, H.-G. Haubold, J. Hormes, G. Köhl, F.T. Mauschick, H. Modrow, R. Mörtel. R. Mynott, B. Tesche, T. Vad, N. Waldöfner und H. Bönnemann:* Nanoskopische Pt-Kolloide im „embryonalen Stadium“. Angew. Chem. **114**, 4213-4216 (2002); Angew. Chem. Int. Ed. **41**, 4041-4044 (2002).
4. *Antes, I., W. Thiel and W.F. van Gunsteren:* Molecular Dynamics Simulations of Photoactive Yellow Protein (PYP) in Three States of its Photocycle: A Comparison with X-ray and NMR Data and Analysis of the Effects of Glu46 Deprotonation and Mutation. Eur. Biophys. J. **31**, 504-520 (2002).
5. *Babik, S.T. and G. Fink:* Propylene polymerization with a bisiminepyridine iron complex: activation with $Ph_3C[B(C_6F_5)_4]$ and AlR_3; iron hydride species in the catalytic cycle. J. Mol. Catal A: Chem. **188**, 245-253 (2002).
6. *Belder, D., A. Deege, F. Kohler and M. Ludwig:* Poly(vinyl acohol)-coated microfluidic devices for high-performance microchip electrophoresis. Electrophoresis **23**, 3567-3573 (2002).
7. *Belder, D., A. Deege, M. Maass and M. Ludwig:* Design and performance of a microchip electrophoresis instrument with sensitive variable-wavelength fluorescence detection. Electrophoresis **23**, 2355-2361 (2002).
8. *Binger, P., A. Brinkmann and P. Wedemann:* Highly Efficient Synthesis of Methylenecyclopropane. Synthesis **2002**, 1344-1346.
9. *Binger, P., P. Müller, S. Podubrin, S. Albus and C. Krüger:* Bis(η^5-cyclopentadienyl)- and bis(η^5-indenyl)metallacycles of titanium and zirconium from methylenecyclopropanes by oxidative coupling. J. Organomet. Chem. **656**, 288-298 (2002).
10. *Bönnemann, H. and W. Brijoux:* Synthesis and Application of Organyl-Cobalt Cocyclization Catalysts. In: Synthetic Methods of Organometallic and Inorganic Chemistry, Vol. 10, (Eds.) W.A. Herrmann, G. Brauer. Thieme Verlag, Stuttgart 2002, 149-157.
11. *Bönnemann, H. and W. Brijoux:* Cyclooligomerization of alkynes. In: Applied Homogeneous Catalysis with Organometallic Compounds, 2. Ed., Vol. 3, (Eds.) B. Cornils, W.A. Herrmann. Wiley-VCH, Weinheim 2002, 1252-1268.
12. *Bönnemann, H., W. Brijoux, H.-W. Hofstadt, T. Ould Ely, W. Schmidt, B. Waßmuth und C. Weidenthaler:* Nasschemische Synthese von β-Nickelaluminid NiAl. Angew. Chem. **114**, 628-632 (2002); Angew. Chem. Int. Ed. **41**, 599-603 (2002).
13. *Bönnemann, H. and R. Richards:* Manufacture of Heterogeneous Mono- and Bimetallic Colloid Catalysts and Their Applications in Fine Chemical Synthesis and Fuel Cells. In: Synthetic Methods of Organometallic and Inorganic Chemistry, Vol. 10, (Eds.) W.A. Herrmann, G. Brauer. Thieme Verlag, Stuttgart 2002, 209-224.
14. *Bönnemann, H., N. Waldöfner, H.-G. Haubold and T. Vad:* Preparation and Characterization of Three-Dimensional Pt Nanoparticle Networks. Chem. Mater. **14**, 1115-1120 (2002).
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16. *Bogdanović, B. and G. Sandrock:* Catalyzed complex metal hydrides. MRS Bull. **27**, 712-716 (2002).

17. *Bolm, C., C. Palazzi, G. Franciò and W. Leitner:* Baeyer-Villiger oxidation in compressed CO_2. Chem. Commun. (Cambridge, U. K.) **2002**, 1588-1589.

18. *Breidung, J. and W. Thiel:* Ab Initio Study of the Charge-Transfer Complex of Xenon and Dicarbon. J. Mol. Spectrosc. **216**, 424-427 (2002).

19. *Bucher, S., J. Hormes, H. Modrow, R. Brinkmann, N. Waldöfner, H. Bönnemann, L. Beuermann, S. Krischok, W. Maus-Friedrichs and V. Kempter:* Interaction between core and protection shell of $N(butyl)_4Cl$- and $N(octyl)_4Cl$-stabilized Pd colloids. Surf. Sci. **497**, 321-332 (2002).

20. *Bühl, M.:* Structure, Dynamics, and Magnetic Shieldings of Permanganate Ion in Aqueous Solution. A Density Functional Study. J. Phys. Chem. A **106**, 10505-10509 (2002).

21. *Bühl, M.:* Density-Functional Computation of ^{55}Mn NMR Parameters. Theor. Chem. Acc. **107**, 336-342 (2002).

22. *Bühl, M. and F.T. Mauschick:* On the mechanism of olefin polymerisation with titanium β-diketonato complexes. A model density functional study. J. Organomet. Chem. **648**, 126-133 (2002).

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24. *Bühl, M., F.T. Mauschik, F. Terstegen und B. Wrackmeyer:* Bemerkenswert starke Geometrie-Abhängigkeit ^{57}Fe-chemischer Verschiebungen. Angew. Chem. **114**, 2417-2420 (2002); Angew. Chem. Int. Ed. **41**, 2312-2315 (2002).

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27. *Choudhury, A.R., U.K. Urs, P.S. Smith, R. Goddard, J.A.K. Howard and T.N. Guru Row:* Study of weak interactions in (4-chlorophenyl)-(4-fluorophenyl)-(4-pyridyl) methanol and bis-(4-fluorophenyl)-(4-pyridyl) methanol. J. Mol. Struct. **641**, 225-232 (2002).

28. *Czuryszkiewicz, T., J. Ahvenlammi, P. Kortesuo, M. Ahola, F. Kleitz, M. Jokinen, M. Lindén and J.B. Rosenholm:* Drug release from biodegradable silica fibers. J. Non-Cryst. Solids **306**, 1-10 (2002).

29. *Dash, A.K., A. Razavi, A. Mortreux, C.W. Lehmann and J.-F. Carpentier:* Amine Elimination Reactions between Homoleptic Silylamide Lanthanide Complexes and an Isopropylidene-Bridged Cyclopentadiene-Fluorene System. Organometallics **21**, 3238-3249 (2002).

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51. *Goddard, R.,H.M. Herzog and M.T. Reetz:* Cation–anion CH···O$^-$ interactions in the metal-free phenolate, tetra-*n*-butylammonium phenol-phenolate. Tetrahedron **58**, 7847-7850 (2002).

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409. *Reetz, M.T., H. Schulenburg, M. Lopez, B. Spliethoff and B. Tesche:* Platinum-Nanoparticles on Different Types of Carbon Supports: Correlation of Electrocatalytic Activity with Carrier Morphology. Chimia **58**, 896-899 (2004).

410. *Reetz, M.T., P. Tielmann, A. Eipper, A. Ross and G. Schlotterbeck:* A high-throughput NMR-based ee-assay using chemical shift imaging. Chem. Commun. (Cambridge, U. K.) **2004**, 1366-1367.

411. *Reetz, M.T., C. Torre, A. Eipper, R. Lohmer, M. Hermes, B. Brunner, A. Maichele, M. Bocola, M. Arand, A. Cronin, Y. Genzel, A. Archelas and R. Furstoss:* Enhancing the Enantioselectivity of an Epoxide Hydrolase by Directed Evolution. Org. Lett. **6**, 177-180 (2004).

412. *Reetz, M.T. and W. Wiesenhöfer:* Liquid poly(ethylene glycol) and supercritical carbon dioxide as a biphasic solvent system for lipase-catalyzed esterification. Chem. Commun. (Cambridge, U. K.) **2004**, 2750-2751.

413. *Romanus, E., N. Matoussevitch, S. Prass, J. Heinrich, R. Müller, D.V. Berkov, H. Bönnemann and P. Weber:* Magnetic characterization of cobalt nanoparticles by temperature-dependent magnetic relaxation measurements. Appl. Organomet. Chem. **18**, 548-552 (2004).

414. *Scheiper, B., M. Bonnekessel, H. Krause and A. Fürstner:* Selective Iron-Catalyzed Cross-Coupling Reactions of Grignard Reagents with Enol Triflates, Acid Chlorides, and Dichloroarenes. J. Org. Chem. **69**, 3943-3949 (2004).

415. *Scheiper, B., F. Glorius, A. Leitner and A. Fürstner:* Catalysis-based enantioselective total synthesis of the macrocyclic spermidine alkaloid isooncinotine. Proc. Natl. Acad. Sci. U.S.A. **101**, 11960-11965 (2004).

416. *Schlichte, K., T. Kratzke and S. Kaskel:* Improved synthesis, thermal stability and catalytic properties of the metal-organic framework compound $Cu_3(BTC)_2$. Microporous Mesoporous Mater. **73**, 81-88 (2004).

417. *Schmidt, M., G. Boettger, M. Eich, W. Morgenroth, U. Huebner, R. Boucher, H.G. Meyer, D. Konjhodzic, H. Bretinger and F. Marlow:* Ultralow refractive index substrates – a base for photonic crystal slab waveguides. Appl. Phys. Lett. **85**, 16-18 (2004).

418. *Schöneboom, J.C., S. Cohen, H. Lin, S. Shaikl and W. Thiel:* Quantum Mechanical/Molecular Mechanical Investigtion of the Mechanism of C-H Hydroxylation of Camphor by Cytochrome $P450_{cam}$: Theory Supports a Two-State Rebound Mechanism. J. Am. Chem. Soc. **126**, 4017-4034 (2004).

419. *Schöneboom, J.C. and W. Thiel:* The Resting State of $P450_{cam}$: A QM/MM Study. J. Phys. Chem. B **108**, 7468-7478 (2004).

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421. *Schrader, W. and H.-W. Klein:* Liquid chromatography/Fourier transform ion cyclotron resonance mass spectrometry (LC-FTICR MS): ab early overview. Anal. Bioanal. Chem. **379**, 1013-1024 (2004).

422. *Schüth, C., N.-A. Kummer, C. Weidenthaler and H. Schad:* Field application of a tailored catalyst for hydrodechlorinating chlorinated hydrocarbon contaminants in groundwater. Appl. Catal., B **52**, 197-203 (2004).

423. *Schüth, F.:* The evolution of ordered mesoporous materials. In: Mesoporous Crystals and Related Nano-Structured Materials. (Ed.) O. Terasaki. Elsevier, Amsterdam. Stud. Surf. Sci. Catal. **148**, 1-13 (2004).

424. *Schüth, F., B. Bogdanović and M. Felderhoff:* Light metal hydrides and complex hydrides for hydrogen storage. Chem. Commun. (Cambridge, U. K.) **2004**, 2249-2258.

425. *Seidel, G., D. Laurich and A. Fürstner:* Iron-Catalyzed Cross-Coupling Reactions. A Scalable Synthesis of the Immunosuppressive Agent FTY720. J. Org. Chem. **69**, 3950-3952 (2004).

426. *Solinas, M., A. Pfaltz, P.G. Cozzi and W. Leitner:* Enantioselective Hydrogenation of Imines in Ionic Liquid/Carbon Dioxide Media. J. Am. Chem. Soc. **126**, 16142-16147 (2004).

427. *Stambuli, J.P., C.D. Incarvito, M. Bühl and J.F. Hartwig:* Synthesis, Structure, Theoretical Studies, and Ligand Exchange Reactions of Monomeric, T-Shaped Arylpalladium(II) Halide Complexes with an Additional, Weak Agostic Interaction. J. Am. Chem. Soc. **126**, 1184-1194 (2004).

428. *Thiel, W.:* Ab Initio Vibration-Rotation Spectroscopy. Chimia **58**, 276-280 (2004).

429. *Varjo, S.J.O., M. Ludwig, D. Belder and M.-L. Riekkola:* Separation of FITC-labeled amines by microchip electrophoresis on uncoated and PVA-coated glass chips with dimethyl sulfoxide based electrolyte. Electrophoresis **25**, 1901-1906 (2004).

430. *Vignola, N. and B. List:* Catalytic Asymmetric Intramolecular α-Alkylation of Aldehydes. J. Am. Chem. Soc. **126**, 450-451 (2004).

431. *Wang, Y., B. Zibrowius, C.-M. Yang, B. Spliethoff and F. Schüth:* Synthesis and characterization of large-pore vinyl-functionalized mesoporous silica SBA-15. Chem. Commun. (Cambridge, U. K.) **2004**, 46-47.

432. *Wendt, R.A., K. Angermund, V. Jensen, W. Thiel and G. Fink:* Ethene Copolymerization with Trialkylsilyl Protected Polar Norbornene Derivatives. Macromol. Chem. Phys. **205**, 308-318 (2004).

433. *Wingen, A., F. Kleitz and F. Schüth:* Ordered Mesoporous Materials: Preparation and Application in Catalysis. In. Basic Principles in Applied Catalysis. (Ed.) M. Baerns. Springer Ser. Chem. Phys. 75. Springer, Berlin 2004, 281-319.

434. *Yang, J.W., M.T. Hechavarria Fonseca und B. List:* Eine metallfreie Transferhydrierung: organokatalytische konjugierte Reduktion von α,β-ungesättigten Aldehyden. Angew. Chem. **116**, 6829-6832 (2004); Angew. Chem. Int. Ed. **43**, 6660-6662 (2004).

435. *Yang, C.-M., J.-H. Smatt, B. Zibrowius and M. Lindén:* Chemical Removal of the Organic Polymers from Sol-gel Derived Highly Porous Silica Monoliths. New J. Chem. **28**, 1520-1525 (2004).

436. *Yang, C.-M., Y. Wang, B. Zibrowius and F. Schüth:* Formation of cyanide-functionalized SBA-15 and its transformation to carboxylate-functionalizd SBA-15. Phys. Chem. Chem. Phys. **6**, 2461-2467 (2004).

437. *Yang, C.-M., H.U. Wüstefeld, M. Kalwei and F. Schüth:* Exploring the Catalytic Activity of Metal Nanoparticles in Functionalized Mesoporous Silica. In: 14th Int. Zeolite Conf., Cape Town, South Africa, 25-30 April 2004. (Eds.) E.W.J. van Steen, L.H. Callanan, M. Claeys, C.T. O'Connor. The Catalysis Society of South Africa, Cape Town, S.A. 2004, 898-899; 2574-2580CD.

438. *Yang, C.-M., B. Zibrowius, W. Schmidt and F. Schüth:* Stepwise Removal of the Copolymer Template from Mesopores and Micropores in SBA-15. Chem. Mater. **16**, 2918-2925 (2004).

439. *Zech, T., J. Klein, S.A. Schunk, T. Johann, F. Schüth, S. Kleditzsch and O. Deutschmann:* Miniaturized Reactor Concepts and Advanced Analytics for Primary Screening in High-Throughput Experimentation. In: High-Throughput Analysis: A Tool for Combinatorial Materials Science, (Eds.) R.A. Potyrailo, E.J. Amis. Kluwer Academic/Plenum Publishers, New York 2004, chapter 23.

440. *Zibrowius, B., C. Bähtz, M. Knapp and U. Ruschwewitz:* Phase transition in K_2C_2 as studies by synchrotron X-ray powder diffraction and solid-state ^{13}C NMR Spectroscopy. Phys. Chem. Chem. Phys. **6**, 5237-5243 (2004).

7.2 List of Invited Talks Given by Members of the Institute (2002-2004)

2002

Babik, S., Institut für Technische Chemie (ITC-CPV) des Forschungszentrums Karlsruhe, DE, 8 February 2002

Belder, D., Universität Siegen, DE, 9 January 2002

Belder, D., University of Twente, MESA$^+$, Enschede, NL, 21 March 2002

Belder, D., The Fourth Asia-Pacific International Symposium on Microscale Separations and Analysis, APCE2002, Shanghai, CN, 11-14 October 2002

Bönnemann, H., ACS Spring Meeting, Orlando, USA, 5-12 April 2002

Bönnemann, H., 4. Deutscher Ferrofluid Workshop, Berlin, DE, 2-5 July 2002

Bönnemann, H., Forschungszentrum Karlsruhe, DE, 19 September 2002

Bönnemann, H., Werkstoffwoche München, DE, 29 September -3 October 2002

Bönnemann, H., EU Project Meeting Apollon, Mailand, IT, 9 October 2002

Bühl, M., F. T. Mauschick, Chemiedozententagung 2002, Köln, DE, 10-13 March 2002

Bühl, M., F. T. Mauschick, Bunsentagung 2002, Potsdam, DE, 9-11 May 2002

Bühl, M., Universität Dortmund, DE, 24 May 2002

Bühl, M., Humboldt-Universität Berlin, DE, 13 June 2002

Bühl, M., Universität Siegen, DE, 25 June 2002

Bühl, M., Technische Universität Berlin, DE, 25 October 2002

Bühl, M., Universität Rostock, DE, 13 December 2002

Fink, G., Universität Essen, DE, 6 February 2002

Fink, G., Max-Planck-Institut für Polymerforschung, Mainz, DE, 15 May 2002

Fink, G., University of Jyväskylä - Jyväskylä Summer School, Jyväskylä, FI, 22-28 August 2002

Fürstner, A., Syngenta, Jealott's Hill, UK, 10 January 2002

Fürstner, A., Royal Society of Chemistry Heterocyclic Group's Annual London Meeting, London, UK, 11 January 2002

Fürstner, A., Serratosa Lecture, Universitat de Barcelona, ES, 21-22 January 2002

Fürstner, A., GDCh, Universität Dresden, DE, 31 January 2002

Fürstner, A., AstraZeneca Research Lecture in Modern Chemistry, Vancouver, CA, 12-13 February 2002

Fürstner, A., 13th Annual Symposium on Frontiers in Chemistry, Scripps Research Institute, La Jolla, USA, 15 February 2002

Fürstner, A., Boehringer Ingelheim, Wien, AT, 14 March 2002

Fürstner, A., Chemisches Synthesekolloquium, Boehringer Ingelheim, Biberach/Riss, DE, 29 April 2002

Fürstner, A., 2èmes Recontres de Chimie Organique de Marseille, Marseille, FR, 16 May 2002

Fürstner, A., Novartis Lecture, Prag, CZ, 27 May 2002

Fürstner, A., Novartis Lecture, Bratislava, SK, 29 May 2002

Fürstner, A., Novartis Lecture, Budapest, HU, 30 May 2002

Fürstner, A., GDCh, Universität Tübingen, DE, 21 June 2002

Fürstner, A., IUPAC - 23rd International Meeting on the Chemistry of Natural Products, Florenz, IT, 30 July 2002

Fürstner, A., Arthur C. Cope Scholar Award, Boston, USA, 20 August 2002

Fürstner, A., Boehringer Ingelheim Lecture, Queen's University, Kingston, CA, 10 September 2002

Fürstner, A., Boehringer Ingelheim, Laval, CA, 11 September 2002

Fürstner, A., Astra Zeneca Lecture, Montreal, CA, 12 September 2002

Fürstner, A., Astra Zeneca Lecture, University of Ottawa, CA, 13 September 2002

Fürstner, A., 1. UC Irvine-Pfizer Symposium on Organic Synthesis, University of California, Irvine, USA, 16 September 2002

Fürstner, A., Roche, Palo Alto, USA, 18 September 2002

Fürstner, A., University of Austin, USA, 20 September 2002

Fürstner, A., Abbott Lecture, Texas A&M University, College Station, USA, 23 September 2002

Fürstner, A., Schering, Berlin, DE, 16 October 2002

Fürstner, A., GDCh, Johannes-Gutenberg Universität Mainz, DE, 28 November 2002

Fürstner, A., BASF, Ludwigshafen, DE, 4 December 2002

Gooßen, L. J., GDCh, Gesamthochschule Wuppertal, DE, 14 February 2002

Gooßen, L. J., GDCh, Universität Dortmund, DE, 25 June 2002

Gooßen, L. J., ORCHEM, Bad Nauheim, DE, 13 September 2002

Gooßen, L. J., Schering AG, Berlin, DE, 6 December 2002

Gooßen, L. J., Akademie der Wissenschaften, Göttingen, DE, 14 December 2002

Haenel, M. W., 4th UK Meeting on Coal Research and Its Applications, Imperial College London, UK, 16-18 September 2002

Kaskel, S., Jagellonian University, Krakau, PL, 25 + 26 April 2002

Kaskel, S., Degussa, Hanau, DE, 6 June 2002

Kaskel, S., hte-company, Heidelberg, DE, 18 October 2002

Kaskel, S., Physikalische Chemie Universität Ulm, DE, 25 October 2002

Kaskel, S., Anorganische Chemie Universität Hannover, DE, 21 November 2002

Kaskel, S., Anorganische Chemie TU München, DE, 16 December 2002

Lehmann, C. W., Deutsche Gesellschaft für Kristallographie, Kiel, DE, 4-7 March 2002

Lehmann, C. W., Universität Aachen, DE, 7 May 2002

Lehmann, C. W., Pfizer Global Research & Development, Ann Arbor, USA, 24 July 2002

Lehmann, C. W., International Union of Crystallography, Geneva, CH, 6-11 August 2002

Lehmann, C. W., Sommerschule Einkristallstrukturanalyse, Hardehausen, DE, 9-13 September 2002

Leitner, W., Dalton Discussion "Inorganic Reaction Mechanism", Kloster Banz, DE, 12 January 2002

Leitner, W., 41. Sitzung des DECHEMA-Arbeitsausschusses "Technische Reaktionen", Frankfurt, DE, 15 January 2002

Leitner, W., Chemistry of Clean Reactions and Processes, Politecnico Milano, IT, 1 March 2002

Leitner, W., XXXV. Jahrestreffen Deutscher Katalytiker; Weimar, DE, 22 March 2002

Leitner, W., Utrecht University, NL, 25 April 2002

Leitner, W., GDCh, Bonn, DE, 28 May 2002

Leitner, W., Graduiertenkolleg, Universität Tübingen, DE, 11 June 2002

Leitner, W., TU Eindhoven, NL, 25 June 2002

Leitner, W., GDCh Festkolloquium, RWTH Aachen, DE, 9 July 2002

Leitner, W., ICCC 35, Heidelberg, DE, 24 July 2002

Leitner, W., 10. Kolloquium "Homogene Katalyse", RWTH Aachen, DE, 30 August 2002

Leitner, W., ORCHEM 2002, Bad Nauheim, DE, 14 September 2002

Leitner, W., Università di Sassari, Sardegna, IT, 23 October 2002

Leitner, W., 4th Symposium on Green Chemistry, Barcelona, ES, 10 November 2002

Marlow, F., Seminarvortrag Münster, DE, 4 July 2002

Marlow, F., Gordon-Conference, South Hedley, USA, 20 June 2002

Marlow, F., Seminarvortrag, Siegen, DE, 17 July 2002

Marlow, F., Int. Conference on Functional Materials, Kiev, UA, 26 September 2002

Marlow, F., DFG-Workshop "Guest-Host Systems" Berlin, DE, 22 October 2002

Marlow, F., Seminarvortrag BAM Berlin, DE, 14 November 2002

Pörschke, K.-R., Jonas, K., 224th ACS National Meeting, Boston, USA, 18-22 August 2002

Reetz, M. T., OC-Kolloquium, Universität Darmstadt, DE, 21 January 2002

Reetz, M. T., GDCh, Universität zu Köln, DE, 1 February 2002

Reetz, M. T., GDCh, Universität Marburg, DE, 6 February 2002

Reetz, M. T., IBC USA's 7th Annual World Congress on Enzyme Technologies, San Francisco, USA, 5 March 2002

Reetz, M. T., University of Austin, Dallas, USA, 22 April 2002

Reetz, M. T., Rice University, Houston, USA, 25 April 2002

Reetz, M. T., William Dauben Lecture, University of California, Berkely, USA, 30 April 2002

Reetz, M. T., SISOUM 2002, University of Montreal, CA, 2 May 2002

Reetz, M. T., Firmenich, Genf, CH, 8 May 2002

Reetz, M. T., ETH Zürich, CH, 27 May 2002

Reetz, M. T., GDCh, Universität des Saarlandes, Saarbrücken, DE, 3 June 2002

Reetz, M. T., Universität Bielefeld, DE, 18 June 2002

Reetz, M. T., BOS 2002, Vilnius, LT, 26 June 2002

Reetz, M. T., 50 Years Catalysis Research, Universität Rostock, DE, 3 July 2002

Reetz, M. T., XXth ICOMC, Corfu, GR, 8 July 2002

Reetz, M. T., ACS Meeting, Boston, USA, 19 August 2002

Reetz, M. T., Boreskov Institute of Catalysis, Novosibirsk, RU, 6 September 2002

Reetz, M. T., Institute for Molecular Science (IMS), Nagoya, JP, 17 September 2002

Reetz, M. T., JCCF Conference, Kawasaki, JP, 19 September 2002

Reetz, M. T., Technische Universität Braunschweig, DE, 28 October 2002

Reetz, M. T., University of Leeds, GB, 4 November 2002

Reetz, M. T., Merck-Lecture, University of Manchester, GB, 5 November 2002

Reetz, M. T., Chemistry Meets Technology II, London, GB, 9 December 2002

Reetz, M. T., GDCh, Frankfurt, DE, 17 December 2002

Richter, W. J., XXV. Bibliothekstagung der MPG, Dresden, DE, 7 May 2002

Richter, W. J., 5. Bibliothekstagung der CPT-Sektion, Heidelberg, DE, 5 November 2002

Schüth, F., GDCh, Universität Erlangen-Nürnberg, DE, 10 January 2002

Schüth, F., GDCh, Tag der Chemie, Universität Stuttgart, DE, 1 February 2002

Schüth, F., GDCh, Universität Magdeburg, DE, 14 February 2002

Schüth, F., Catalysis Meeting, Technische Universität Eindhoven, NL, 18 February 2002

Schüth, F., Euresco Conference, Zeolite Molecular Sieves, Obernai, FR, 15-18 March 2002

Schüth, F., GDCh, Philipps-Universität Marburg, DE, 10 March 2002

Schüth, F., UOP/Honeywell Invitation Lecture Series, Des Plaines, Illinois, USA, 1-4 June 2002

Schüth, F., GDCh, Universität Karlsruhe, DE, 27 June 2002

Schüth, F., Fakultät für Chemie, TU Berlin, DE, 28 June 2002

Schüth, F., Nordrhein-Westfälische Akademie der Wissenschaften, Düsseldorf, DE, 3 July 2002

Schüth, F., 3rd International Mesostructured Materials Symposioum, Jeju, KR, 8-11 July 2002

Schüth, F., 2nd International FEZA Conference, Taormina, IT, 1-5 September 2002

Schüth, F., Italian Association of Zeolites (AIZ), Taormina, IT, 6 September 2002

Schüth, F., 552. Dechema Kolloquium, Frankfurt, DE, 7 November 2002

Theyssen, N., Celanese Chemicals Europe GmbH, Standort Ruhrchemie, Oberhausen, DE, 11 July 2002

Theyssen, N., 4. AK-Tagung: Ressourcen und umweltschonende Synthesen und Prozesse, FSU Jena, DE, 2 September 2002

Thiel, W., Competence Center for Computational Chemistry, ETH Zürich, CH, 10 January 2002

Thiel, W., IBM Research Center Rüschlikon, Zürich, CH, 11 January 2002

Thiel, W., Moscowitz Lecture, University of Minnesota, Minneapolis, USA, 5 April 2002

Thiel, W., GDCh, Universität Mainz, DE, 16 May 2002

Thiel, W., GDCh, Universität München, DE, 18 June 2002

Thiel, W., Hinze-Kolloquium, Universität Bielefeld, DE, 28 June 2002

Thiel, W., Gordon Conference for Computational Chemistry, New London, USA, 1 July 2002

Thiel, W., Department of Chemistry, University of Auckland, NZ, 9 July 2002

Thiel, W., Physical Chemistry Seminar, University of Auckland, NZ, 16 July 2002

Thiel, W., Theoretical Chemistry Seminar, University of Auckland, NZ, 17 July 2002

Thiel, W., School of Biological Sciences, University of Auckland, NZ, 18 July 2002

Thiel, W., SPHERS Summer School, Han-sur-Lesse, BE, 18-19 September 2002

Thiel, W., MINERVA Symposium: Computational Quantum Chemistry, Berlin, DE, 27 September 2002

Thiel, W., Symposium: Computational Organic Chemistry, Uppsala, SE, 4 October 2002

Thiel, W., DFG-Workshop, Universität Köln, DE, 12 October 2002

Thiel, W., GDCh, Universität Erlangen, DE, 19 December 2002

Vyboishchikov, S., Institut de Química Computacional, Universitat de Girona, ES, 23 May 2002

Vyboishchikov, S., Unitat de Química Física, Universitat Autònoma de Barcelona, ES, 17 June 2002

Vyboishchikov, S., Universitet Leiden, NL, 17 November 2002

Zibrowius, B., SFB 294, Universität Leipzig, DE, 19 June 2002

2003

Babik, S., Universität Konstanz, DE, 5 August 2003

Belder, D., Universität Tübingen, DE, 30 January 2003

Belder, D., Forschungszentrum Jülich, DE, 26 March 2003

Belder, D., Bergische Universität Wuppertal, DE, 1 July 2003

Belder, D., GDCh-Jahrestagung Chemie, München, DE, 9 October 2003

Bocola, M., BIOTRANS 2003, Olomouc, CZ, 30 June 2003

Bocola, M., CERC3 Young Chemists Workshop, Computer Modeling of Chemical and Biological Systems, Porto, PR, 4 April 2003

Bönnemann, H., EU Project Meeting Apollon, Madrid, ES, 8-12 January 2003

Bönnemann, H., MPI Magdeburg, DE, 5 March 2003

Bönnemann, H., Universität Hamburg, DE, 23 April 2003

Bönnemann, H., EU Project Meeting Apollon, Prag, CZ, 28-29 June 2003

Bönnemann, H., FECHEM Conference, Zürich, CH, 10-13 August 2003

Bönnemann, H., ECIS Colloid Meeting, Florenz, IT, 20-27 September 2003

Bönnemann, H., ACS Fall Meeting, New York, USA, 6-12 September 2003

Bönnemann, H., GDCh Jahrestagung, München, DE, 6-11 October 2003

Bönnemann, H., Wacker Chemie, München, DE, 24 October 2003

Bühl, M., Universität Niteroí bei Rio de Janeiro, BR, 30 April 2003

Bühl, M., IX Auremn-Congress (NMR users' meeting), Angra dos Reis, BR, 5-9 May 2003

Bühl, M., Max-Planck-Institut für Bioanorganische Chemie, Mülheim/Ruhr, DE, 4 July 2003

Fink, G., Acedemia Nazionale dei Lincei, Rom, IT, 12-13 March 2003

Fink, G., EUPOC 2003, Mailand, IT, 8-12 June 2003

Fink, G., Universität Konstanz, DE, 5 August 2003

Fink, G., German-Chinese Bilatral Symposium, Mülheim/Ruhr, DE, 14-18 August 2003

Fürstner, A., Jour Fixe der Gesellschaft Österreichischer Chemiker, TU Graz, AT, 8 January 2003

Fürstner, A., Novartis Young Investigator Award, Basel, CH, 28 January 2003

Fürstner, A., Abbott Laboratories Distinguished Lecture, University of Notre Dame, IN, USA, 3 March 2003

Fürstner, A., 2002/2003 Bristol-Myers Squibb Lecturer, Stanford University, USA, 5 March 2003

Fürstner, A., 3rd Bristol Synthesis Meeting, Bristol, UK, 14 April 2003

Fürstner, A., Merck Sharp & Dohme, Harlow, UK, 15 April 2003

Fürstner, A., GDCh-Programm "Historische Stätten der Wissenschaft", Gießen, DE, 16 May 2003

Fürstner, A., AstraZeneca Course, Mölndal, SE, 19-21 May 2003

Fürstner, A., GDCh, Universität Paderborn, DE, 26 May 2003

Fürstner, A., Universidad de Santiago de Compostela, ES, 26-27 June 2003

Fürstner, A., 14th Summer Chemistry Symposium, Pfizer, Sandwich, UK, 15 July 2003

Fürstner, A., 15th International Symposium on Olefin Metathesis and Related Chemistry (ISOM XV), Kyoto, JP, 29 July 2003

Fürstner, A., Bayer Yakuhin, Kyoto, JP, 31 July 2003

Fürstner, A., Tetrahedron Prize Award Symposium, New York, USA, 8 September 2003

Fürstner, A., 226th ACS National Meeting, Carbohydrate Division, New York, USA, 9 September 2003

Fürstner, A., One-Day-Symposium "New Trends in Bioorganic and Medicinal Chemistry", Oslo, NO, 31 October 2003

Fürstner, A., International Symposium on Catalysis, BayKomm, Leverkusen, DE, 14 November 2003

Fürstner, A., DSM Nutritional Products, Basel, CH, 19 November 2003

Fürstner, A., 3rd Solvias Science Day, New Methods and Developments in Catalysis, Basel, CH, 20 November 2003

Fürstner, A., Altana Pharma KG, Konstanz, DE, 21 November 2003

Fürstner, A., GDCh, Universität zu Köln, DE, 5 December 2003

Fürstner, A., 2nd Centre for Synthesis and Chemical Biology Symposium on Recent Advances in Synthesis and Chemical Biology, Dublin, IE, 12 December 2003

Glorius, F., Chemiedozententagung, Chemnitz, DE, 18 March 2003

Glorius, F., Steinheimer Gespräche, Steinheim, DE, 9 May 2003

Glorius, F., Regionales FCI-Stipendiatentreffen, Dortmund, DE, 23 May 2003

Glorius, F., Universität Dortmund, DE, 17 June 2003

Glorius, F., 13th European Symposium on Organic Chemistry (ESOC 13), Cavtat-Dubrovnik, HR, 11 September 2003

Gooßen, L. J., OC Kolloquium, Universität Bochum, DE, 10 January 2003

Gooßen, L. J., OC Kolloquium IfOK Rostock, DE, 15 January 2003

Gooßen, L. J., Novo Nordisk, Kopenhagen, DK, 24 January 2003

Gooßen, L. J., OC Kolloquium, Universität Göttingen, DE, 10 February 2003

Gooßen, L. J., 4SC AG, Martinsried, DE, 24 February 2003

Gooßen, L. J., OC Kolloquium, Universität Karlsruhe, DE, 28 March 2003

Gooßen, L. J., Steinheimer Gespräche des FCI, Steinheim, DE, 9 May 2003

Gooßen, L. J., FCI Stipendiatentreffen, Dortmund, DE, 23 May 2003

Gooßen, L. J., OC Kolloquium, Universität Wuppertal, DE, 2 July 2003

Gooßen, L. J., OC Kolloquium, Universität Freiburg, DE, 7 July 2003

Gooßen, L. J., OC Kolloquium, Universität Zürich, CH, 26 July 2003

Gooßen, L. J., FECHEM, Zürich, CH, 10 August 2003

Gooßen, L. J., Bayer AG, Leverkusen, DE, 23 September 2003

Haenel, M. W., Vortragsveranstaltung der DGMK-Bezirksgruppe Ruhr, Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, DE, 20 November 2003

Kaskel, S., 15. Deutsche Zeolithtagung, 5-7 March 2003

Kaskel, S., Degussa, Darmstadt, DE, 17 April 2003

Kaskel, S., Anorganisch Chemisches Kolloquium, Ruhr-Universität Bochum, DE, 27 June 2003

Kaskel, S., 8. Arbeitstreffen Polymerkeramik, TU Darmstadt, DE, 15 July 2003

Kaskel, S., Technische Chemie Universität Stuttgart, DE, 18 July 2003

Kaskel, S., Technische Chemie TH Aachen, DE, 31 July 2003

Kaskel, S., 2. Interdisziplinäre Schule für Nachhaltigkeit in der Chemie, Volkenroda, DE, 23-26 September 2003

Knoke, S., XXXVI. Jahrestreffen deutscher Katalytiker, Weimar, DE, 19-21 March 2003

Lehmann, C. W., 23rd International Conference on X-ray Analysis, Durham, UK, 14-17 September 2003

Lehmann, C. W., Universität Paderborn, DE, 3 November 2003

Lehmann, C. W., Universidad Nacional de La Plata, AR, 11-14 November 2003

Lehmann, C. W., BASF Ludwigshafen, DE, 4 December 2003

Leitner, W., Netherlands Catalysis Conference 2th, NL, 10 March 2003

Leitner, W., ACHEMA, Frankfurt, DE, 21 May 2003

Leitner, W., Novel Technolgie Conference, Manchester, UK, 3 June 2003

Leitner, W., Symrise, Holzminden, DE, 13 June 2003

Leitner, W., OMCOS – 12, Toronto, CA, 8 July 2003

Leitner, W., Gordon Conference "Organometallic Chemistry", Salve Regina University, Newport, Rhode Island, 22 July 2003

Leitner, W., DuPont, Wilmington, USA, 28 July 2003

Leitner, W., 28th International Conference on Solution Chemistry, Debrecen, HU, 26 August 2003

Leitner, W., 226th ACS Meeting, New York, USA, 8 September 2003

Leitner, W., 13th European Symposium on Organic Chemistry, Dubrovnik, HR, 12 September 2003

Leitner, W., DECHEMA/GVC-Jahrestagung, Mannheim, DE, 18 September 2003

Leitner, W., Degussa, Frankfurt/Wolfgang, DE, 2 October 2003

Leitner, W., DSM, Geleen, NL, 7 October 2003

Leitner, W., 7. SFB Seminar, Jülich, DE, 17 October 2003

Leitner, W., Le Nouvelles Forces de la Catalyse, Rennes, FR, 3 November 2003

Leitner, W., Greiss Lectureship, University of Nottingham, UK, 12 November 2003

Leitner, W., Greiss Lectureship, University of Loughborough, UK, 13 November 2003

Leitner, W., Greiss Lectureship, University of Leicester, UK, 14 November 2003

Leitner, W., Universiteit van Amsterdam, NL, 26 November 2003

Leitner, W., Institute of Chemical and Engineering Sciences, Singapore, 15 December 2003

Leitner, W., Singapore International Chemistry Conference, SG, 17 December 2003

List, B., NSF-Workshop, Asilomar, USA, 12 July 2003

List, B., SFB-Symposium, Jülich, DE, 17 October 2003

List, B., Universität (TH) Darmstadt, DE, 10 November 2003

List, B., Universität Freiburg, DE, 24 November 2003

List, B., Universität Karlsruhe, DE, 25 November 2003

List, B., Universität Köln, DE, 1 December 2003

List, B., Universität Göttingen, DE, 8 December 2003

List, B., Universität Basel, CH, 18 December 2003

Marlow, F., BMBF/PCOC-Meeting, Karlsruhe, DE, 25 January 2003

Marlow, F., Seminarvortrag, Braunscheig, DE, 19 June 2003

Marlow, F., Euromat2003, Lausanne, CH, 1-5 September 2003

Marlow, F., Seminarvortrag Chemnitz, DE, 13 December 2003

Pörschke, *K.-R.,* M. Bühl, C. Gemel, R. Goddard, A. Rufińska, XVth FECHEM Conference on Organometallic Chemistry, Zürich, CH, 10–15 August 2003

Reetz, M. T., Felix Serratosa Lecture, University of Barcelona, ES, 20/21 January 2003

Reetz, M. T., GDCh, Universität Hannover, DE, 6 February 2003

Reetz, M. T., Degussa, Hanau, DE, 14 February 2003

Reetz, M. T., University of Southampton, GB, 3 March 2003

Reetz, M. T., Centenary Lecture, University of Bristol, GB, 5 March 2003

Reetz, M. T., University of Nottingham, GB, 7 March 2003

Reetz, M. T., University of Edinburgh, GB, 10 March 2003

Reetz, M. T., University of Cambridge, GB, 12 March 2003

Reetz, M. T., H. C. Brown Lecture, Purdue University, Lafayette, USA, 5 April 2003

Reetz, M. T., Bürgenstock, CH, 27 April 2003

Reetz, M. T., UCLA-Amgen Lecture, Los Angeles, USA, 7 May 2003

Reetz, M. T., Chiral Europe 2003, London, GB, 13 May 2003

Reetz, M. T., Achema, Frankfurt, DE, 19 May 2003

Reetz, M. T., GDCh, Technische Universität München, Garching, DE, 20 May 2003

Reetz, M. T., Universität Wien, AT, 28 May 2003

Reetz, M. T., Gordon Conference Bioorganic Chemistry, Andover, New Hampshire, USA, 18 June 2003

Reetz, M. T., DuPont, Wilmington, USA, 20 June 2003

Reetz, M. T., Boehringer Ingelheim Pharma AG, Biberach, DE, 26 June 2003

Reetz, M. T., Philipps-Universität Marburg, DE, 18 June 2003

Reetz, M. T., 10th Brazilian Meeting on Organic Synthesis, Sao Paulo, BR, 28 August 2003

Reetz, M. T., Silver Anniversary 2003 Fall Organic Symposium of the Princeton ACS Section, University of New Jersey, Piscataway, USA, 19 September 2003

Reetz, M. T., Regio-Symposium für Organische Synthese und Katalyse, Albert-Ludwig-Universität Freiburg, DE, 24 September 2003

Reetz, M. T., GDCh-Jahrestagung, München, DE, 8 October 2003

Reetz, M. T., Nordrhein-Westfälische Akademie der Wissenschaften, Düsseldorf, DE, 15 October 2003

Reetz, M. T., Internationales Katalyse-Symposium, Bayer AG, Leverkusen, DE, 14 November 2003

Reetz, M. T., ACC Workshop, Royal Netherlands Academy of Arts and Science, Amsterdam, NL, 18 November 2003

Reetz, M. T., Hans Herloff Inhoffen-Vorlesung, Universität Braunschweig, DE, 26 November 2003

Reetz, M. T., Schweizer Jungchemikerforum, Universität Basel, CH, 11 December 2003

Rentzsch M., IUPAC 2003, Ottawa, CA, 11 August 2003

Richter, W. J., 6. Bibliothekstagung der CPT-Sektion, Leipzig, DE, 29 October 2003

Schöneboom, J., Arbeitstagung Theoretische Chemie, Mariapfarr, AT, 21 February 2003

Schöneboom, J., Stipendiatentreffen des Fonds der Chemischen Industrie, Dortmund, DE, 22 May 2003

Schöneboom, J., Computational Chemistry Workshop, Bayer Pharma, Wuppertal, DE, 3 November 2003

Schrader, W., Institut für organische Katalyse, Rostock, DE, 26 February 2003

Schrader, W., Max-Planck-Institut für Bioanorganische Chemie, Mülheim/Ruhr, DE, 18 September 2003

Schüth, F., GDCh- Kolloquium Universität des Saarlandes, Saarbrücken, DE, 3 February 2003

Schüth, F., Österreichische Akademie der Wissenschaften, Graz, AT, 21 March 2003

Schüth, F., XXXVI. Jahrestreffen Deutscher Katalytiker, Weimar, DE, 19-21 March 2003

Schüth, F., Schmalenbach-Gesellschaft für Betriebswirtschaft, Bingen, DE, 31 March 2003

Schüth, F., GDCh, Universität Hamburg, DE, 17 April 2003

Schüth, F., French-German Summer School Research, Lyon University, Lyon, FR, 3 July 2003

Schüth, F., Gordon Conference, Colby College, Waterville, Maine, USA, 13-18 July 2003

Schüth, F., EuropaCat-VI, Innsbruck, AT, 31 August - 4 September 2003

Schüth, F., International Graduate School of Chemistry, Münster, DE, 9 September 2003

Schüth, F., 2nd European Organosilicon Days, München, DE, 11 September 2003

Schüth, F., The Netherlands Graduate School for Catalysis Research (NIOK), Utrecht, NL, 25 September 2003

Schüth, F., Conference on Functional Nanostructures (CFN03), Universität Karlsruhe, DE, 29 September 2003

Schüth, F., Jahrestagung Chemie 2003, München, DE, 9-10 October 2003

Schüth, F., BMBF-Werkstofftage, Weimar, DE, 31 October 2003

Schüth, F., Debye-Lecture, Universität Utrecht, NL, 7 November 2003

Schüth, F., GDCh, Universität Bonn, DE, 11 November 2003

Schüth, F., 2nd Symposium of Hightech Research Center, Okayama University of Science, JP, 23-26 November 2003

Schüth, F., Kolloquium Universität Bielefeld, DE, 2 December 2003

Senn, H. M., SPHERS Network Meeting, Sevilla, ES, 18 January 2003

Senn, H. M., Inorganic Chemistry Seminar, University of Zürich, CH, 16 April 2003

Senn, H. M., Intergroup Seminar Inorganic/Physical Chemistry, ETH Zürich, CH, 4 July 2003

Tesche, B., 31. DGE-Conference, Dresden, DE, 7-12 September 2003

Thiel, S., Theoretisch-Chemisches Kolloquium, Ruhr-Universität Bochum, DE, 29 October 2003

Thiel, S., Computational Chemistry Workshop, Bayer Pharma, Wuppertal, DE, 11 November 2003

Thiel, W., DECHEMA Katalysetagung, Frankfurt, DE, 17 January 2003

Thiel, W., Workshop on Theoretical Chemistry, Mariapfarr, AT, 18–20 February 2003

Thiel, W., SPHERS Network Meeting, Bad Peterstal, DE, 30 August 2003

Thiel, W., German-Chinese Symposium on Olefin Polymerization, Mülheim/Ruhr, DE, 16 September 2003

Thiel, W., 39th Symposium on Theoretical Chemistry, Gwatt, CH, 1 October 2003

Thiel, W., GDCh-Jahrestagung: Theorie-Symposium, München, DE, 8 October 2003

Thiel, W., Physikalisch-chemisches Seminar, Universität München, DE, 22 October 2003

Thiel, W., SFB 624 Symposium on Templates, Universität Bonn, DE, 27 October 2003

Thiel, W., GDCh, Universität Kiel, DE, 6 November 2003

Thiel, W., COST Meeting on Olefin Polymerization, Mülheim /Ruhr, DE, 14 November 2003

Thiel, W., GDCh, Universität Stuttgart, DE, 27 November 2003

Vyboishchikov, S., AM-2003 Workshop, Barcelona, ES, 16 May 2003

Vyboishchikov, S., Fachbereich Chemie, Universität Marburg, DE, 5 July 2003

Wiesenhöfer W., 1st Meeting on Sustainable Chemistry in Spain, Barcelona, ES, 12 November 2003

2004

Belder, D., Analytica Conference, München, DE, 12 May 2004

Belder, D., Philipps Universität Marburg, DE, 14 June 2004

Belder, D., Universität Frankfurt, DE, 25 June 2004

Belder, D., University of Helsinki, FI, 17 August 2004

Bocola, M., BIOCAT 2004, Hamburg, DE, 30 August 2004

Bönnemann, H., Particles 2004, Orlando, USA, 6-11 March 2004

Bönnemann, H., CAMD, Baton Rouge, USA, 12-15 March 2004

Bönnemann, H., Dye Solar Cells Project Meeting, Titisee, DE, 10 May 2004

Bönnemann, H., EU Project Meeting Apollon, Ljubljana, SL, 7-9 July 2004

Bönnemann, H., Dechema, Frankfurt, DE, 14 July 2004

Bönnemann, H., Groves Fuel Cell Meeting, München, DE, 5-8 October 2004

Bönnemann, H., Nanomaterials 2004, Stamford, USA, 20-29 October 2004

Bühl, M., Max-Planck-Institut für Eisenforschung, Düsseldorf, DE, 15 January 2004

Bühl, M., Second Joint HLRB and KONWIHR Result and Reviewing Workshop, München, DE, 2-3 March 2004

Bühl, M., Chemiedozententagung, Dortmund, DE, 7-10 March 2004

Bühl, M., Bunsentagung, Dresden, DE, 20-22 May 2004

Bühl, M., Technische Universität Dresden, DE, 24 May 2004

Bühl, M., Ecole Nationale Supérieure de Chimie de Paris, FR, 9 June 2004

Bühl, M., Second Humboldt Conference on Computational Chemistry, Nessebar, BUL, 1-5 September 2004

Bühl, M., Université de Strasbourg, FR, 8 September 2004

Bühl, M., S. Grigoleit, 40th Symposium for Theoretical Chemistry, Suhl, DE, 19-23 September 2004

Bühl, M., Universität Frankfurt/Main, DE, 30 September 2004

Bühl, M., Universität Genf, CH, 2 December 2004

Fink, G., European Technology Forum Workshop "Ziegler Catalysis"- Crompton GmbH, Bergkamen, DE, 13 February 2004

Fink, G., Universität Düsseldorf - GDCh-Fachgruppe Makromolekulare Chemie, Düsseldorf, DE, 15-16 March 2004

Fink, G., Institut für Polymerforschung, Dresden, DE, 28 April 2004

Fink, G., MOSPOL, Moskau, RUS, 22-25 June 2004

Fink, G., Institut für Technische und Makromolekulare Chemie, RWTH Aachen, DE, 1 July 2004

Fink, G., TICONA GmbH, Frankfurt-Höchst, DE, 30 September 2004

Fürstner, A., GDCh, Universität Hamburg, DE, 27 January 2004

Fürstner, A., RSC Centenary Lecture, University of Strathclyde, UK, 3 February 2004

Fürstner, A., RSC Centenary Lecture, University of Newcastle upon Tyne, UK, 4 February 2004

Fürstner, A., RSC Centenary Lecture, University of Swansea, UK, 6 February 2004

Fürstner, A., RSC Centenary Lecture, University of Loughborough, UK, 9 February 2004

Fürstner, A., RSC Centenary Lecture, University of Manchester, UK, 11 February 2004

Fürstner, A., DIP-Symposium, MPI für Kohlenforschung, Mülheim/Ruhr, DE, 12 March 2004

Fürstner, A., University of Edmonton, CA, 15 March 2004

Fürstner, A., AMRI, Albany, USA, 17 March 2004

Fürstner, A., Chemistry as a Life Science, State University of New Jersey, USA, 19 March 2004

Fürstner, A., International Symposium on Advances in Synthetic, Combinatorial and Medicinal Chemistry, ASCMC 2004, Moskau, R, 5 May 2004

Fürstner, A., Merck Lecture, University of Cambridge, UK, 24 May 2004

Fürstner, A., Merck Lecture, Merck, Sharp & Dohme, Harlow, UK, 26 May 2004

Fürstner, A., Merck Lecture, University of Cambridge, UK, 28 May 2004

Fürstner, A., 7th International Symposium on Carbanion Chemistry, ISCC-7, Alicante, ES, 9 July 2004

Fürstner, A., 10th Belgian Organic Synthesis Symposium (BOSS-10), Louvain-la-Neuve, BE, 12 July 2004

Fürstner, A., GDCh, Universität Konstanz, DE, 15 July 2004

Fürstner, A., Altana Pharma KG, Konstanz, DE, 16 July 2004

Fürstner, A., 15th International Conference of Organic Synthesis, ICOS-15, Nagoya, JP, 3 August 2004

Fürstner, A., 123. Versammlung der GDNÄ, Passau, DE, 21 September 2004

Fürstner, A., 12th Chemistry Day, Institut de Recherche Pierre Fabre, Castres, FR, 8 October 2004

Fürstner, A., Österreichische Akademie der Wissenschaften, Wien, AT, 11 October 2004

Fürstner, A., GlaxoSmithKline, Stevenage, UK, 14 October 2004

Fürstner, A., SFB 623 der Ruprecht-Karls-Universität Heidelberg, DE, 29 October 2004

Fürstner, A., Aventis, Frankfurt am Main, DE, 4 November 2004

Fürstner, A., Wyeth Lecture, Wyeth, Cambridge, USA, 8 November 2004

Fürstner, A., Wyeth Lecture, Massachusetts Institute of Technology, Cambridge, USA, 9 November 2004

Fürstner, A., Merck-Frosst Lecturer, Merck, Montréal, CA, 11 November 2004

Fürstner, A., Merck-Frosst Lecturer, University of Montréal, CA, 12 November 2004

Glorius, F., Merck KGaA, Darmstadt, DE, 22 January 2004

Glorius, F., Chemiedozententagung in Dortmund, DE, 9 March 2004

Glorius, F., Universität Marburg, DE, 1 June 2004

Glorius, F., Solvias AG, Basel, CH, 3 June 2004

Glorius, F., Universität Basel, CH, 4 June 2004

Glorius, F., Universität Heidelberg, DE, 14 June 2004

Glorius, F., Universität Stuttgart, DE, 15 June 2004

Glorius, F., Universität Karlsruhe, DE, 13 July 2004

Glorius, F., Universität Bonn, DE, 20 July 2004

Glorius, F., Merck & Co., New Jersey, USA, 20 August 2004

Glorius, F., 228. ACS-Meeting, Philadelphia, USA, 24 August 2004

Glorius, F., 228. ACS-Meeting, Philadelphia, USA, 25 August 2004

Glorius, F., Bayer Pharma, Wuppertal, DE, 7 September 2004

Glorius, F., ORCHEM-Tagung, Bad Nauheim, DE, 9 September 2004

Glorius, F., BASF AG, Ludwigshafen, DE, 1 October 2004

Glorius, F., Universität Hamburg, DE, 19 October 2004

Glorius, F., Universität Münster, DE, 21 October 2004

Glorius, F., Boehringer-Ingelheim, Biberach, DE, 27 October 2004

Glorius, F., Universität Darmstadt, DE, 1 November 2004

Glorius, F., Universität Freiburg, DE, 8 November 2004

Glorius, F., Freie Universität Berlin, DE, 9 November 2004

Glorius, F., Humboldt-Universität Berlin, DE, 10 November 2004

Glorius, F., Universität Wuppertal, DE, 11 November 2004

Gooßen, L. J., OC Kolloquium, RWTH Aachen, DE, 10 February 2004

Gooßen, L. J., OC Kolloquium, EPFL Lausanne, CH, 25 February 2004

Gooßen, L. J., OC Kolloquium, Universität Kaiserslautern, DE, 7 April 2004

Gooßen, L. J., Leo Bioscience, Kopenhagen, DK, 29 April 2004

Gooßen, L. J., OC Kolloquium, University of Kopenhagen, DK, 30 April 2004

Gooßen, L. J., OC Kolloquium, Universität Marburg, DE, 27 May 2004

Gooßen, L. J., Schering AG, Berlin, DE, 28 May 2004

Gooßen, L. J., UMICORE AG, Hanau, DE, 28 May 2004

Gooßen, L. J., OC Kolloquium, Universität Stuttgart, DE, 16 November 2004

Gooßen, L. J., OC Kolloquium, Universität Hamburg, DE, 30 November 2004

Haenel, M. W., DGMK, 60. Sitzung des Arbeitskreises Kohlenveredlung, Velen/Westf., DE, 19 April 2004

Haenel, M. W., DGMK, 61. Sitzung des Arbeitskreises Kohlenveredlung, Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, DE, 12 November 2004

Lehmann, C. W., National Tsing Hua University, TW, 23 June 2004

Lehmann, C. W., Academia Sinica, Taipeh, TW, 25 June 2004

Lehmann, C. W., Sommerschule Einkristallstrukturanalyse, Hardehausen, DE, 13-17 September 2004

Lehmann, C. W., Polymorphism & Crystallisation, IQPC, Frankfurt, DE, 25 October 2004

Leitner, W., 4th Green and Sustainable Chemistry Workshop, GSCN, Tokyo, JP, 9 March 2004

Leitner, W., Verantwortlich handeln - wieviel Nachhaltigkeit will sich die chemische Industrie leisten?, Leverkusen, DE, 11 March 2004

Leitner, W., XXXVII. Jahrestreffen Deutscher Katalytiker, Weimar, DE, 18 March 2004

Leitner, W., FZ Karlsruhe, DE, 2 April 2004

Leitner, W., Advances in Flavours and Fragrances, Manchester, UK, 12 May 2004

Leitner, W., 18th Canadian Symposium on Catalysis, Montreal, CA, 17 May 2004

Leitner, W., Canada-US Joint Workshop on Innovative Chemistry in Clean Media McGill University, Montreal, CA, 20 May 2004

Leitner, W., TU Graz, AT, 6 June 2004

Leitner, W., Bayer AG, Leverkusen, DE, 25 June 2004

Leitner, W., Chemisch-Technisches Kolloquium, Dortmund, DE, 23 July 2004

Leitner, W., Georgia Institute of Technology, Atlanta, USA, 19 October 2004

Leitner, W., University of Berkeley, USA, 21 October 2004

Lindén, M., Partnering-Event zur erwarteten BMBF-Ausschreibung des Forschungsbereiches "Chemische Nanotechnologie", Dechema, Frankfurt, DE, 14 July 2004

List, B., Bayer Chemicals AG, Leverkusen, DE, 7 January 2004

List, B., Humboldt Universität Berlin, DE, 8 January 2004

List, B., Schering AG, Berlin, DE, 9 January 2004

List, B., Universität Tübingen, DE, 20 January 2004

List, B., Universität Bonn, DE, 3 February 2004

List, B., Chemistry Lecturer Conference, Dortmund, DE, 10 March 2004

List, B., Merck KG, Darmstadt, DE, 11 March 2004

List, B., SFB-Symposium "Frontiers in Advanced Synthesis", Münster, DE, 14 May 2004

List, B., GlaxoSmithKline, Stevenage, UK, 19 May 2004

List, B., Canadian Society of Chemistry Conference, CA, 29 May 2004

List, B., Wacker, Consortium für Elektrochemie, München, DE, 7 June 2004

List, B., Degussa Fine Chemical Price Lecture, Chiral Europe, Mainz, DE, 15 June 2004

List, B., Universität Helsinki, FI, 17 June 2004

List, B., Universität Wuppertal, DE, 21 June 2004

List, B., Belgian Organic Synthesis Symposium, Louvain-la-Neuve, BE, 14 July 2004

List, B., German-American Frontiers in Chemistry, München, DE, 16 July 2004

List, B., Technische Universität München, DE, 22 July 2004

List, B., ICHAC, Shanghai, CN, 21 August 2004

List, B., Mulzer Symposium, Universität Wien, AT, 3 September 2004

List, B., French-German Summer School, Saarbrücken, DE, 30 September 2004

List, B., BASF Research Seminar 2004, Ludwigshafen, DE, 13 October 2004

List, B., GlaxoSmithKline, Research Triangle Park, USA, 18 October 2004

List, B., Abott Laboratories, Abbott Park, USA, 19 October 2004

List, B., JNJ, Springhouse, USA, 21 October 2004

List, B., GlaxoSmithKline, Tonbridge, UK, 11 November 2004

List, B., Lieseberg Price Lecture, Universität Heidelberg, DE, 30 November 2004

Marlow, F., BMBF/PCOC-Meeting, Aachen, DE, 7 April 2004

Marlow, F., Seminarvortrag, Universität Hamburg, DE, 17 May 2004

Marlow, F., Workshop "Nanoporöse Kristalle", Delmenhorst, DE, 10 June 2004

Marlow, F., Seminarvortrag, IPHT Jena, DE, 1 November 2004

Pörschke, K.-R., R. Goddard, A. Rufińska, M. Bühl, 227th ACS National Meeting, Anaheim, USA, 28 March – 1 April 2004

Reetz, M. T., Chemspeed Ltd., Basel, CH, 22 January 2004

Reetz, M. T., Novartis Chemistry Lectureship, Basel, CH, 3 February 2004

Reetz, M. T., Novartis Chemistry Lectureship, London, UK, 25 February 2004

Reetz, M. T., 42. Tutzing-Symposium, Tutzing, DE, 3 March 2004

Reetz, M. T., Novartis Chemistry Lectureship, Wien, AT, 16 March 2004

Reetz, M. T., Technische Universität, Graz, CH, 17 March 2004

Reetz, M. T., Carlsberg-Seminar, Kopenhagen, DK, 19 March 2004

Reetz, M. T., Jungchemikerforum, Heidelberg, DE, 31 March 2004

Reetz, M. T., Werdelmann-Vorlesung, Universität Duisburg-Essen, DE, 28 April 2004

Reetz, M. T., New International Conference on Modern Synthetic Methods - Reaction to Reality, Berlin, DE, 6 May 2004

Reetz, M. T., Aventis, Vitry-sur-Seine, FR, 13 May 2004

Reetz, M. T., F. Hoffmann-La Roche Ltd., Basel, CH, 7 June 2004

Reetz, M. T., ISBOC-7, Sheffield, UK, 1 July 2004

Reetz, M. T., ISHC-14, Universität München, DE, 8 July 2004

Reetz, M. T., 13th International Congress of Catalysis, Université Pierre et Marie Curie, Paris, FR, 13 July 2004

Reetz, M. T., Aventis Pharma Deutschland GmbH, Frankfurt, DE, 2 September 2004

Reetz, M. T., Scripps Research Institute, La Jolla, USA, 30 September 2004

Reetz, M. T., Diversa Corporation, San Diego, USA, 1 October 2004

Reetz, M. T., Caltech-Merck Symposium on Organic Synthesis, Pasadena, USA, 2 October 2004

Reetz, M. T., 50 Jahre organische Synthese in Berlin-Adlershof, Berlin, DE, 15 October 2004

Reetz, M. T., Bohlmann-Vorlesung, Berlin, DE, 8 November 2004

Reetz, M. T., Molecular evolution: from enzymes to genomes, Institut Pasteur, Paris, FR, 10 November 2004

Richter, W. J., XXVII. Bibliothekstagung der MPG, Stuttgart, DE, 4 May 2004

Richter, W. J., 7. Bibliothekstagung der CPT-Sektion, München, DE, 26 October 2004

Schrader W., Universität Münster, DE, 9 December 2004

Schüth, F., Festkörpertag am Zentrum für Festkörperchemie und neue Materialien (ZFM), Universität Hannover, DE, 30 January 2004

Schüth, F., GDCh-Kolloquium Universität GH Siegen, DE, 10 February 2004

Schüth, F., Max-Planck-Society/UCSB Workshop, Santa Barbara, USA, 22-25 February 2004

Schüth, F., Fifth Netherlands Catalysis and Chemistry Conference (NCCC V), Noordwijkerhout, NL, 9 March 2004

Schüth, F., Symposium on "Transition metal oxides", Humboldt-Universität Berlin, DE, 23 March 2004

Schüth, F., 1st Anniversary of the BASF Research Laboratory at ISIS-ULP and Symposium on Nanostructured Polymeric Materials, Strasbourg, FR, 29-30 March 2004

Schüth, F., Symposium on Mesoporous Crystals and Related nano-structured Materials and Workshop by/for/of young scientists, Arrhenius Laboratory, Stockholm University, SE, 1-5 June 2004

Schüth, F., MH2004 – International Symposium on Metal-Hydrogen Systems, Krakau, PL, 9-10 September 2004

Schüth, F., French-German Summer School of Research, Saarbrücken, DE, 29 September 2004

Schüth, F., Deutscher Business Angels Tag 2004, Mainz, DE, 4 October 2004

Schüth, F., Department of Chemistry, Istanbul University, Istanbul, TR, 5 October 2004

Schüth, F., GVC/Dechema-Jahrestagungen, Karlsruhe, DE, 13 October 2004

Schüth, F., GDCh-Kolloquium, Technische Universität München, DE, 2 November 2004

Schüth, F., 2004 MRS Fall Meeting, Boston, USA, 28-30 November 2004

Theyssen, N., Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, DE, 17 May 2004

Theyssen, N., Green Solvents for Synthesis, Bruchsal, DE, 5 October 2004

Thiel, S., Competence Center for Computational Chemistry, ETH Zürich, CH, 21 October 2004

Thiel, W., TACC-2004 Conference: Theory and Applications of Computational Chemistry, Gyeongju, Korea, KO, 20 February 2004

Thiel, W., Peking University, Department of Chemistry, Peking, CN, 23 February 2004

Thiel, W., Peking University, Theoretical Chemistry Seminar, Peking, CN, 24 February 2004

Thiel, W., University of Science and Technology of China, Hefei, CN, 26 February 2004

Thiel, W., Xiamen University, Department of Chemistry, Xiamen, CN, 27 February 2004

Thiel, W., Fudan University, Department of Chemistry, Shanghai, CN, 1 March 2004

Thiel, W., German-Israeli DIP Symposium on Asymmetric Catalysis, Mülheim/Ruhr, DE, 12 March 2004

Thiel, W., National Meeting of the American Chemical Society, Dewar Memorial Symposium, Anaheim, USA, 28 March 2004

Thiel, W., GDCh, Universität Karlsruhe, DE, 3 June 2004

Thiel, W., National Meeting of the American Chemical Society, Symposium: Quantum/Classical Simulations in Chemistry and Biophysics, Philadelphia, USA, 25 August 2004

Thiel, W., National Meeting of the American Chemical Society, Schaefer Symposium, Philadelphia, USA, 26 August 2004

Thiel, W., Summer School: New Developments in Catalysis, Saarbrücken, DE, 1 October 2004

Thiel, W., Jug-Symposium, Universität Hannover, DE, 16 October 2004

Thiel, W., Consortium für elektrochemische Industrie, Workshop, München, DE, 20 October 2004

Thiel, W., GDCh, Universität Göttingen, DE, 28 October 2004

Thiel, W., GDCh, Technische Universität München, DE, 16 November 2004

Thiel, W., Max-Planck-Institut für chemische Physik fester Stoffe, Anorganisch-chemisches Kolloquium, Dresden, DE, 7 December 2004

Thiel, W., Lise Meitner Symposium, Technion, Haifa, IL, 19 December 2004

Yurchenko, S. N., Academy of Sciences of the Czech Republic, Prag, CS, 12 September 2004

7.3 Scientific Honors, Lectureships, Awards

Bönnemann, H.
- Scientific Member of Forschungszentrum Karlsruhe since August 2003

Bühl, M.
- Heisenberg fellow until November 2004
- Visiting professor at the Université de Strasbourg

Fürstner, A.
- Member of Deutsche Akademie der Naturforscher Leopoldina, 2002
- Merck Academic Development Program Award, 2002
- Arthur C. Cope Scholar Award of the American Chemical Society, 20 August 2002
- Serratosa Lecture, Universitat de Barcelona, ES, 21-22 January 2002
- AstraZeneca Research Lecture in Modern Chemistry, Vancouver, CA, 12-13 February 2002
- Novartis Lecture, Prag, CZ, 27 May 2002; Bratislava, SK, 29 May 2002; Budapest, HU, 30 May 2002
- Boehringer Ingelheim Lecture, Queen's University, Kingston, CA, 10 September 2002
- Astra Zeneca Lecture, Montreal, CA, 12 September 2002; University of Ottawa, CA, 13 September 2002
- Abbott Lecture, Texas A&M University, College Station, USA, 23 September 2002
- Novartis Young Investigator Award, Basel, CH, 28 January 2003
- Abbott Laboratories Distinguished Lecture, University of Notre Dame, IN, USA, 3 March 2003
- 2002/2003 Bristol-Myers Squibb Lecturer, Stanford University, USA, 5 March 2003
- RSC Centenary Lecture, University of Strathclyde, UK, 3 February 2004; University of Newcastle upon Tyne, UK, 4 February 2004; University of Swansea, UK, 6 February 2004; University of Loughborough, UK, 9 February 2004; University of Manchester, UK, 11 February 2004
- Merck Lecture, University of Cambridge, UK, 24 May 2004; Merck, Sharp & Dohme, Harlow, UK, 26 May 2004; University of Cambridge, UK, 28 May 2004
- Wyeth Lecture, Wyeth, Cambridge, USA, 8 November 2004; Massachusetts Institute of Technology, Cambridge, USA, 9 November 2004
- Merck-Frosst Lecturer, Merck, Montréal, CA, 11 November 2004; University of Montréal, CA, 12 November 2004
- Member of Nordrhein-Westfälische Akademie der Wissenschaften, 2004
- Member of Österreichische Akademie der Wissenschaften, 2004
- Tetrahedron Chair, 12 July 2004

Glorius, F.
- Liebig scholarship of the "Fonds der Chemischen Industrie" until November 2004
- Thieme Journal Award 2002
- ORCHEM-Award 2004 for Scientists
- Lilly Lecture Award 2004

Gooßen, L.
- Thieme Literature Prize 2002
- Academy Prize of the Academy of Sciences (Göttingen) 2002
- Jochen-Block Prize of the DECHEMA for Catalysis Research 2003
- Leo-Lectureship, Leo Pharma, Denmark April 2004
- Heisenberg Scholarship of the "Deutsche Forschungsgemeinschaft" September 2004
- Award of the "Fonds der Chemischen Industrie" for exceptional research:"Dozentenstipendium", November 2004

Kaskel, S.
- Awardee of the "Nanotechnology" BMBF Junior Competition

Leitner, W.
- Griess Lectureship of the Royal Society of Chemistry 2003

List, B.
- Carl-Duisberg-Memorial Award 2003
- Lecturer's Award of the Endowment of the Chemical Industry 2004
- Lieseberg Prize 2004
- Degussa Prize for Chiral Chemistry 2004
- Honorary Professorship at the Universität Köln 2004

Reetz, M. T.
- William Dauben Lecture, University of California, Berkely, USA, 30 April 2002
- Merck-Lecture, Leeds, GB, 4 November 2002; Manchester, GB, 5 November 2002
- Felix Serratosa Lecture, University of Barcelona, ES, 20-21 January 2003
- Centenary Lecture, Bristol, GB, 5 March 2003
- H. C. Brown Lecture, Purdue University, Lafayette, USA, 5 April 2003
- UCLA-Amgen Lecture, Los Angeles, USA, 7 May 2003
- Novartis Chemistry Lectureship 2004, Basel, CH, 3 February 2004; London, UK, 25 February 2004; Vienna, AT, 16 March 2004
- Werdelmann Lecture, Essen, DE, 28 April 2004
- Bohlmann Lecture, Berlin, DE, 8 November 2004
- Hans Herloff Inhoffen-Medaille, Universität Braunschweig, DE, 26 November 2003
- Member of the Kuratorium der Alfried Krupp von Bohlen und Halbach-Stiftung (since 2003)

Schöneboom, J.
- Otto-Hahn-Medaille, Max-Planck-Society, 2004

Schüth, F.
- Gottfried-Wilhelm Leibniz-Preis of Deutsche Forschungsgemeinschaft, DFG 2003
- UOP/Honeywell Invitation Lecture Series, Des Plaines, Illinois, USA, 1-4 June 2002
- Debye-Lecture, Universität Utrecht, NL, 7 November 2003

Theyssen, N.
- Borchers-Plakette, RWTH Aachen, 2004

Thiel, W.
- Schrödinger Medal 2002 of the World Association of Theoretical Chemists
- Moskowitz Lecture, University of Minnesota, USA, 5 April 2002
- Visiting Professor at the University of Auckland, NZ, July 2002

7.4 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 2002 – 2004 the following lectures/workshops were held:

Angermund, K., Kristallographie und Molecular Modeling, Ruhr-Universität Bochum, DE, SS 2002, WS 2002/2003, SS 2003, WS 2003/2004, SS 2004, WS 2004/2005

Belder, D., Instrumentelle Analytik für Fortgeschrittene: Chromatographie und Kapillarelektrophorese, Bergische Universität Gesamthochschule Wuppertal, SS 2002

Belder, D., Methoden der Strukturaufklärung: Moderne Techniken der Massenspektrometrie, Bergische Universität Gesamthochschule Wuppertal, SS 2002, SS 2003, SS 2004

Belder, D., Instrumentelle Analytik für Fortgeschrittene: Analytik mit Mikrochips, Bergische Universität Gesamthochschule Wuppertal, SS 2003

Belder, D., Methoden der Strukturaufklärung: Analytik mit Mikrochips, Bergische Universität Wuppertal, SS 2004

Benn, R., Methoden der Strukturuntersuchungen II, Universität/Gesamthochschule Siegen, SS 2002

Bönnemann, H., Darstellung und Charakterisierung von Übergangsmetallkatalysatoren, Rheinisch-Westfälische Technische Hochschule Aachen, SS 2002, WS 2002/2003

Bühl, M., Analytische Chemie, Universität-Gesamthochule Essen, WS 2002/2003

Bühl, M., Theoretische Chemie, Universität-GH Wuppertal, WS 2003/2004

Bühl, M., Tutorial Computational Chemistry, Universität-GH Wuppertal, WS 2003/2004

Bühl, M., Dichtefunktionaltheorie - Grundlagen und Anwendungen, Universität-Gesamthochschule Wuppertal, WS 2004/2005

Fink, G., Makromolekulare Chemie (along with practical training), Heinrich-Heine-Universität Düsseldorf, WS 2001/2002, SS 2002

Fink, G., Experimentelle Übungen zur Makromolekularen Chemie, Heinrich-Heine-Universität Düsseldorf, WS 2001/2002, SS 2002, WS 2002/2003, SS 2003, WS 2003/2004, SS 2004

Fink, G., Spezielle Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf, SS 2002

Fink, G., Spezielle Makromolekulare Chemie, Stereospezifische Polymerisation und Stereochemie von Polymeren, Heinrich-Heine-Universität Düsseldorf, WS 2002/2003

Fink, G., Spezielle Makromolekulare Chemie, Polymer Reaction Engineering, Heinrich-Heine-Universität Düsseldorf, SS 2003

Fink, G., Spezielle Makromolekulare Chemie, Reaktionskinetik und Mechanismen, Heinrich-Heine-Universität Düsseldorf, WS 2003/2004

Fink, G., Spezielle Makromolekulare Chemie, Stereospezifische Polymerisation und Polymer Reaktionstechnik, Heinrich-Heine-Universität Düsseldorf, WS 2003/2004

Fürstner, A., Naturstoffsynthese, Universität Dortmund, DE, WS 2001/2002, WS 2003/2004

Fürstner, A., Moderne Synthesemethoden, Technische Universität Graz, AT, WS 2001/2002, WS 2002/2003

Fürstner, A., Naturstoffsynthese II, Universität Dortmund, DE, SS 2002, SS 2004

Fürstner, A., Stereoselektive Synthesen I, Universität Dortmund, DE, WS 2002/2003, WS 2004/2005

Fürstner, A., Stereoselektive Synthesen II, Universität Dortmund, DE, SS 2003

Glorius, F., Asymmetric catalysis, Universität Dortmund, WS 2003/2004

Glorius, F., Chemistry of heterocycles, Universität Dortmund, SS 2004

Gooßen, L. J., Metallorganische Katalyse, Bergische Universität Wuppertal, WS 2003/2004, WS 2004/2005

Haenel, M. W., Übergangsmetalle in der Organischen Synthese, Heinrich-Heine-Universität Düsseldorf, WS 2001/2002, WS 2002/2003, WS 2003/2004, WS 2004/2005

Haenel, M. W., Spezielle Aromatenchemie: Cyclophane – polycyclische Aromaten – Fullerene – Nanotubes, Heinrich-Heine-Universität Düsseldorf, SS 2002, SS 2003

Haenel, M. W., Organische Chemie II: Chemie der Aromaten und Heterocyclen, Heinrich-Heine-Universität Düsseldorf, SS 2004

Lehmann, C. W., Fortgeschrittenen Praktikum Anorganische Chemie (Röntgenkurs), Bergische Universität Wuppertal, SS 2002

Lehmann, C. W., Methoden der Strukturuntersuchung, Bergische Universität Wuppertal, SS 2003, SS 2004

List, B., Organokatalyse, Universität Köln, SS 2003, WS 2003/2004, SS 2004, WS 2004/2005

Marlow, F., Physical Chemistry in Nanostructured Systems I (Molecular Nanostructures, engl.),

Freie Universität Berlin, WS 2001/2002

Marlow, F., Physical Chemistry in Nanostructured Systems II (Photonic Crystals, engl.), Freie Universität Berlin, SS 2002, WS 2002/2003, SS 2003, SS 2004

Marlow, F., Pflichtvorlesung Molekulare Materialien im Bachelor-Studiengang Chemie/Molekulare Materialien,Universität Duisburg-Essen, WS 2003/2004, WS 2004/2005

Pörschke, K.-R., Metallorganische Komplexchemie, Heinrich-Heine-Universität Düsseldorf, SS 2002, WS 2002/2003, SS 2004, WS 2004/2005

Reetz, M. T., Course on directed evolution of enzymes, University of Technology, Delft, NL, 2002, 2003, 2004

Schrader, W., Einführung in die moderne Massenspektrometrie für die quantitative Analytik, Westfälische Wilhelms-Universität Münster, SS 2002, SS 2003

Schrader W., Introduction into modern Mass Spectrometry, Wilhelms-Universität Münster, SS 2004

Schüth, F. and Kaskel S., Grundzüge der Chemie für Studierende des Maschienenbaus und des Studiengangs Umwelttechnik und Resourcenmanagement, Ruhr-Universität Bochum, WS 2002/2003

Schüth, F., Präparation fester Katalysatoren, Teil I und II, Ruhr-Universität Bochum, WS 2002/2003

Schüth, F., Wissenschaftliche Präsentation, (fächerübergreifende Lehrveranstaltung, Blockveranstaltung), Ruhr-Universität Bochum, SS 2003

Schüth, F. and Kaskel S., Maschinenbauer, Ruhr-Universität Bochum, WS 2003/2004

Schüth, F., Präparation fester Katalysatoren, Lehrverbund Katalyse, Universität Dortmund, WS 2004

Thiel, W., Theoretische Chemie II, Universität Düsseldorf, WS 2002/2003

Thiel, W., Molekülmodellierung, Universität Düsseldorf, SS 2004

Thiel, W., Workshop on Theoretical Chemistry, Universität Graz, Mariapfarr, AT, February 2003

7.5 List of Talks Given by Guests (2002 - 2004)

2002

5 February 2002	Professor X.-L. Hou (Shanghai Institute of Organic Chemistry, CN) *Ferrocene ligands with multi-chiralities: Synthesis and applications in asymmetric catalysis*
26 February 2002	Dr. R. Mahrwald (Humboldt-Universität, Berlin, DE) *Stereoselektive Aldolprozesse mit Titanreagenzien*
26 March 2002	Dr. E. J. M. Hensen (University Eindhoven, NL) *Realistic planar silica-based models for industrial hydrotreating catalysts*
9 March 2002	Professor G. Férey (University Versailles-Saint-Quentin, FR) *From building blocks to very large pores via scale chemistry*
12 April 2002	Dr. G. Nikonov (Lomonosov-University, Moskau, RU) *New types of non-classical interligand H-Si interactions in transition metal hydrides*
18 April 2002	Professor E. J. Beckmann (University of Pittsburgh, USA) *Design of highly* CO_2*-soluble materials*
22 April 2002	Professor D. Goldfarb (Weizmann Institut, Rehovot, IL) *Metal substitution and complex encapsulation in porous materials through the "eyes" of high field pulsed EPR*
21 May 2002	Professor P. Kocovsky (University of Glasgow, UK) *Asymmetric synthesis with transition-metal catalysts and metal-free organocatalysts*
22 May 2002	Dr. S. Mecking (Freiburger Materialsforschungszentrum, DE) *Katalyse und Polymerisation in unkonventionellen Mehrphasensystemen*
28 May 2002	Professor K. Szabo (University of Stockholm, SE) *Palladium-catalyzed electrophilic substitution of functionalized allylic substrates.Mechanism, regiochemistry and synthetic applications*
7 June 2002	Dr. M. Lindén (Abo Akademie, FI) *The use of mixed templates in the synthesis of porous oxides*
11 June 2002	Professor G. Panov (Boreskov Institute of Catalysis, Novosibirsk, RU) *Active state of iron in catalytic oxidation with nitrous oxide*
19 June 2002	Dr. S. Doye (Universität Hannover, DE) *Komplexe der 4. Nebengruppe als Hydroaminierungskatalysatoren*
26 June 2002	Dr. A. Theisen (Wyatt Technology Deutschland GmbH, DE) *Molmassenbestimmung und Strukturaufklärung mit der GPC-Lichtstreukopplung an synthetischen Polymeren*
15 July 2002	Dr. C. Dwyer (Sastech R&D, Sasolburg, ZA) *Hydroformylation studies using high pressure NMR spectroscopy*
16 July 2002	A. Volbach (MDL, DE) *Das elektronische Laborjournal, das Softwareprodukt ELAN*

17 July 2002	Dr. B. List (Scripps Research Institute, La Jolla, USA) *Asymmetrische Aminokatalyse*
18 July 2002	Dr. T. Weber (Patentanwaltbüro Kreisler, Köln, DE) *Abfassung von Patentanmeldungen*
12 August 2002	Professor Okubo (University of Tokyo, JP) *Crystal growth behavior of zeolites on atomic scale*
27 August 2002	Professor B. Kolbesen (Universität Frankfurt, DE) *Nitridierung von Übergangsmetallen und intermetallischen Phasen mittels thermischer Kurzzeitprozesse ('Rapid Thermal Processing')*
3 September 2002	Professor X. Zhang (Pennsylvania State University, USA) *Developing a practical chiral toolbox for asymmetric catalytic reactions*
14 October 2002	Professor G. Stucky (University of California Santa Barbara, USA) *Organizing domains in composite systems – synthesis, structure, function*
25 November 2002	Dr. S. Polarz (University of Toronto, CA) *Ordered mesoporous materials: Prototypes for nanoreactor systems*
26 November 2002	Dr. H. Amenitsch (Österreichische Akademie der Wissenschaften, Graz, AT) *SAXS from bulk to surfaces*
27 November 2002	Dr. T. Heine (Universität Dresden, DE) *From electronic structure calculations to simple rules of thumb for stability and properties of ‚aromatic‘ molecules*
17 December 2002	Dr. S. Mintova (Universität München, DE) *Synthesis and applications of nanosized molecular sieves*
18 December 2002	Professor D. Astruc (University of Bordeaux, FR) *Organometallic chemistry and catalysis at the nanoscopic scale*

German Chemical Society (GDCh), Ruhr Section

7 February 2002	Professor R. Kniep (MPI für chemische Physik fester Stoffe, Dresden, DE) *Morphogenese von Apatit-Gelatine-Kompositen*
11 April 2002	Professor N. Krause (Universität Dortmund, DE) *Funktionalisierte Allene in der Organischen Synthese*
25 April 2002	Professor G. N. Schrauzer (University of California San Diego, USA) *Mechanismus der biologischen Stickstoff-Fixierung*
20 June 2002	Professor M. Karas (Universität, Frankfurt, DE) *Stimmt die Chemie, kommen die Ionen – Zum aktuellen Verständnis von MALDI*
29 August 2002	Professor S.-I. Murahashi (Okayama University of Science, JP) *Ruthenium and iridium catalysts for organic synthesis. A way to green chemistry*
7 November 2002	Professor R. Boeckman (University of Rochester, USA) *New methodology for asymmetric synthesis with applications to the construction of complex molecules*
26 November 2002	Professor C. C. Cummins (MIT, Cambridge, USA) *The remarkable world of molybdaziridine and niobaziridine hydrides*

2003

19 February 2003	Dr. J. Kornatowski (Universität München, DE) *Morphology dependences in the crystals of zeolitic materials*
4 March 2003	Dr. M. Stöcker (SINTEF, Oslo, NO) *Standard reaction of the International Zeolite Association (IZA) for Acidity Characterization Ethylbenzene disproportionation over NaLaY*
4 March 2003	Dr. A. Hill (CSIRO Clayton, AU) *Pore-size distribution of mesoporous and nanoporous materials probed by Positron Annihilation Lifetime Spectroscopy*
5 March 2003	Dr. F. Furche (Universität Karlsruhe, DE) *Time-dependent density functional methods for excited state properties: Energetics, structure, vibrational spectra*
11 March 2003	Professor Zexing Cao (Xiamen University, CN) *Dinitrogen activation*
19 March 2003	Professor C. Marian (Universität Düsseldorf, DE) *Spin-orbit coupling in organic and organometallic molecules*
20 March 2003	Dr. Y. Röder (Wacker Siltronic AG, Burghausen, DE) *Berufseinstieg als Trainee – Umwege oder Überholspur?*
1 April 2003	Professor M. Linscheid (Humboldt-Universität, Berlin, DE) *DNA-Metallkomplexe mit Platin und Palladium – Untersuchungen mit Ionenfallen*
7 May 2003	Dr. D. Gleich (Universität Zürich, CH) *Computational approaches to activity in rhodium-catalyzed hydroformylation*
14 May 2003	Professor T. Livinghouse (Montana State University, Bozman, USA) *Stereocontrolled organic synthesis via substrate-metal complexation*
27 May 2003	Professor B. Engels (Universität Würzburg, DE) *Modellierung von Systemen mit unterschiedlicher Komplexität –von gespannten Allenen bis SARS*
10 June 2003	Dr. J. Francisco (Purdue University, USA) *The structure and reactivity of open-shell complexes: New frontiers in atmospheric chemistry*
11 June 2003	Dr. J. Autschbach (Universität Erlangen, DE) *Relativistic DFT calculations of NMR properties of heavy nuclei: spin-spin coupling constants, and shielding and coupling anisotropies*
16 June 2003	Professor D. Avnir (The Hebrew University Jerusalem, IL) *New applications of sol-gel materials*
16 July 2003	Professor S. Shaik (The Hebrew University, Jerusalem, IL) *Two-state reactivity and its manifestations: How can radicals be both present and absent in oxidations by Heme enzymes and catalysts*
4 August 2003	Professor M. Landau (Ben Gurion University of the Negev, IL)

	Transition metal based phase dispersions inside mesoporous silica nanotubes: Structure, assembling and functionality
22 August 2003	Professor T. R. Ward (Université de Neuchatel, CH) *Artificial Metalloenzymes for Enantioselective Catalysis based on the Biotin-Avidin Technology*
10 September 2003	Dr. J. Haas (Universität Basel, CH) *New chiral amine-ICI complexes: A combined computational and synthetic approach*
12 September 2003	Professor Z. Guan (University of California Irvine, USA) *Chain walking: A new strategy to control polymer technology*
16 September 2003	Dr. S. Yurchenko (Steacie Institute of Molecular Sciences, Ottawa, CA) *Theoretical model for the rovibrational description of non-rigidpyramidal XY3-type molecules: application to NH3*
1 October 2003	Professor C. J. Forsyth (University of Minnesota, USA) *Total synthesis of complex natural products*
13 October 2003	Dr. U. Kolb (Universität Mainz, DE) *Combining X-ray powder and electron diffraction – A key to nanostructural analysis?*
4 November 2003	Professor K. K. Unger (Universität Mainz, DE) *The next generation of adsorbents for life science applications: How to design silica adsorbents for liquid phase separation processes in proteomics?*
11 November 2003	Professor I. Stary (Academy of Sciences, Prag, CZ) *Molecular screws: From alkynes to helicenes*
12 November 2003	Professor R. Bernhardt (Universität Saarbrücken, DE) *Cytochrom P450 Systeme: Struktur, Funktion und potentielle Anwendungen in der Biotechnologie und Medizin*
10 December 2003	Dr. O. Trapp (Standford University, USA) *Reaktionschromatographie – eine neue Perspektive für die Katalyseforschung*

German Chemical Society (GDCh), Ruhr Section

23 January 2003	Professor W. Steglich (Universität München, DE) *Synthesen nach dem Vorbild der Pilze und Schwämme*
30 January 2003	Professor P. Jutzi (Universität Bielefeld, DE) *Strategien in der Cyclopentadienyl-Chemie von p-Block-Elementen*
20 February 2003	Professor D. Oesterhelt (MPI für Biochemie, Martinsried, DE) *Eine Chloridpumpe bei der Arbeit: Halorhodopsin*
10 April 2003	Professor H. Knözinger (Universität München, DE) *Isomerisierung von n-Alkanen – Charakterisierung und Funktionsweise von Wolfram-basierten Katalysatoren*
15 May 2003	Professor H. F. Schaefer (University of Georgia, Athens, USA) *Unsaturated binuclear homoleptic carbonyls:* $M_2(CO)_x$ *(M = Cr, Mn, Fe, Co, Ni, Cu; x = 5-11). Are multiple bonds between transition metals possible for these systems?*

12 June 2003	Professor M. Brookhart (University of North Carolina, USA) *Olefin polymerizations using late transition metal complexes*
3 July 2003	Professor H. G. Schmalz (Universität Köln, DE) *Übergangsmetalle als Werkzeuge in der Wirkstoffsynthese*
6 November 2003	Professor C. M. Niemeyer (Universität Dortmund, DE) *Fabrication of micro- and nanostructured devices from DNA and proteins*
17 November 2003	Professor L. Böhm (Basell Polyolefine GmbH, Frankfurt, DE) *Die Ethylen-Polymerisation mit Ziegler-Katalysatoren: 50 Jahre nach der Entdeckung*
27 November 2003	Professor Herbert Mayr (Ludwig-Maximilians-Universität München, DE) *Systematik polarer organischer Reaktionen: Theorie und Anwendung*
18 December 2003	Professor M. Stratmann (MPI für Eisenforschung, Düsseldorf, DE) *Neues vom Stahl: von ungewöhnlichen Legierungen bis zu maßgeschneiderten Oberflächen*

2004

3 January 2004	Dr. R. E. Zillich (University of California, Berkeley, USA) *Spectroscopy of Molecules in Superfluid Helium-4 Clusters*
20 January 2004	Professor Z. Gross (Israel Institute of Technology, Haifa, IL) *Asymmetric Catalysis by Chiral and Bio-conjugated Corrole Metal Complexes*
27 January 2004	Dr. M. Elstner (Universität Paderborn and Deutsches Krebszentrum Heidelberg, DE) *Calculating Absorption Spectra of Retinal Proteins: A Challenge for Quantum Chemistry*
17 February 2004	Dr. R. Anwander (Technische Universität München, DE) *Von molekularen zu nanostrukturierten Ziegler-Mischkatalysatoren*
16 March 2004	Dr. M. Thommes (Quantachrome, Boynton Beach, USA) *Adsorption hysteresis of simple gases in ordered and disordered mico/mesoporous silica materials*
19 March 2004	Professor O. Terasaki (University of Stockholm, SE) *Characterization of guest-functionalized porous systems by X-ray diffraction and electron microscopy*
23 March 2004	Professor A. Liese (Universität Münster, DE) *Scope and limitations of biocatalysis*
26 March 2004	Professor M. R. Buchmeiser (Universität Innsbruck, AT) *Übergangsmetall-katalysierte Synthese polymerer Trenn- und Trägermaterialien: Konzepte und Anwendungen in den Proteomics/Genomics und in der Heterogenkatalyse*
6 April 2004	Professor Jürgen Caro (Universität Hannover, DE) *Zeolithmembranen in der membranunterstützten Katalyse und Hochtemperaturstofftrennung – von den Labormustern bis hin zu den ersten technischen Anlagen*

11 May 2004	Professor E. Kraka (University of Goeteborg, SE) *The importance of computational chemistry in drug design – a CADD approach to non-toxic enediyne anti-cancer drug*
14 May 2004	Professor P. Pyykkö (University of Helsinki, FI) *Theoretical prediction of new species:* WAu_{12} *and other unusual compounds*
18 May 2004	Dr. S. Patchkovskii (Steacie Institute for Molecular Sciences, Ottawa, CA) *Predicting thermodynamic properties of hydrogen storage materials*
4 June 2004	Dr. S. Hecht (Freie Universität Berlin, DE) *Controlling oligomer/polymer backbone conformation: From tubular design to recognition and sensing*
28 June 2004	Professor M. G. Finn (Scripps Institute, La Jolla, USA) *New ways to make biological and polymeric connections*
12 July 2004	Professor Y. Yamamoto (Tohoky University, JP) *New synthetic methodologies with Lewis acids and palladium catalysts*
14 July 2004	Dr. V. G. Malkin (Slovak Academy of Sciences, Bratislava, SK) *Recent progress in calculation and interpretation of NMR and EPR parameters*
27 July 2004	Professor D. Shantz (A&M University, Texas, USA) *Polypeptide templated nanostructured oxides*
17 August 2004	Dr. L. A. Solovyov (Krasnoyarsk, RU) *Mesostructure analysis: problems and solutions*
24 August 2004	Professor B. Chemelka (UC Santa Barbara, USA) *Hierarchially ordered inorganic-organic and porous materials*
8 September 2004	Dr. J. Kästner (Technische Universität Clausthal, DE) *Unraveling biological nitrogen fixation: Insights from first-principles calculations*
14 September 2004	Dr. K. Gross (Sandia National Labs, USA) *Hydrogen sorption property measurements*
21 September 2004	Professor S.-W. Tsai (National Cheng Kung University, RC) *Carica papaya lipase: A versatile biocatalyst for the kinetic resolution of chiral acids*
28 September 2004	Professor M. Isobe (Nagoya University, JP) *Synthetic and bioorganic studies on protein phosphatase inhibition*
13 October 2004	Dr. P. Strodel (Universität Paderborn, DE) *Describing photochemistry in complex systems: OM2 plus CHARMM*
26 October 2004	Professor S. Förster (Universität Hamburg, DE) *Assembling polymers into ordered and compartimented structures*
27 October 2004	Dr. N. Gaston (Massey University, Auckland, NZ) *Mercury clusters – from van Waals to metallic systems*
9 November 2004	Dr. S. Vasenkov (Universität Leipzig, DE)

	Transport optimization of novel nanostructured materials processing hierarchically organized porous systems: Application for catalysis, storage and separations
8 December 2004	Professor A. Yamamoto (Institute of Technology, Tokyo, JP) *Development of new strategies based on the concept of palladium-promoted C-O bond cleavage*

German Chemical Society (GDCh), Ruhr Section

13 May 2004	Professor U. Rosenthal (Universität Rostock, DE) *Metalle machen's möglich: Der Weg von Dreiringen zu Fünfring-Exoten und deren Katalysen*
17 June 2004	Professor R. Mülhaupt (Universität Freiburg, DE) *Herausforderung Polymerisationskatalyse: Neue polymere Werk- und Effektstoffe*
7 October 2004	Professor J.-E. Bäckvall (Universität Stockholm, SE) *Recent advances in combination of metal and enzyme catalysis for asymmetric synthesis*
18 November 2004	Professor F. Diederich (Zürich, CH) *Molekulare Erkennung mit biologischen ETH Rezeptoren: Strukturbasierte Entwicklung nichtpeptidischer Enzyminhibitoren*
16 December 2004	Professor A. Manz (ISAS, Dortmund und Berlin, DE) *Continuous-flow chemical reactions and separations on chip*

7.6 Alexander von Humboldt Senior Awardees Hosted by the Institute

Professor Dr. John J. Eisch
State University of New York at Binghamton
Department of Chemistry
Binghamton, NY 13902-6000
USA

Professor Dr. Peter G. Schulz
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
Department of Chemistry and Biochemistry
Biomolecular Science and Engineering Program
Materials Department
University of California, Santa Barbara, CA 93106
USA

7.7 Local Activities of the Young Chemists Forum (JCF) of the German Chemical Society (GDCh)

List of Talks Given by Guests

10 January 2002	Dr. M. Willuhn (Schering AG, DE) *Berufseinstieg bei Schering*
4 June 2002	Professor Neumann-Mahlkau (Geologisches Landesamt NRW, DE) *Treibhaus oder Kühlung – Das Klima der Erde*
19 September 2002	W. Peters, W. Lubert (Enjoyventure Management GmbH, DE) *Venturekapital und junge Unternehmer*
26 September 2002	Priv.-Doz. Dr. U. Deichmann (Universität Köln, DE) *Chemiker und Biochemiker in der NS-Zeit*
5 December 2002	Professor G. Schwedt (Technische Universität Clausthal, DE) *Chemische Experimente mit Supermarktprodukten*
9 January 2003	Dr. B. Guenzel (Degussa AG, DE) *Promotion! – Was nun?*
16 January 2003	Dr. A. Düffels (Henkel KgaA, Düsseldorf, DE) *Patentreferent bei Henkel*
20 March 2003	Dr. Y. Röder (Wacker Siltronic AG, Burghausen, DE) *Berufseinstieg als Trainee - Umweg oder Überholspur?*
8 May 2003	Dr. E. Guggolz (Nachrichten aus der Chemie, Frankfurt, DE) *Wissenschaftsjournalismus*
30 June 2003	Dr. C. Temme (GKSS Forschungszentrum Geesthacht, DE) *365 Tage am Rande der Antarktis – Quecksilberanalytik unter widrigen Umständen*
10 July 2003	Dr. K.-J. Haack (Bayer CropScience GmbH, DE) *Schädlingsbekämpfung: Moderne Wirkstoffe, Wirkmechanismen und Herstellwege*
13 November 2003	Dr. M. Grauert (Boehringer Ingelheim Chemical Research Biberach, DE) *Crobenetine (BIII0890CL), a novel use-dependent sodium-channel blocker for the treatment of stroke* and Dr. G. Roth (same affiliation as above) *Research and drug-finding processes at Boehringer Ingelheim*
18 December 2003	Professor D. De Keukeleire (Ghent University, BE) *Hops and Beer: A healthy combination*
11 March 2004	Dr. C. Brehm (Altana Pharma AG, DE) *Wer ist Altana Pharma? Mein Berufseinstieg bei Altana Pharma*
4 November 2004	Dr. J. Ragot / Dr. D. Heimbach (Bayer HealthCare AG, Pharma Research Elberfeld, DE) *Mein erstes Jahr bei Bayer / A medical case study*

15 December 2004	Professor T. Vilgis (MPI für Polmerforschung, Mainz, DE) *Molecular Cooking: Science with pleasure*
21 December 2004	Professor A. Fenster (McGill University, CA) *Crime and Detection: The Story of Forensic Science*

Excursion

2 December 2004	Study trip to Henkel, Düsseldorf, DE 15 participants from the MPI für Kohlenforschung and Bioinorganic Chemistry The trip consists of a general presentation of the Henkel company. Subsequently a young employee of Henkel will present career opportunities and answers questions of the participants.

7.8 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