SANTANDER
INTERNATIONAL SUMMER SCHOOLS
FOR DOCTORAL STUDENTS

UNIVERSITÄT
HEIDELBERG
ZUKUNFT
SEIT 1386

MOLECULAR CATALYSTS
TOOLS FOR CHEMICAL SYNTHESIS
PROGRAMME BOOK

JULY 13 TO 24, 2015
HEIDELBERG CENTER FOR LATIN AMERICA (HCLA),
SANTIAGO DE CHILE

COOPERATION PARTNERS

Pontificia Universidad Católica de Chile
University of Notre Dame (USA)

Santander
UNIVERSIDADES

INTERNATIONAL SUMMER
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MOLECULAR CATALYSTS
TOOLS FOR CHEMICAL SYNTHESIS

CONTENT

PONTIFICIA
UNIVERSIDAD
CATÓLICA
DE CHILE


MUSEUM
MUSEUM

Universität Heidelberg,
University Square

UNIVERSITÄT HEIDELBERG

Heidelberg University, founded in 1386, is Germany's oldest university and one of the strongest research universities in Europe. The successes in both rounds of the Excellence Initiative of the German federal and state governments and in international rankings prove its leading role in the scientific community. In terms of educating students and promoting promising young academics, Heidelberg relies on research-based teaching and a well-structured training for doctoral candidates.

Heidelberg University is a comprehensive university with the full spectrum of subjects including medicine. It aims to strengthen the individual disciplines, to further interdisciplinary cooperation and to make research results usable for society and industry.

Heidelberg also draws its strength from its cooperation with local non-university research institutions. In addition, the university is tied into a worldwide network of research and teaching collaborations which give evidence of its marked global interconnectedness.

International Profile
Heidelberg University is tied into a worldwide network of research and teaching collaborations. Exchange programmes have been established with more than 400 universities worldwide. Heidelberg's marked global interconnectedness is also evidenced by its 19 university partnerships and three International Research Training Groups as well as its membership in European networks such as the League of European Research Universities (LERU) and the Coimbra Group.

A myriad of research and teaching collaborations are also established at the faculty, institute and chair levels. Additionally, Heidelberg has a satellite campus in Latin America as well as liaison offices in North America and Asia. The university also offers courses in Eastern Europe.

Heidelberg's international prominence is reflected in its student population: approximately 20 percent of Heidelberg's students and a third of the enrolled doctoral candidates come from abroad. According to a DAAD survey, Heidelberg is the favoured German university for international doctoral candidates.

SANTANDER UNIVERSIDADES

Santander, Committed to Higher Education
The university plays a fundamental role in the knowledge society. It acts as a guide towards an innovative society, contributing to economic and social change and supporting scientific and technological progress.

Through its Santander Universities Global Division, Banco Santander has collaborated with universities for more than 16 years on a unique global initiative which distinguishes it from other national and international banks and financial institutions.

In 1996, Emilio Botín (†), at that time Chairman of Santander, decided that the bank should be useful to the societies in which it operates. With the conviction that the university is a vital cornerstone of development and progress, it was decided that Santander's long term commitment would be materialised through creating a programme to help the academic world in its role as a guardian of knowledge and a key agent in achieving progress in terms of economic competitiveness and social wellbeing.

Santander Universities maintains a stable alliance with more than 1,040 universities from America, Asia and Europe.

In 2011, through Santander Universities, Banco Santander contributed over 110 million euros to cooperation projects with universities of America, Asia and Europe.

More than 2,130 professionals coordinate and manage Santander's commitment to higher education through Santander Universities Global Division. In the words of Emilio Botín, former Chairman of Santander: »Increased employment and welfare provision is based on education, research and effort.«

Academic institutions are receiving support from Santander for the development of academic initiatives relating to scholarships, mobility grants, research programmes, university-enterprise relations, new technologies.


BADEN - WÜRTTEMBERG
HEIDELBERG CENTER PARA AMERICA LATINA
CENTRO DE ESTUDIOS DE POSTGRADO Y POSTITULO
DE LA UNIVERSIDAD DE HEIDELBERG EN SANTIAGO DE CHILE

PROGRAMME OVERVIEW

MON 13	TUE 14	WED 15	THU 16	FRI 17	SAT 18	SUN 19	MON 20	TUE 21	WED 22	THU 23	FRI 24	SA 25
Arrival participants	9:30-10:30 h **Welcome Session** Gade, Toro-Labbé, Eckel, Eisenmann	9:30-10:30 h **Tutorial Lecture** Enders	9:30-10:30 h **Research Lecture** Toro-Labbé	9:30-10:30 h **Research Lecture** Hashmi	10:30-22:00 h **Excursion Cajón del Maipo**		9:30-11:00 h **Tutorial Lecture** Straub	9:30-10:30 h **Research Lecture** Gade	9:30-10:30 h **Research Lecture** Iluc	9:30-10:30 h **Research Lecture** Rojas	10:00-11:00 h **Tutorial Lecture** Gade	Departure participants
	10:30-11:30 **Introductory Lecture** Gade											
	12:00-13:00 h **Tutorial Lecture** Muñiz	11:00-12:00 h **Tutorial Lecture** Brown	11:00-12:00 h **Tutorial Lecture** Toro-Labbé	11:00-12:00 h **Tutorial Lecture** Brown			11:30-13:00 h **Tutorial Lecture** Straub	11:00-12:00 h **Research Lecture** Dupont	11:00-12:00 h **Tutorial Lecture** Rojas	11:00-12:00 h **Research Lecture** Bellemin-Laponnaz	11:30-12:30 h **Research Lecture** Mazet	
		12:00-13:00 h **Tutorial Lecture** Brown	12:00-13:00 h **Research Lecture** Brown	12:00-13:00 h **Research Lecture** Enders				12:00-13:00 h **Research Lecture** Straub	12:00-13:00 h **Student questions & answers** Rojas	12:00-13:00 h **Tutorial Lecture** Mazet		
	Lunch	Lunch	Lunch	Lunch			Lunch	Lunch	Lunch	Lunch	Lunch	
		15:00-16:00 h **Student poster presentations 1-4**	15:00-16:00 h **Student poster presentations 5-8**	15:00-16:00 h **Student poster presentations 9-12**			15:00-16:00 h **Student poster presentations 13-16**	15:00-16:00 h **Student poster presentations 17-20**		15:00-16:00 h **Tutorial Lecture** Gade	15:00-16:00 h **Roundtable Discussion**	
16:00-18:00 h HCLA Welcome Desk & Poster Setup	16:00-17:00 h PUC **Public Lecture** Hashmi	16:30-17:30 h **Research Lecture** Muñiz	16:30-17:30 h **Tutorial Lecture** Hashmi	16:30-17:30 h **Tutorial Lecture** Aliaga & Pavez			16:30-18:00 h **Tutorial Lecture** Dupont	16:30-18:00 h **Tutorial Lecture** Iluc		16:30-18:00 h **Tutorial Lecture** Bellemin-Laponnaz		
			17:30-18:00 h **Poster Session/ Discussion**	17:30-18:00 h **Poster Session/ Discussion**			**Student questions & answers**	**Student questions & answers**		**Student questions & answers**		
		Dinner	Dinner	Dinner			Dinner	Dinner		Dinner		
18:30 h HCLA Welcome Dinner											19:00 h HCLA Farewell Dinner	

DETAILED PROGRAMME

MONDAY, JULY 13, 2015

	Arrival participants
16:00 – 18:00	Welcome Desk at HCLA & Poster Setup
18:30 – 20:30	**Welcome Dinner,** HCLA

TUESDAY, JULY 14, 2015

09:30 – 10:30	**WELCOME SESSION**
	Lutz H. Gade, Alejandro Toro-Labbé, Walter Eckel, Isabel Eisenmann
10:30 – 11:30	**INTRODUCTORY LECTURE**
	Lutz H. Gade, Universität Heidelberg: »Molecular Catalysts: Tools for Chemical Synthesis«
11:30 – 12:00	*Coffee break*
12:00 – 13:00	**TUTORIAL LECTURE**
	Kilian Muñiz, Institut Català d'Investigació Química: »Fun with Physical-Organic Control Experiments«
13:00 – 15:00	*Lunch*
15:00 – 15:30	*Shuttle transfer from HCLA to Pontificia Universidad Católica de Chile (PUC)*
16:00 – 17:00	**PUBLIC LECTURE,** PUC
	A. Stephen K. Hashmi, Universität Heidelberg: »Gold – Nugget, Necklace, Nanotechnology«
17:00 – 17:30	*Shuttle transfer from Pontificia Universidad Católica de Chile (PUC) to HCLA*

Product analysis
in catalyst screening

WEDNESDAY, JULY 15, 2015

09:30 – 10:30	**TUTORIAL LECTURE** **Markus Enders,** Universität Heidelberg: »Non-Metallocene Olefin Polymerisation Catalysis«
10:30 – 11:00	*Coffee break*
11:00 – 12:00	**TUTORIAL LECTURE** **Seth Brown,** University of Notre Dame: »Catalysis as a Kinetic Phenomenon: Statement and Implications«
12:00 – 13:00	**TUTORIAL LECTURE** **Seth Brown,** University of Notre Dame: »Case Studies in the Pleasures and Perils of Mechanistic Analysis of Catalytic Reactions«
13:00 – 15:00	*Lunch*
15:00 – 16:00	**STUDENT POSTER PRESENTATIONS (1-4)**
16:00 – 16:30	*Coffee break*
16:30 – 17:30	**RESEARCH LECTURE** **Kilian Muñiz,** Institut Català d'Investigació Química: »Iodine-Catalysed Amination Reactions«
18:00 – 19:00	*Dinner*

THURSDAY, JULY 16, 2015

09:30 – 10:30	**RESEARCH LECTURE** **Alejandro Toro-Labbé,** Pontificia Universidad Católica de Chile: »Some Hints from Conceptual DFT to Chemical Catalysis«
10:30 – 11:00	*Coffee break*
11:00 – 12:00	**TUTORIAL LECTURE** **Alejandro Toro-Labbé,** Pontificia Universidad Católica de Chile: »Some Hints from Conceptual DFT to Chemical Catalysis«
12:00 – 13:00	**RESEARCH LECTURE** **Seth Brown,** University of Notre Dame: »Not Just a Scaffold: Ligand Involvement in Oxidation-Reduction Reactions«
13:00 – 15:00	*Lunch*
15:00 – 16:00	**STUDENT POSTER PRESENTATIONS (5-8)**
16:00 – 16:30	*Coffee break*
16:30 – 17:30	**TUTORIAL LECTURE** **A. Stephen K. Hashmi,** Universität Heidelberg: »Basic Principles of Gold Catalysis«
17:30 – 18:00	**POSTER SESSION / DISCUSSION**
18:00 – 19:00	*Dinner*

FRIDAY, JULY 17, 2015

09:30 – 10:30 **RESEARCH LECTURE**
A. Stephen K. Hashmi, Universität Heidelberg: »New Horizons in Gold Catalysis«
10:30 – 11:00 *Coffee break*
11:00 – 12:00 **TUTORIAL LECTURE**
Seth Brown, University of Notre Dame:
»Envisioning the Invisible: The Art of Inference in the Experimental Study of Catalysis«
12:00 – 13:00 **RESEARCH LECTURE**
M. Markus Enders, Universität Heidelberg:
»Organochromium Catalysts for Polymerisation or Selective Trimerisation of Ethylene«
13:00 – 15:00 *Lunch*
15:00 – 16:00 **STUDENT POSTER PRESENTATIONS (9-12)**
16:00 – 16:30 *Coffee break*
16:30 – 17:30 **TUTORIAL LECTURE**
Paulina Pavez & Margarita E. Aliaga, Pontificia Universidad Católica de Chile:
»Kinetics and mechanisms in homogeneous catalytic reactions«
17:30 - 18:00 **POSTER SESSION / DISCUSSION**
18:00 – 19:00 *Dinner*

SATURDAY, JULY 18, 2015

10:30 – 22:00 **Excursion to the canyon Cajón del Maipo**
> Weather-proof clothing and adequate shoes are recommended! <

10:30 – 12:30 *Bus trip from HCLA to Cajón del Maipo*
12:30 – 13:30 *Snack Lunch*
13:30 – 17:00 Free time: Trekking, Horse Riding, Rafting…
17:00 – 20:30 Wine tasting and Dinner at La Tribu, Cascada de las Ánimas
20:30 – 22:00 *Bus trip from Cajón del Maipo to HCLA*

SUNDAY, JULY 19, 2015

Free time

MONDAY, JULY 20, 2015

09:30 – 11:00 **TUTORIAL LECTURE**
Bernd Straub, Universität Heidelberg: »Electronic Structure of Reactive Transition Metal Intermediates«
11:00 – 11:30 *Coffee break*
11:30 – 13:00 **TUTORIAL LECTURE**
Bernd Straub, Universität Heidelberg: »Unravelling Reaction Mechanisms«
13:00 – 15:00 *Lunch*
15:00 – 16:00 **STUDENT POSTER PRESENTATIONS (13-16)**
16:00 – 16:30 *Coffee break*
16:30 – 18:00 **TUTORIAL LECTURE**
Jairton Dupont, Universidade Federal do Rio Grande do Sul: tba
SUBSEQUENTLY: STUDENT QUESTIONS & ANSWERS
18:00 – 19:00 *Dinner*

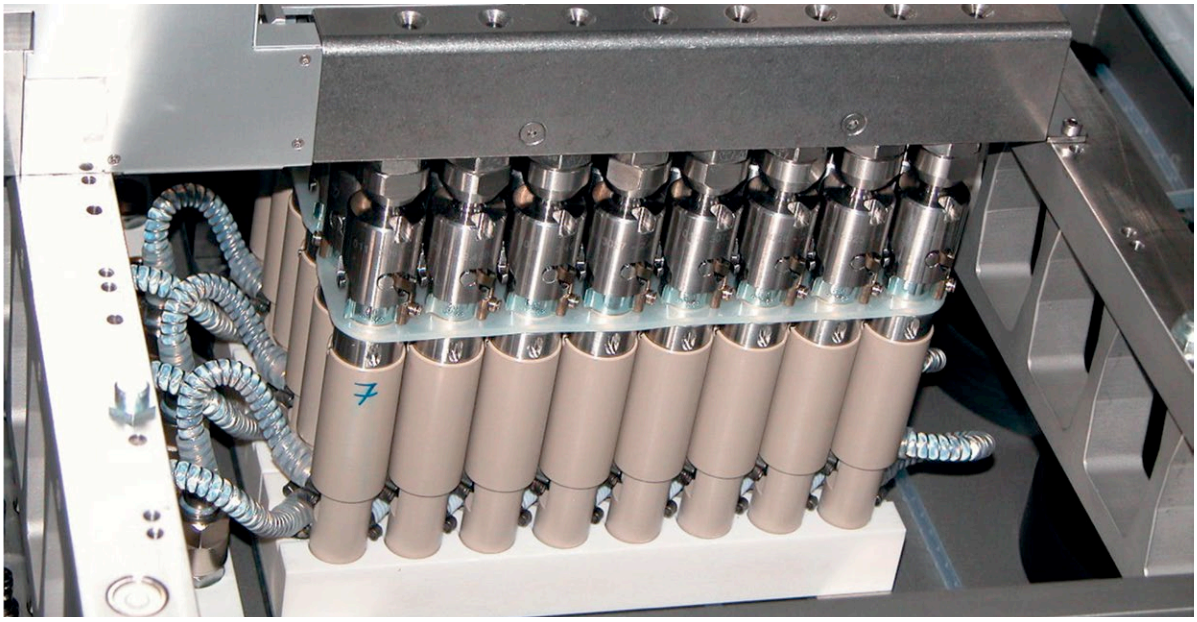
High throughput screening
in catalyst development

TUESDAY, JULY 21, 2015

09:30 – 10:30	**RESEARCH LECTURE**
	Lutz H. Gade, Universität Heidelberg: »Enantioselective Catalysis with 3d Transition Metal Complexes: Chiral Pincers as Stereodirecting Ligands«
10:30 – 11:00	*Coffee break*
11:00 – 12:00	**RESEARCH LECTURE**
	Jairton Dupont, Universidade Federal do Rio Grande do Sul: »Supported Ionic Liquid Phase Nanoparticle Catalysts«
12:00 – 13:00	**RESEARCH LECTURE**
	Bernd Straub, Universität Heidelberg: »Intermediates in Homogeneous Coinage Metal Catalysis«
13:00 – 15:00	*Lunch*
15:00 – 16:00	**STUDENT POSTER PRESENTATIONS (17-20)**
16:00 – 16:30	*Coffee break*
16:30 – 18:00	**TUTORIAL LECTURE**
	Vlad M. Iluc, University of Notre Dame: »Applications of metal-ligand cooperation in catalysis«
	SUBSEQUENTLY: STUDENT QUESTIONS & ANSWERS
18:00 – 19:00	*Dinner*

WEDNESDAY, JULY 22, 2015

09:30 – 10:30	**RESEARCH LECTURE**
	Vlad M. Iluc, University of Notre Dame: »Metal-Ligand Interactions: E-H Activation and Metal-Element Multiple Bonding«
10:30 – 11:00	*Coffee break*
11:00 – 12:00	**TUTORIAL LECTURE**
	René Rojas, Pontificia Universidad Católica de Chile: »Pre-olefin polymerization catalysts: Activation modes and impact on reactivity of the active site«
12:00 – 13:00	**STUDENT QUESTIONS & ANSWERS**
13:00 – 14:00	*Lunch*
Afternoon	*Free time*



THURSDAY, JULY 23, 2015

09:30 – 10:30	**RESEARCH LECTURE**
	René Rojas, Pontificia Universidad Católica de Chile:
	»Nickel complexes, Lewis acids influence on the reactivity towards ethylene and terminal olefins«
10:30 – 11:00	*Coffee break*
11:00 – 12:00	**RESEARCH LECTURE**
	Stéphane Bellemin-Laponnaz, Université de Strasbourg:
	»Catalytic Performance and Recycling of Oxazoline-Based Catalysts«
12:00 – 13:00	**TUTORIAL LECTURE**
	Clément Mazet, University of Geneva: »C_1-symmetry in Transition Metal-based Asymmetric Catalysis«
13:00 – 15:00	*Lunch*
15:00 – 16:00	**TUTORIAL LECTURE**
	Lutz H. Gade, Universität Heidelberg: »Threefold Rotational Symmetry as a Construction Principle in Asymmetric Catalysis«
16:00 – 16:30	*Coffee break*
16:30 – 18:00	**TUTORIAL LECTURE**
	Stéphane Bellemin-Laponnaz, Université de Strasbourg:
	»Kinetic Resolution: Concepts and Applications«
	SUBSEQUENTLY: STUDENT QUESTIONS & ANSWERS
18:00 – 19:00	*Dinner*

FRIDAY, JULY 24, 2015

10:00 – 11:00	**TUTORIAL LECTURE**
	Lutz H. Gade, Universität Heidelberg: »Non-Linear Effects in Asymmetric Catalysis«
11:00 – 11:30	*Coffee break*
11:30 – 12:30	**RESEARCH LECTURE**
	Clément Mazet, University of Geneva: »Recent Advances in Selective Isomerizations«
13:00 – 15:00	*Lunch*
15:00 – 16:00	**ROUNDTABLE DISCUSSION**
	»Molecular Catalysis: Challenges for the Future«
16:00 – 16:30	*Coffee break*
16:30 – 19:00	*Free time*
19:00	**Farewell Dinner,** HCLA

SATURDAY, JULY 25, 2015

Departure participants

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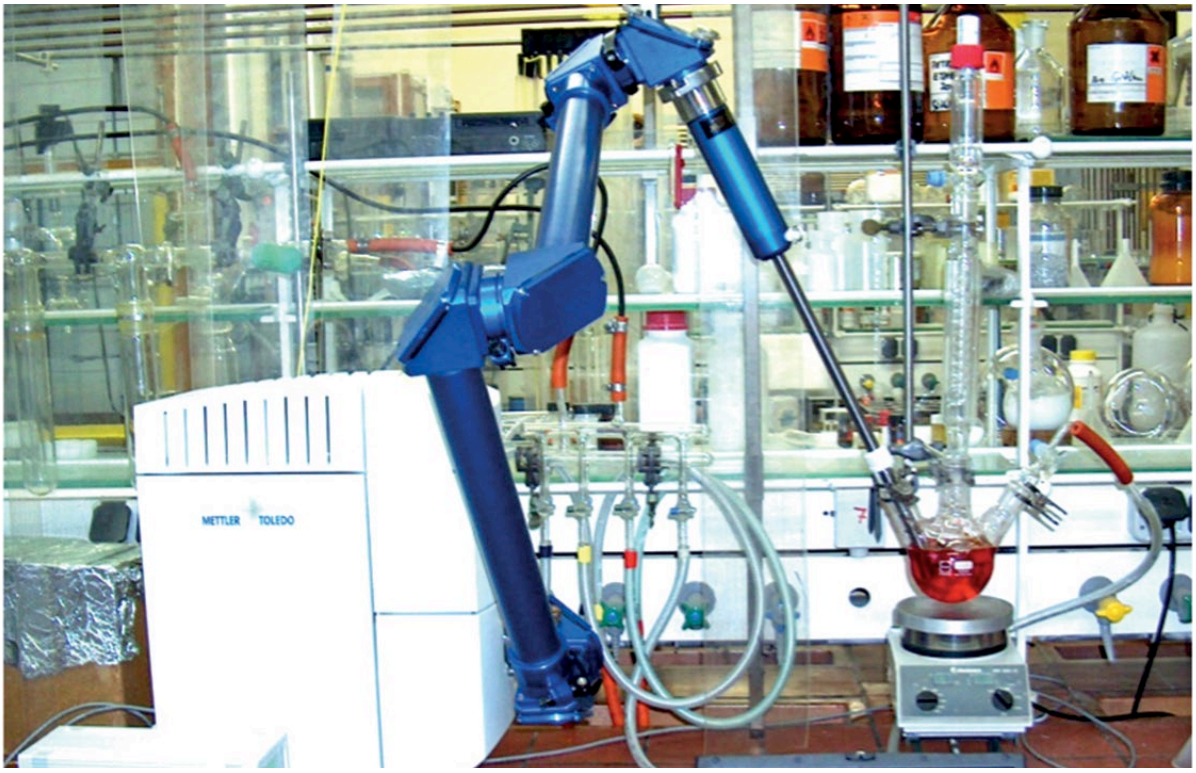

Catalytic reaction set up with
in situ IR spectroscopy

SPEAKERS

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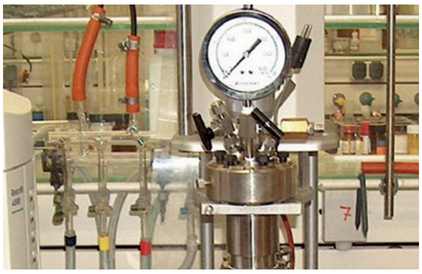

In situ high pressure infrared spectroscopy to monitor catalytic conversions

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ABSTRACTS OF SPEAKERS

STÉPHANE BELLEMIN-LAPONNAZ, UNIVERSITÉ DE STRASBOURG
RESEARCH LECTURE
Catalytic Performance And Recycling of Oxazoline-Based Catalysts
Asymmetric catalysis constitutes a privileged approach for the production of enantiopure compounds. However, homogeneous asymmetric catalytic systems frequently exhibit relatively low activity for a large-scale application and they also suffer from two drawbacks: (i) possible product contamination and, (ii) inability to reuse the homogeneous catalyst. Due to the high cost of both the chiral ligand and the metal, it is highly desirable to develop catalytic systems that are active at a very low catalytic level and/or that allow an easy separation from reaction mixture and efficient recycling. These points will be discussed in this research lecture.

[1] a) Gade, L. H.; Bellemin-Laponnaz, S. Chem. Eur. J. 2008, 14, 4152; b) Foltz, C.; Stecker, B.; Marconi, G.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade L. H. Chem. Eur. J. 2007, 13, 9912; c) Foltz, C.; Enders, M; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. Chem. Eur. J. 2007, 13, 5994.
[2] Gaab, M.; Bellemin-Laponnaz, S.; Gade, L. H. Chem. Eur. J. 2009, 15, 5450.
[3] a) Torres, M.; Heinrich, B.; Miqueu, K.; Bellemin-Laponnaz, S.; Eur. J. Inorg. Chem. 2012, 3384; b) Torres, M.; Maisse-François, A.; Bellemin-Laponnaz, S. ChemCatChem 2013, 5, 3078; c) Torres, M.; Nano, A.; Maisse-François, A.; Bellemin-Laponnaz,
S. New J. Chem. 2014, 38, 4748.

TUTORIAL LECTURE
Kinetic Resolution. Concepts and applications
The kinetic resolution of racemic compounds is a fundamental method for obtaining enantiomerically enriched molecules.[1] In this tutorial lecture, we will discuss recent advances in the use of chiral catalysts for the kinetic resolution and dynamic kinetic resolution of racemic substrates. Successful examples that afford products in high enantiomeric excess are included and some mechanistic details will also be discussed. Selected examples will illustrate the wide range of different reaction scenarios where kinetic resolution was found to be an efficient synthetic strategy.

[1] Fiaud, J.C.; Kagan, H.B. (1988). »Kinetic Resolution«. In Eliel, E.L.; Wilen, S.H. Topics in Stereochemistry 18. New York: John Wiley and Sons, Inc. pp. 249–340.

SETH N. BROWN, UNIVERSITY OF NOTRE DAME
RESEARCH LECTURE
Not Just a Scaffold: Ligand Involvement in Oxidation-Reduction Reactions
Ligands play a crucial role in catalytic reactions mediated by soluble metal complexes by tuning the electronic and steric environment of the metal, thereby enhancing the reactivity or selectivity of the catalyst. Traditionally, though, they are not directly involved in bond-making or bond-breaking processes. Here I will describe some of our recent work on metal complexes containing ligands based on 2-amidophenoxides, where reactions can potentially involve redox changes on the ligands rather than the metal. Such complexes can undergo reactions where both bonding changes and redox changes take place at the metal center; where both take place at the ligands; and where redox changes take place at the ligands but bonding changes take place at the metal. Examples of all three types of reactivity will be described.

Catalysis on industrial scale

TUTORIAL LECTURES

Catalysis as a Kinetic Phenomenon: Statement and Implications

Catalysis is defined as the acceleration of a chemical reaction; its elucidation thus necessitates detailed consideration of reaction rates. In this lecture, I will briefly summarize the basic ideas of chemical kinetics of stoichiometric reactions, including the connection between mechanism and rate law; the notion of a rate-determining step; saturation kinetics and the steady-state approximation; and the measurement and interpretation of activation parameters. These ideas will then be extended to catalytic systems, focusing on aspects of selectivity and reactivity unique to catalytic reactions.

Case Studies in the Pleasures and Perils of Mechanistic Analysis of Catalytic Reactions

Given the truism that one cannot prove a reaction mechanism, it is perhaps no surprise that mechanistic studies are fraught with traps for the unwary. Studies of catalytic reactions, which are generally both more important and more complex than those of stoichiometric reactions, are even more so. This lecture will explore two classes of pitfalls that lurk in such studies. (1) *What you see is not what you get.* Catalysis is often carried out by species present in minute concentration, or are present adventitiously. The principal case study here will be the classic examination of enantioselective rhodium catalysts for the hydrogenation of enamides, where the major enantiomer is the opposite of what is observed in solution. (2) *What you want to see is not what you get.* Formulating a hypothesis is essential in chemistry, but the peril of this is that one becomes too attached to one's hypothesis to view the evidence dispassionately. Here the principal case study will be the exploration of the metallaoxetane mechanism for the dihydroxylation of alkenes. Of particular interest is the chemistry – and psychology – of what kinds of experiments prove compelling and what kinds do not.

Envisioning the Invisible: The Art of Inference in the Experimental Study of Catalysis

The most important species in a catalytic reaction – reactive intermediates and transition states – by their nature make only fleeting appearances in a reaction flask and thus cannot usually be studied directly. What we know about them must be garnered indirectly, by inference. Here I will discuss three main tools in this enterprise. The first is the interpretation of reaction kinetics, including structure-activity relationships on reaction rates. The second is the direct observation of intermediates by spectroscopic techniques such as NMR, EPR, or UV-visible spectroscopy. The third involves measuring chemo-, regio-, or stereoselectivity of reactions. A special case here involves the measurement of isotope effects, which can be particularly powerful. Each of these methods has strengths and limitations, so a complete study must weave together a variety of techniques to establish a compelling tapestry that illuminates a catalytic mechanism.

JAIRTON DUPONT, UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

RESEARCH LECTURE

Supported Ionic Liquid Phase Nanoparticle Catalysts

Ionic liquids (ILs), in particular imidazolium-based ILs, have proven to be suitable media for the generation and stabilisation of soluble metal nanoparticles (NPs). Indeed, transition-metal NPs with small sizes, narrow size distribution and different shapes have been prepared by reduction of organometallic compounds with molecular hydrogen, decomposition of transition-metal complexes in the zero-valent state, metal bombardment or simple transfer for previously prepared water- or classical organic solvent-soluble colloids to the ILs. The formation and stabilisation of NPs in these highly hydrogen bonded organised supramolecular fluids occur with the re-organisation of the hydrogen bond network and the generation of nanostructures with polar and non-polar regions, including the NPs. The IL forms a protective layer, which is probably composed of imidazolium aggregates located immediately adjacent to the nanoparticle surface, which provides both steric and electronic protection against aggregation and/or agglomeration. These stable transition-metal NPs immobilised in the ILs have proven to be efficient green catalysts for several reactions in multiphase conditions. The catalytic properties (activity and selectivity) of these soluble metal NPs indicate that they possess a pronounced surface-like (multi-site) rather than single-site-like catalytic properties. In particular, the preparation, stabilisation and catalytic properties of mono and bimetallic NPs in ILs for the partial hydrogenation of benzene will be discuss in details.

TUTORIAL LECTURE
TBA.

MARKUS ENDERS, UNIVERSITÄT HEIDELBERG
RESEARCH LECTURE

Organochromium Catalysts for Polymerisation or Selective Trimerisation of Ethylene

Chromium is an outstanding element for the polymerization of ethylene as well as for the selective trimerization and is used in heterogeneous catalysts in large scale industrial processes. Consequently molecular chromium complexes have been studied in order to supplement their heterogeneous counterparts. We have developed Cp (Cp = Cyclopentadienyl) based single-site organochromium complexes which catalyze the formation of ultra-high molecular weight polyethylene with high productivities.[1] In addition to that we prepared chromium complexes with simple bidentate ligands which serve as pre-catalysts for the selective trimerization of ethylene.[2] The combination of the different complexes leads to hybrid-catalysts which allow the tandem-catalytic formation of all-polyethylene nano-composite materials with currently unsurpassed properties.[3]

[1] M. Enders, *Macromol. Symp.* 2006, *236,* 38 - 47.
[2] M. Ronellenfitsch, H. Wadepohl, M. Enders, *Organometallics* 2014, *33*, 5758 - 5766.
[3] M. Stürzel, Y. Thomann, M. Enders, R. Mülhaupt, *Macromolecules* 2014, 47, 4979–4986.

TUTORIAL LECTURE

Non-Metallocene Olefin Polymerisation Catalysis

The production of polyolefin plastics is still dominated by heterogeneous Ziegler-type catalysts although very active molecular catalysts of the metallocene type (i. e. bis-cyclopentadienyl complexes of group 4 metals) have been developed in the mid 80's of last century. Triggered by the search for new plastics material properties but also by patent issues, many new polymerization catalysts have been developed which do not embed bis-cyclopentadienyl ligands (i.e non-Metallocene Complexes). In the meantime such catalysts are used in industrial polyolefin synthesis.[1] The lecture will give an overview about the common and the special features of several types of non-metallocene catalysts.

[1] M.C. Baier, M.A. Zuideveld, S. Mecking, *Angew. Chem. Int. Ed. Engl.* 2014, *53*, 9722-9744.

LUTZ H. GADE, UNIVERSITÄT HEIDELBERG
INTRODUCTORY LECTURE

Molecular Catalysts: Tools for Chemical Synthesis

Molecular catalysis is a key methodology in modern chemical synthesis. Ideally, it allows the energy and atom efficient generation of complex target compounds with high selectivity. The development of new catalytic systems, including new catalytic phases which allow novel chemical transformations and/or render known catalytic reactions more efficient and selective, has been identified as a key scientific and technological goal of chemical research in the decades to come.

Truly novel catalysts still tend to be discovered rather than developed by design. However, an ever increasing insight into the mechanisms of the more or less complicated reaction networks, frequently referred to simplistically as »catalytic cycles«, may provide the foundation for more rational approaches.

The lecture will highlight historically important developments in the field, key applications of molecular catalysis in industrial production processes as well as future developments.

RESEARCH LECTURE

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

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

During the past decade, we developed chiral bis(oxazolinylmethyl)pyrroles as well as bis(pyridylimino)isoindole (bpi) derivatives which have been used as stereodirecting ligands inter alia in Fe-catalyzed enantioselective hydrosilylations of ketones, Co-catalyzed cyclopropanations and Ni-catalyzed hydrodehalogenations of prochiral geminal dihalides. More recently, we developed bis(oxazolinylmethylidene)isoindoline (»Boxmi«) ligands which have been used in a variety of enantioselective transformations including alkylations of β-ketoesters and their subsequent cyclization to spirolactones, as well as the trifluoromethylation, trifluoromethylthiolation[6c,e] and azidation of β-ketoesters and oxindoles.

TUTORIAL LECTURES

Threefold Rotational Symmetry as a Construction Principle in Asymmetric Catalysis

The development of catalysts for new chemical transformations or catalytic systems with improved performance for known reactions is one of the key challenges of current chemical research. There is no universal approach to the design and/or discovery of new molecular catalysts with improved performance. Selectivity in catalytic transformations is based on a selection process in a key step of the catalytic cycle, and high selectivity may be obtained by »forcing« the system into one specific reaction pathway. This provides the challenge in the quest for new catalysts.

The exploitation of C_3 chirality in the design of chiral stereodirecting ligands for homogeneous catalytic transformations has been the focus of considerable research efforts and conceptual debate. The use of highly symmetrical stereodirecting ligands may reduce the number of transition states and diastereomeric reaction intermediates and, in favourable cases, this degeneration of alternative reaction pathways may lead to high stereoselectivity in catalytic reactions and greatly simplifies the analysis of such transformations.

Non-Linear Effects in Asymmetric Catalysis

The tutorial lecture will focus on the observation of non-linear effects in enantioselective catalysis and the information they provide about the active catalytic species. Particular emphasis will be placed on the underlying theoretical models, and Henri Kagan's ML_2-Model, representing the most frequently encountered case, will be presented in detail. Finally, the relevance of non-linearity for autocatalytic reactions will be discussed and the way in which this provides a model for the emergence of homochirality in the chemical evolution of biopolymers.

A. STEPHEN K. HASHMI, UNIVERSITÄT HEIDELBERG

RESEARCH LECTURE

New Horizons in Gold Catalysis

The initial phase of homogeneous gold catalysis focussed on the interaction of the organic substrates with one gold complex.[1] In the near past the reactions involving two gold complexes[2] in the activation of the substrate allowed entirely new conversions. This, for example, allowed the synthesis of benzofulvene, dibenzopentalenes, benzocyclobutenes and even gold-catalyzed selective reactions of unactivated sp^3-C,H bonds could be achieved. Also, diaurated intermediates and dinuclear organometallic compounds could be isolated. Recent reports indicate that dinuclear gold complexes can be useful in photoredox catalysis.[3,4]

The lecture will cover these fascinating aspects of homogeneous gold catalysis and also include computational results.

[1] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* 2006, *45*, 7896-7936.
[2] A. S. K. Hashmi, I. Braun, M. Rudolph, F. Rominger, *Organometallics* 2012, *31*, 644–661.
[3] G. Revol, T. McCallum, M. Morin, F. Gagosz, L. Barriault, *Angew. Chem. Int. Ed.* 2013, *52*, 13342-13345.
[4] J. Xie, S. Shi, T. Zhang, N. Mehrkens, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* 2015, *54*, 6046-6050.

TUTORIAL LECTURE

Basic Principles of Gold Catalysis

For a long time gold was neglected in homogeneous catalysis, only very few scattered singular mentioning could be found in the literature. Then, followed a first »pre-peak« of activity, addressing the first-ever catalytic asymmetric aldol reactions,[1] but after a few years of focus on that one reaction type, the activity in the field stopped.

In the year 2000 two publications, one on hydroarylation reactions and one on furan-yne cycloisomerizations (a subgroup of the enyne cyclization reactions) indicated a high potential of homogeneous gold catalysts for organic reactions.[2,3]

This initiated a »gold rush« in homogeneous catalysis, even today, 15 years later, almost every issue of the important journals on organic chemistry contains at least one publication on the subject.

This lecture will in detail explain the different reactivity patterns we find in the catalytic cycles of the new and synthetically interesting reactions.[4,5]

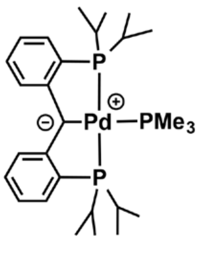
[1] Y. Ito, M. Sawamura, T. Hayashi, J. *Am. Chem. Soc.* 1986, *108*, 6405-6406.
[2] A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* 2000, *122*, 11553-11554.
[3] A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem. Int. Ed. Engl.* 2000, *39*, 2285-2288.
[4] A. S. K. Hashmi, *Chem. Rev.* 2007, *107*, 3180-3211.
[5] M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* 2012, *41*, 2448-2462.

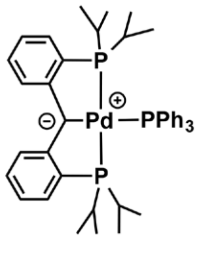
VLAD M. ILUC, UNIVERSITY OF NOTRE DAME

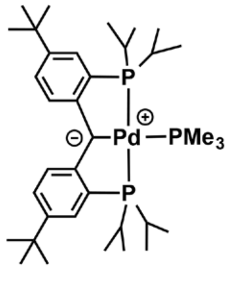
RESEARCH LECTURE

Metal-Ligand Interactions: E-H Activation and Metal-Element Multiple Bonding

Three formal palladium carbene complexes, $[PC(sp^2)P]Pd(PR_3)$ (R = Me, Ph) and $[PC(sp^2)P]^{tBu}Pd(PMe_3)$ were isolated and characterized. Structural studies and DFT calculations indicate that the interaction between palladium and carbon is best described as a single bond, associated with nucleophilic character at that carbon atom. The characteristics of these carbene were probed by reactions with electrophiles (MeI), acids (MeOH and HCl), and para-toluidine. The reactions of $[PC(sp^2)P]Pd(PMe_3)$ and $[PC(sp^2)P]^{tBu}Pd(PMe_3$ with the strong Lewis acid $B(C_6F5)_3$ afforded two zwitterionic products. One of them features a remote nucleophilic attack at the para-carbon of the supporting ligand, while the other indicates C–F activation of $B(C_6F5)_3$. Both behaviours are reminiscent of the reactivity of frustrated Lewis pairs due to the steric inaccessibility of the nucleophilic carbon center, but are unprecedented for transition metal carbene complexes. Furthermore, when those reactions are carried out in the presence of H_2, products resulting from H_2 splitting are observed.







TUTORIAL LECTURE

Applications of metal-ligand cooperation in catalysis

The properties of a metal complex are the result of the interaction of the metal centre and its surrounding ligands. In some cases, a classification of ligands in categories such as hybrid ligands, hemilabile ligands, or noninnocent ligands may be based on their intrinsic properties. This tutorial lecture will cover this special class of ligands and their unique properties. Homogenous catalysts containing transition metals are useful in a wide range of transformations. Tuning the steric and electronic properties of the ancillary ligands was successfully used to enhance the reactivity of the metal centre, for the selectivity of the products or for mechanistic studies. On the other hand metal-ligand cooperation can bring a new dimension to the observed reactivity of these metals by participating in the chemical transformation of the substrate.

CLÉMENT MAZET, UNIVERSITY OF GENEVA

RESEARCH LECTURE

Recent Advances in Selective Isomerizations

Catalytic isomerization reactions are – in essence – ideal transformations as they allow complete refunctionalization of a given substrate upon an internal redox process and usually do not require the use of expensive and potentially toxic reagents and additives.[1] The isomerizations developed in our laboratory rely on the use of well-defined, highly reactive, late transition metal hydride complexes. We recently developed novel iridium hydride catalysts for the enantio- and diastereoselective isomerization of primary allylic alcohols into chiral aldehydes.[2] In a complementary approach, we discovered that well-defined palladium hydrides are efficient catalysts in the isomerization of terminal epoxides and alkenyl alcohols.[3] Highlights of these methodologies along with some of their mechanistic features will be discussed.

[1] (a) Trost, B. M. *Science* 1991, *254*, 1471; (b) Wender, P. A.; Verma, V. A.; Paxton, T. J.; Pillow, T. H. *Acc. Chem. Res.* 2008, *41*, 40; (c) Burns, N. Z.; Baran, P. S.; Hoffmann, R. W. *Angew. Chem. Int. Ed.* 2009, *48*, 2854.

[2] (a) Mantilli, L.; Mazet, C. *Tetrahedron Lett.* 2009, *50*, 4141; (b) Mantilli, L.; Gérard, D.; Torche, S.; Besnard, C.; Mazet, C. *Angew. Chem. Int. Ed.* 2009, *48*, 5143; (c) Mantilli, L.; Mazet, C. *Chem. Commun.* 2010, *46*, 445; (d) Mantilli, L.; Gérard, D.; Torche, S.; Besnard, C.; Mazet, C. *Chem. Eur. J.* 2010, *16*, 12736; (e) Li, H.; Mazet, C. *Org. Lett.*, 2013, *15*, 6170.

[3] Vyas, D. J.; Larionov, E.; Besnard, C.; Guénée, L.; Mazet, C. *J. Am. Chem. Soc.* 2013, *135*, 6177; (b) Larionov, E.; Lin, L.; Besnard, C.; Mazet, C. *J. Am. Chem. Soc.* 2014, *136*, 16882.

TUTORIAL LECTURE

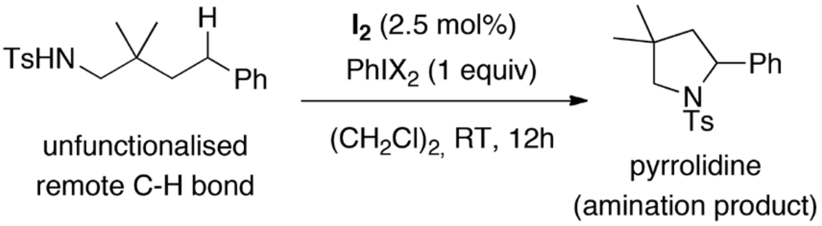
C_1-symmetry in Transition Metal-based Asymmetric Catalysis

In this Tutorial Course, we will discuss the historical developments in the design of chiral ligands in enantioselective transition metal catalysis. Next, the counter-intuitive benefits of moving away from the C_2-symmetry dogma will be discussed by placing emphasis on chiral ligands with a C_1-symmetry. A survey of the most remarkable achievements in the area will be presented and the mechanistic rationales discussed in details.

KILIAN MUÑIZ, INSTITUTE FOR CHEMICAL RESEARCH OF CATALONIA
RESEARCH LECTURE

Iodine-Catalysed Amination Reactions

Iodine reagents have been identified as economically and ecologically benign synthetic alternatives to transition metals, although their application as molecular catalysts in challenging C-H oxidation has remained elusive. An attractive iodine oxidation catalysis is now shown to promote the convenient conversion of ubiquitous carbon-hydrogen into carbon-nitrogen bonds with unprecedented complete selectivity. This reaction represents the realisation of the first catalytic Hofmann-Löffler reaction.[1] It proceeds within two interlocked catalytic cycles comprising a radical chain reaction, which is initiated by visible light as energy source. This unorthodox synthetic oxidation strategy of direct amination of alkyl groups has no biosynthetic precedence and provides an efficient and straightforward access to a general class of saturated nitrogenated heterocycles.



[1] C. Martínez, K. Muñiz, *Angew. Chem. Int. Ed.*, in press.

TUTORIAL LECTURE

Fun with Physical-Organic Control Experiments

For the understanding and improvement of (catalytic) reactions, insight into mechanistic details is of utmost importance. While theory can often offer an explanation for the involved reaction pathways, physical-organic control experiments can provide a very accurate description of the mechanistic context of a given reaction. In this tutorial lecture, we will discuss general aspects to arrive at quick mechanistic information using a set of common control experiments.[1-3]

[1] P. Sykes, Guidebook to Mechanism in Organic Chemistry, 6th ed., Pearson, 1996.
[2] N. Isaacs, Physical Organic Chemistry, 2nd ed., Longman, 1995.
[3] E. V. Anslyn, D. A. Dougherty, Modern Physical Organic Chemistry, 3rd ed., USC, 2006.

PAULINA PAVEZ & MARGARITA E. ALIAGA, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
RESEARCH LECTURE

Kinetics and mechanisms in homogeneous catalytic reactions

Kinetic aspects and mechanisms in homogeneous catalytic reactions summarizes the results obtained over the last three years in our laboratory in this field, including mechanisms of organic and inorganic reactions. The topics covered include:

- Solvent properties of ionic liquids as an approach to the kinetics of catalytic systems.[1]
- Reaction mechanisms, related to Michael addition in homogeneous catalysis,[2] among others.
- Biomimetic studies related to enzymatic transformations, namely the potential of Cu(II)-disulfide complexes to act as SOD and catalase-like molecules.[3]

[1] (a) Pavez P., Millán D., Morales J., Castro E.A., Lopez A. C., Santos J.G. *J. Org. Chem.* 2013, *78*, 9670; (b) Pavez P., Millán D., Cocq C., Santos J.G., Nome F. *New J. Chem.* 2015, *39*, 1953.
[2] García-Beltrán O., Santos J.G., Fuentealba S., De la Torre P., Pavez P., Mena N., Nuñez M.T., Aliaga M.E. *Tetrahedron Lett.* 2015, *56*, 2437-2440.
[3] Aliaga M.E., Andrade-Acuña D., López-Alarcón C., Sandoval-Acuña C., Speisky H. *J. Inorg. Biochem.* 2013, *129*, 119.

ACKNOWLEDGMENTS
Project ICM-P10-003-F CILIS, granted by »Fondo de Innovación para la Competitividad« from Ministerio de Economía, Fomento y Turismo, Chile and FONDECYT, grants 1130065 and 1130062.

RENÉ ROJAS, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE

RESEARCH LECTURE

Nickel complexes, Lewis acids influence on the reactivity towards ethylene and terminal olefins

It will be shown and discussed recent development results of organometallic complexes of nickel based on bidentate ligands with additional functionality, that alone, or by the action of Lewis acids such as $B(C_6F_5)_3$, BF_3, are able to activate ethylene and terminal olefins. It will be addressed in detail strategies to access stable complexes and therefore, with high feasibility of synthesis, versus effective activation strategies to access systems capable of coordinating monomers and selectively generating terminal olefins, isomerization of olefins and / or polymers with unique features.

TUTORIAL LECTURE

Pre-olefin polymerization catalysts: Activation modes and impact on reactivity of the active site

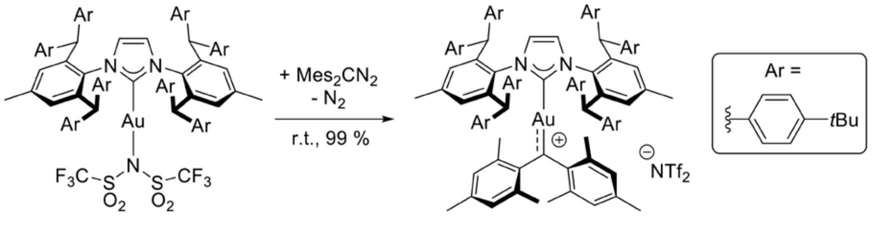
Synthesis strategies and methods of characterization of organometallic and coordination complexes of early and late transition metal, capable of being activated to homo- and copolymerizing ethylene and terminals olefins, that have had a major impact on the development of polyolefin materials will be addressed. It will be given special emphasis in the strategies of activation of metal centers by action of Lewis acids or other components and also on the way the characteristics of the ligands influence the reactivity of the metal to different monomers, determining the type of material that can be accessed from activation of these monomers.

BERND STRAUB, UNIVERSITÄT HEIDELBERG

RESEARCH LECTURE

Intermediates in Homogeneous Coinage Metal Catalysis

Steric shielding by the IPr** ancillary ligand and the carbene's two mesityl substituents rendered possible the synthesis, isolation, and full characterization of an emerald-green gold carbene complex with a significant Au=C back-bonding.[1] Relativistic effects can be derived from the comparison with the isostructural copper and silver complexes.

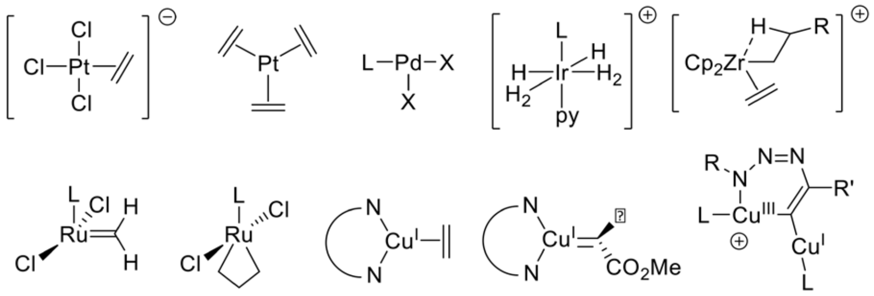


[1] M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub, *Angew. Chem.* 2014, *126*, 9526-9529; *Angew. Chem. Int. Ed.* 2014, *53*, 9372-9375.

TUTORIAL LECTURES

Electronic Structure of Reactive Transition Metal Intermediates

The interrelation of geometry and electronic structure determines the intrinsic reactivity of a transition metal complex.[1] Local minima, dynamics, and isolobal analogies of coordinatively unsaturated species are of particular importance for the understanding of metal-mediated and metal-catalyzed transformations, thereby »building bridges between inorganic and organic chemistry«.[2]



[1] T. A. Albright, J. K. Burdett, M-H. Whangbo, Orbital Interactions in Chemistry, Second Edition, 2013, John Wiley & Sons, New Jersey, USA.

[2] Roald Hoffmann, nobel lecture 1981, www.nobelprize.org/nobel_prizes/chemistry/laureates/1981/

Unravelling Reaction Mechanisms

»Can reaction mechanisms be proven?«[1] In the strict sense, one certainly cannot.[2] Several elucidations of reaction mechanisms are discussed, thereby providing an insight into strategies to unravel molecular pathways. Anecdotic examples include transition metal-catalyzed reactions with several options of metal oxidation state and ligation,[3-6] and a symmetry-forbidden organic rearrangement that gives facile conversion nonetheless.[7] Relationships are established to Occam's razor principle, to Karl R. Popper's falsification approach, to Thomas S. Kuhn's proposal of incommensurable competing paradigms, and to Richard P. Feynman's cargo cult analogy.

[1] a) A. Buskirk, H. Baradaran, *J. Chem. Educ.* 2009, *86*, 551-554;b) T. L. Brown, *J. Chem. Educ.* 2009, *86*, 552; c) D. E: Lewis, *J. Chem. Educ.* 2009, *86*, 554.

[2] https://en.wikipedia.org/wiki/Philosophy_of_science

[3] B. F. Straub, C. Gollub, *Chem. Eur. J.* 2004, *10*, 3081-3090.

[4] a) B. F. Straub, *J. Am. Chem. Soc.* 2002, *124*, 14195-14201; b) G. Berthon-Gelloz, M. Marchant, B. F. Straub, I. E. Marko, *Chem. Eur. J.* 2009, *10*, 2923-2931.

[5] B. F. Straub, *Angew. Chem. Int. Ed.* 2005, *44*, 5974-5978.

[6] A. Makarem, R. Berg, F. Rominger, B. F. Straub, *Angew. Chem. Int. Ed.* 2015, *54*, DOI: 10.1002/anie.201502368.

[7] N. Blank, B. F. Straub, T. Opatz, *Eur. J. Org. Chem.* 2011, 7355-7365.

ALEJANDRO TORO-LABBÉ, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE

RESEARCH & TUTORIAL LECTURE

Some Hints from Conceptual DFT to Chemical Catalysis

Density functional theory has provided a solid ground to define global and local chemical concepts that help characterize the reactivity of atoms and molecules [1]. Electronegativity, molecular hardness, electrophilicity, etc. are global reactivity descriptors that indicate if a given system is prone to produce a chemical reaction when interacting with another system. In the case of molecules, the electron density, Fukui functions, local softness and Dual Descriptor of chemical reactivity and selectivity are local descriptors indicating the region of the molecule where the reaction will take place [2]. Both global and local reactivity descriptors are better characterized within the framework of few reactivity principles such as the Sanderson's electronegativity equalization, Pearson and Parr's maximum hardness or Pearson's hard and soft acid and bases [2], principles that rule the intrinsic reactivity of molecular systems. In this lecture a quantitative theory introducing reactivity descriptors for characterizing the intrinsic reactivity of molecular catalyst as well as the mechanisms of catalytic reactions in which they participate is presented. Applications of catalyst design and the characterization of the mechanism of olefin polymerization catalytic reactions will be discussed in detail [3,4].

[1] Parr, R. G.; Yang, W.: Density Functional Theory of Atoms and Molecules; Oxford University Press and Clarendon Press: New York and Oxford, 1989.
[2] Geerlings, P.; De Proft, F.; Langenaeker, W.: Chem. Rev. 2003, 103, 1793-1873.
[3] Martínez-Araya, J.; Quijada, R.; Toro-Labbé, A.: J. Phys. Chem. C, 2012, 116, 21318–21325.
[4] Martínez-Araya, J.; Toro-Labbé, A.: J. Phys. Chem. C, 2015, 119, 3040–3049.

ABSTRACT OF PUBLIC LECTURE

PROF. A. STEPHEN K. HASHMI, UNIVERSITÄT HEIDELBERG
Gold – Nugget, Necklace, Nanotechnology
Gold has always fascinated mankind. Apart from very young children, probably every human being on the planet has heard about gold. Probably most people are not aware of the fact that, in addition, there is a fascinating side of this noble metal which goes far beyond simple gold nuggets, gold bars in a safe of a bank, or beautiful jewellery and art: Important scientific milestones are connected to gold, and many applications in different technological sectors of modern societies are based on gold. The price of gold is not prohibitive for many of these applications. The lecture will cover the different aspects of this shiny metal.

GOLD – NUGGET, NECKLACE, NANOTECHNOLOGY

PUBLIC LECTURE

A. STEPHEN K. HASHMI,
UNIVERSITÄT HEIDELBERG

JULY 14, 2015, 4 P.M.

PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE,
CASA CENTRAL, SALÓN DE HONOR
AV. LIBERTADOR BERNARDO O’HIGGINS 340, SANTIAGO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DESCRIPTION OF DOCTORAL PROJECTS

AFRAH ALDAWSARI, UNIVERSITY OF OXFORD, UNITED KINGDOM
Microwave assisted heavy oil cracking
Microwave frequency radiation can be used as an efficient alternative to traditional energy sources. Furthermore as a processing tool for functional materials, and also a method for determining their electronic properties. My current research focuses on understanding the interaction between crude oil and microwaves. Also convert crude oil and naphtha to high-value chemicals in a single operational unit using microwaves. Employing »designer« microwave catalysts and principles of microwave electric and magnetic heating, new approaches to the assisted conversion of crude and heavy oils are being developed in order to overcome major industrial challenges.

BRITTANY BARRETT, UNIVERSITY OF NOTRE DAME, USA
Flexible Coordination of PC=CP Ligands to Late Transition Metals
The coordination chemistry of a class of 2,2’-bis(di-*iso*-propylphosphino)-stilbene ligands with late transition metals was investigated. The coordination mode was found to vary with the electronic requirements of the metal center resulting in the observation of hemilability and backbone activation. The *cis* analogue of the ligand was utilized to support the formation of a palladium carbene species and its chemistry was explored.

SONJA BATKE, UNIVERSITÄT HEIDELBERG, GERMANY
Reactive Amidophosphine Complexes of Group V and VI
Based on the successful synthesis of a novel benzylene-linked trisamidophosphine scaffold, my dissertation focusses on the exploration of new metal complexes of this ligand and their application in catalysis. So far, coordination compounds of the early transition metals have been synthesized and intramolecular cyclometalations have been observed in some cases. These cyclometalated species might be of use in catalytic dehydrocoupling reactions, although the lofty goal of this research is set on the activation of more challenging substrates, such as nitriles, alkynes or even molecular dinitrogen.

LUIS GUILLERMO BORJA HIDALGO, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
(Doctoral research project in preparation)

MATHILDE BOUCHÉ, UNIVERSITÉ DE STRASBOURG, FRANCE
Novel N-heterocyclic carbene platinum complexes: from catalysis to therapy
NHC-metal complexes are recognized as a powerful class of complexes for applications ranging from medicinal chemistry to catalysis. Indeed NHC-ligands allow easy and tunable derivatizations, which make them suitable candidates for various applications. A range of functionalized $[(NHC)Pt(I)_2L]$ complexes have been obtained and depict high efficiency against a variety of cancer cell-lines. Enlarging the scope of these auspicious complexes, further catalytic studies are currently underway (hydrosilylation, hydrovinylation, cycloisomerization…).

Setup for monitoring high pressure catalytic reactions

CARLA CASADEVALL, INSTITUT CATALÀ D'INVESTIGACIÓ QUÍMICA (ICIQ), SPAIN

Light-driven metal catalyzed organic transformations

My doctoral project aims to expand the catalytic reactivity of first row transition metal complexes such as [Co(Py$_2^{Ts}$tacn)(OTf)](OTf) in combination with photoredox catalysts towards new organic transformations using light as a source of energy. Moreover, we will either establish new methods to control the quimio-, regio- and enantioselectivity and get deep insights in the mechanisms involved by characterization of intermediates, kinetics and DFT studies.

SEBASTIÁN CORREA, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE

Synthesis of graphene/polyethylene composite produced by ethylene polymerization with solid-supported single-site Ni(II) catalysts

Due to the unique combination of structural, mechanical, electrical, and thermal properties of graphene, a lot of attention is presently focused on the application of graphene as fillers to improve properties of polymers and obtaining advanced multifunctional composite materials. Despite the potential advantages, in this project the idea is obtained well-dispersed graphene in polyethylene matrix using Ni(II) catalysts.

MARIAN DRYZHAKOV, UNIVERSITÉ DE STRASBOURG, FRANCE

Supramolecular H-Bond Catalysis: Template-Induced Assembly of Strong H-Bond Donors

Nitro compounds are found to accelerate the rate and change the kinetic order of several Brønsted acid catalyzed reactions. Kinetic and spectroscopic analysis have led us to the conclusion that nitro compounds act as templates to induce self-assembly of strong H-bond donors. This discovery has allowed several stoichiometric transformations to be rendered catalytic for the first time, including the direct azidation of tertiary aliphatic alcohols and C-C, C-N and C-S bond forming reactions of tertiary aliphatic fluorides.

ROCÍO DURÁN GUAJARDO, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE

Theoretical computational chemistry for catalysis

Develop computational theoretical chemistry as a tool to study different types of relevant chemical processes in all areas of chemistry. The scientific work is focused on the development of mathematical models to characterize chemical reactions through the analysis of different electronic and structural properties, and achieve set and predict experimentally observed behavior.

LAURA FRA FERNÁNDEZ, INSTITUT CATALÀ D'INVESTIGACIÓ QUÍMICA (ICIQ), SPAIN

Development of new synthetic methodology for iodine mediated amination reactions

My research deals with the development of new synthetic methodology. In particular, I am interested in the development of new molecular iodine-based reagents and catalysts to provide nitrogenated molecules through oxidative amination reactions of alkenes and alkanes. Transformations of this type aim to compliment common transition metal based processes and are of particular interest to biological and pharmaceutical application.

HERNÁN GIL BERNAL, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
Computational Astrochemistry: Interactions and Catalysis in the Interstellar Medium
We have been interested in characterizing mechanisms taking place in the interstellar medium, our solar system and exoplanets, thermodynamic and kinetics aspects of chemical reactions through the adequate methodological elements that are provided by the Reaction Force analysis that partition the reaction coordinate in regions where different reaction mechanism may take place.

DANIELA GUZMÁN ANGEL, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
Theoretical model for the computational analysis of catalytic reactions
The main purpose of the project is to develop catalysts theoretical model for studying many type of chemical reactions, mainly polimerization of oleofins. Our models are based on the determination of the structure and reactivity of molecules, performing a detailed characterization of the system in different ways.

ANGELA MESÌAS, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
(Doctoral research project in preparation)

RAFAELY NASCIMENTO LIMA, UNIVERSIDADE DE SÃO PAULO, BRAZIL
Biocatalysis in the preparation of fatty ceramides for cosmetic applications
Biocatalysis applied for production of antioxidant compounds is a clean and eco-friendly methodology for organic compounds production, requires mild conditions and results highly selective products. The objective of the work is synthesizing fatty amides (ceramides) in the presence of amines, lipase and fatty esters by aminolysis reactions. Biological tests will be made with synthesized compounds and those how presented antioxidant properties can be used as prototypes for the manufacture of cosmetic products.

DANAY OSORIO, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
Synthesis and Characterization of bisamidine systems of Al, B, Mg and Zn: CO2 activation and copolymerization with epoxides
On my thesis project I proposed a serial of symmetric bisamidines as ligands in order to get di-nuclear complexes or adducts with a serial of Lewis acids such as B, Al, Mg and Zn. Because of their characteristics, this bisamidinates will be able to coordinate CO2 and other small molecules, in this way we can get more labile CO2 for its conversion on new materials, for example in my case I proposed to convert it on polycarbonate through its copolymerization with epoxides.

GUDRUN PLUNDRICH, UNIVERSITÄT HEIDELBERG, GERMANY
Reactivity studies of group 4 metal complexes supported by a (PNP)-ligand
My doctoral project is about the synthesis and coordination chemistry of group 4 transition metal complexes based on a monoanionic PNP pincer ligand. A key aspect of this thesis constitutes of the isolation and characterization of a η^6-arene complex, which was found to act as a zirconium (II) synthon. Low valent zirconium (II) complexes play an important role as intermediates in catalytic transformations and the activation of small molecules.

CELSO NOE QUINTERO RAMIREZ, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
The Donor/Aceptor interaction of mono and polinclear complexes with β-diketiminates, amidinates and Cp-derivates; Application in olefin catalysis
The study of Donor/Aceptor interaction of novel Zirconium and Titanium metal complex with **β**-diketiminates, amidinates and cp-derivatives and their application in olefin catalysis.

YERSICA RIOS YEPES, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
(Doctoral research project in preparation)

NICOLA SCAFURI, UNIVERSITÉ MONTPELLIER, FRANCE
Design of homogeneous catalyst in silico
The doctoral project concerns the rational design through computational study of improved transition-metal catalysts. More specifically the thesis concentrates on Pd-catalyzed cross-coupling reactions with two essentially complimentary goals:

1. get a better understanding of the electronic influence of the nature and relative positions of the various ligands on the crucial steps of the catalytic cycle through Natural Bonding Orbital analysis of the wavefunctions;
2. estimate the influence of including dispersion corrections when actual experimental systems are considered.

ANNE SCHÖFFLER, UNIVERSITÄT HEIDELBERG, GERMANY
Dinuclear CuAAC Catalysts
The aim of the research project is the development and the synthesis of new, air-tolerant dinuclear copper complexes and their application as catalysts in azide-alkyne cycloadditions (CuAAC) to 1,2,3-triazoles. Particular emphasis is placed on the catalysts' efficient preparation, and on the catalytic activity of these complexes in various solvent environments in order to serve a growing number of CuAAC users.

ELOISA SERRANO, INSTITUT CATALÀ D'INVESTIGACIÓ QUÍMICA (ICIQ), SPAIN
Metal-catalyzed reductive coupling of heterocumulenes
The entitled doctoral thesis deals with the development of new metal-catalyzed cross electrophile reductive couplings of readily available reagents with heterocumulenes while avoiding the use of stoichiometric organometallic species. The developed protocols are characterized by their mild conditions as well as the employment of cheap, available and easy to handle metal catalysts. The current project is focused on the design of a Ni-catalyzed reductive amidation of unactivated alkyl bromides with isocyanates.

CHARLENE SOUZA DOS ANJOS, UNIVERSIDADE DE SÃO PAULO, BRAZIL
Isolation of microorganisms associated with the orange crop of Araraquara-São Paulo region for biodegradation of pesticides used in citrus
The project goal is to isolate microorganisms (fungi and bacteria) associated with the culture of orange. In a second step these microorganisms will be evaluated for their ability to promote pesticide biodegradation reactions commonly used in the citrus. The promising microorganisms can be used in bioremediation, as well as biological insecticides (bio-pesticides).

MIGUEL ESTEBAN VERDUGO ESPAÑA, PONTIFICIA UNIVERSIDAD CATÓLICA DE CHILE
(Doctoral research project in preparation)

JANE YATES, UNIVERSITY COLLEGE LONDON, UNITED KINGDOM
Computational Screening of Supported Metal Films
The catalytically efficient utilization of Pt in hydrogen fuel cells is crucial for the development of low cost, clean energy. This project has used DFT to screen carbides as possible components for core-shell nanoparticles with the ability to tune Pt activity. We have identified carbides which should produce enhanced catalytic activity towards ORR and metallic tie layers which improve Pt adhesion. Screening allows rapid assessment of new materials to identify targets for synthetic development.

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