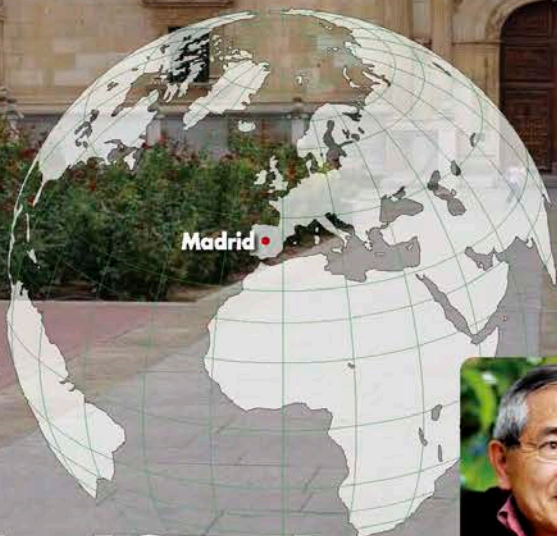


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ICAT International Symposium in Madrid

ASYMMETRIC C-C BOND FORMATION & ORGANOMETALLICS

November. 30. 2015
Universidad de Alcalá



Madrid



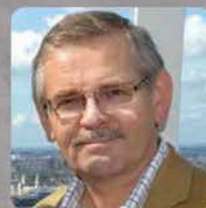
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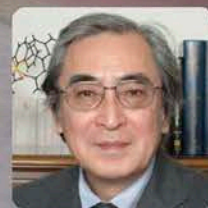
Invited Speakers



Ei-ichi Negishi
Purdue University, USA



Manfred Bodmann
University of East Anglia, UK



Masakatsu Shibasaki
BIKAKEN, Japan



Hisashi Yamamoto
University of Chicago, USA
and Chubu University, Japan



Carmen Nájera
University of Alicante, Spain



Armin de Meijere
University of Göttingen, Germany



Eduardo Peris
Universitat Jaume I, Spain



Tamio Hayashi
IMRE, Singapore

Organizer:
Institute for Catalysis (ICAT), Hokkaido Univ(HU)

Contact Information:
Tamotsu Takahashi
Institute for Catalysis, Hokkaido University, Japan
Phone:+81-11-706-9149 Fax+81-11-706-9150
E-mail:tamotsu@cat.hokudai.ac.jp
Web site:<http://www.cat.hokudai.ac.jp>

Co-Organizer:
Universidad de Alcalá
公益財団法人 総合工学振興財団 (FIST, Japan)

Contacts:
Prof. Tomás Cuenca Agreda
Departamento de Química Inorgánica
Universidad de Alcalá
Edificio de Farmacia
Campus Universitario
Phone:34-91-885-4655 Fax:34-91-885-468
E-mail: tomas.cuenca@uah.es

ASYMMETRIC C-C BOND FORMATION & ORGANOMETALLICS

ICAT International Symposium in Madrid

ASYMMETRIC C-C BOND FORMATION & ORGANOMETALLICS

Date: November 30, 2015

Venue: Universidad de Alcalá

Organizer:

Institute for Catalysis (ICAT), Hokkaido University

Co-Organizer:

Universidad de Alcalá

公益財団法人 総合工学振興財団 (FIST)

Contact Information:

Prof. Tamotsu

Takahashi

Institute for Catalysis, Hokkaido University,

Kita-21, Nishi-10, Kita-ku, Sapporo, 001-0021 JAPAN

Phone: +81-11-706-9149, Fax: +81-11-706-9150

E-mail: tamotsu@cat.hokudai.ac.jp

Web site:

<http://www.cat.hokudai.ac.jp/>

Contacts:

Prof. Tomás Cuenca Agreda

Departamento de Química Inorgánica

Universidad de Alcalá

Edificio de Farmacia

Campus Universitario

Phone: 34-91-885-4655 Fax:34-91-885-468

E-mail: tomas.cuenca@uah.es

**ICAT International Symposium in Madrid:
ASYMMETRIC C-C BOND FORMATION & ORGANOMETALLICS
Universidad de Alcalá, Spain, November 30, 2015**

09:00 - 09:30 Opening ceremony

Paraninfo Room. University of Alcalá

----- 09:30 - 09:45 Coffee Break -----

Scientific Session 1

Salón de Actos Room. University of Alcalá

Chairperson: Professor Luis Oro Giral

09:45 - 10:30 Professor Ei-ichi Negishi (Purdue University, USA)

10:30 - 11:15 Professor Manfred Bochmann (University East Anglia, UK)

11:15 - 12:00 Professor Masakatsu Shibasaki (BIKAKEN, Japan)

----- 12:00 - 13:30 Lunch Break -----

13:30 - 14:30 Poster

Scientific Session 2

Chairperson: Professor Gerardo Jiménez Pindado

14:30 - 15:15 Professor Hisashi Yamamoto (University Chicago, USA ; Chubu University, Japan)

15:15 - 16:00 Professor Carmen Nájera (University of Alicante, Spain)

16:00 - 16:45 Professor Armin de Meijere (University of Göttingen, Germany)

----- 16:45 - 17:00 Coffee Break -----

Scientific Session 3

Chairperson: Professor Eva Royo Cantabrana

17:00 - 18:00 Young Chemists Presentation (10 min + 2 min)

Alejandro Arrese (University of Zaragoza, Spain)

Julio Fernández-Cestau (University of East Anglia, UK) Yuki Mizukami
(Hokkaido University, Japan)

María Fernández Millán (University of Alcalá, Spain)

Scientific Session 4

Chairperson: Professor Marta Elena González Mosquera

18:00 - 18:45 Professor Eduardo Peris (Universitat Jaume I, Spain)

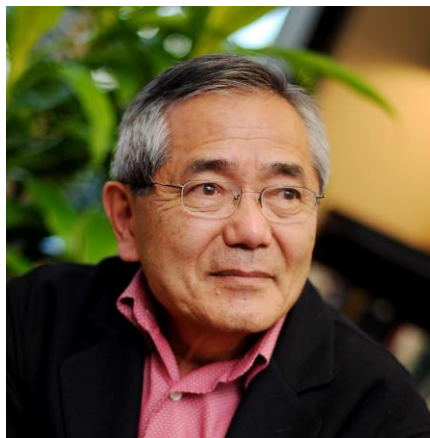
18:45 - 19:30 Professor Tamio Hayashi (IMRE, Japan)

19:30 - Closing Remarks

20:00 - 21:00 Tour of World Heritage Site

21:00 - Dinner Banquet

**CAT International Symposium in Madrid:
Asymmetric C-C Bond Formation & Organometallics**



Name: Ei-ichi Negishi

Organization: Department of Chemistry, Purdue University Profile Weblink:

<http://www.chem.purdue.edu/negishi/> Short Biography:

Ei-ichi Negishi, H. C. Brown Distinguished Professor of Chemistry, Purdue University, grew up in Japan and received his Bachelor's degree from the University of Tokyo in 1958. From 1958-1966, while working as a Research Chemist at Teijin, Ltd., Japan, Negishi spent 3 years (1960-1963) as a Fulbright-Smith-Mund Scholar at the University of Pennsylvania and obtained his Ph.D. in Chemistry. In 1966, he joined Professor H. C. Brown's Laboratories at Purdue as a Postdoctoral Associate and was appointed Assistant to Professor Brown in 1968. Negishi went to Syracuse University as Assistant Professor in 1972 and began his life-long investigations of *transition metal-catalyzed organometallic reactions for organic synthesis*. Negishi was promoted to Associate Professor at Syracuse University in 1976 and invited back to Purdue University as Full Professor in 1979. In 1999 he was appointed the inaugural H. C. Brown Distinguished Professor of Chemistry. He has received various awards, with the most representative being the 1996 Chemical Society of Japan Award, 1998 ACS Award in Organometallic Chemistry, 1998–2001 Alexander von Humboldt Senior Researcher Award, Germany, 2000 Sir Edward Frankland Prize, Royal Society of Chemistry, UK, 2007 Yamada-Koga Prize, Japan, 2010 ACS Award for Creative Work in Synthetic Organic Chemistry, 2010 Japanese Order of Culture, 2010 Nobel Prize in Chemistry, and 2011 Fellow of the American Academy of Arts and Sciences.

ZACA–LyCA–Cross Coupling Cascade for Catalytic Asymmetric Synthesis of Enantiomerically Pure Compounds of Feeble Chirality

Ei-ichi Negishi

Herbert C. Brown Laboratories of Chemistry, Purdue University, 560 Oval Drive,
West Lafayette, Indiana 47907-2084, U.S.A.

Email: negishi@purdue.edu

The zirconium-catalyzed asymmetric carboalumination of alkenes (ZACA) was discovered in 1995 [1,2] by overcoming three major pitfalls, namely (i) cyclic carbometallation, (ii) H-transfer hydrometallation, and (iii) Ziegler-Natta-type alkene polymerization. The ZACA reaction represents a prototypical example of catalytic enantioselective carbon–carbon bond forming reactions of alkenes of one-point binding without requiring any other functional groups, even though various functional groups may be present. Its subsequent development mainly over the past several years has made this ZACA reaction a practically satisfactory synthetic tool for the conversion of terminal alkenes of one-point binding into a wider scope of chiral organic compounds of high enantiomeric purity ($\geq 99\%$ ee) [3,4].

Some details of the discovery and development of the ZACA reaction will be discussed with emphasis on its application to efficient and selective synthesis of chiral natural products and feebly chiral compounds.

References:

- [1] D. Y. Kondakov, E. Negishi, “Zirconium-Catalyzed Enantioselective Methylaluminum of Monosubstituted Alkenes”, *J. Am. Chem. Soc.* 117 (1995) 10771–10772.
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- [3] E. Negishi, “Discovery of ZACA Reaction: Zr-Catalyzed Asymmetric Carboalumination of Alkenes”, *Arkivoc.* viii (2011) 34–53.
- [4] S. Xu, C. T. Lee, G. Wang, E. Negishi, “Widely Applicable Synthesis of Enantiomerically Pure ($\geq 99\%$ ee) Tertiary Alkyl-containing 1-Alkanols via ZACA–Pd- or Cu-Catalyzed Cross- Coupling”, *Chem. Asian J.* 8, (2013) 1829–1835.

**ICAT International Symposium in Madrid:
Asymmetric C-C Bond Formation & Organometallics**



Manfred Bochmann received his Diploma degree from the University of Marburg in 1977, followed by a PhD at Imperial College London in 1979 under the guidance of Professor Sir Geoffrey Wilkinson. He then worked in ICI central research until 1983, before taking up a lectureship in inorganic chemistry at the University of East Anglia. He was elected FRSC in 1993 and promoted to a personal chair in 1994. He was Head of Inorganic and Structural Chemistry at the University of Leeds 1995 – 2000. On his return to UEA he served as Head of the School of Chemical Sciences and Pharmacy 2006-9 and as Head of the School of Chemistry until 2011. He was awarded the RSC Medal for Organometallic Chemistry in 2003, a Leverhulme Senior Research fellowship in 2011 and an ERC Advanced Grant (2014-19). He has published over 280 research articles, several books and numerous patents, mainly on Group 4 metallocene-based olefin polymerisation catalysts. In the last few years his research has concentrated on the organometallic chemistry of gold.

Catalysis-Relevant Au(III) Chemistry: From Au-O to Au-H, Au-R and Au-CO

Manfred Bochmann

School of Chemistry, University of East Anglia, Norwich NR4 7TJ, UK.

E-mail address: m.bochmann@uea.ac.uk

Given the dramatic rise in the importance of gold catalysts in homogeneous and heterogeneous applications, it is surprising that many of the essential but hitherto postulated intermediates of catalytic systems remain unknown. We will present here the synthesis and structure of the first examples of gold(III) alkene, hydride, and peroxide complexes, several of which were known only as “in-computo” structures. We will discuss the nature and energetics of Au-H, Au-C and Au-O bonds with the aid of DFT studies. Most unusually, it can be shown that, unlike its Pt(II) analogues, Au(III) hydroxides can act as oxidising agents, forming gold hydrides in the process: $\text{Au-OH} \rightarrow \text{Au-H}$. This transformation is unique in transition metal chemistry.

Heterogeneous gold catalysts are highly active in CO oxidations and the Water-Gas-Shift (WGS) reaction. However, the mechanism is very much a matter of debate since homogeneous models were not available. Whereas Pt(II) CO complexes were first reported in 1868, Au(III) analogues were unknown. We present the first isolable examples of Au(III)-CO complexes. These show dramatic reactivity differences to the isoelectronic Pt(II)-CO analogues; in particular, they allow key steps of the WGS cycle to be demonstrated. The mechanistic implications for the likely nature of the active species in heterogeneous gold WGS catalysts will be discussed. The results demonstrate that it is the donation/back-donation ratio, not the IR frequency, that explains the reactivity differences between gold and platinum.

References

1. A Thermally Stable Gold(III) Hydride: Synthesis, Reactivity, and Reductive Condensation as a new Route to Au^{II} Complexes. D.-A. Roşca, D. A. Smith, D. L. Hughes, M. Bochmann, *Angew. Chem. Int. Ed.* **2012**, *51*, 10643–10646.
2. Gold peroxide complexes and the conversion of hydroperoxides into gold hydrides by successive oxygen-transfer reactions. D.-A. Roşca, J. A. Wright, D. L. Hughes, M. Bochmann, *Nature Commun.* **2013**, *4*, 2167.
3. Reactivity of gold hydrides: O₂ insertion into the Au-H bond. D.-A. Roşca, J. Fernandez-Cestau, D. L. Hughes, M. Bochmann, *Organometallics* **2015**, *34*, 2098–2101.
4. Gold(III) CO and CO₂ Complexes and Their Role in the Water-Gas Shift Reaction. D.-A. Roşca, J. Fernandez-Cestau, J. Morris, J. A. Wright, M. Bochmann, *Science Adv.* **2015**, *1*, e1500761. DOI: 10.1126/sciadv.1500761.
5. Synthesis and Luminescence Modulation of Pyrazine-Based Gold(III) Pincer Complexes. J. Fernandez-Cestau, B. Bertrand, M. Blaya, G. A. Jones, T. J. Penfold, M. Bochmann, *Chem. Commun.*, ASAP. DOI: <http://dx.doi.org/10.1039/C5CC07523H>.

ICAT International Symposium in Madrid: Asymmetric C-C Bond Formation & Organometallics



Name: Masakatsu Shibasaki

Organization: Institute of Microbial Chemistry, Tokyo (BIKAKEN)

Profile Weblink

http://www.bikaken.or.jp/research/group/shibasaki/shibasaki-lab/index_e.html Short Biography:

Masakatsu Shibasaki earned his Bachelor Degree in 1969 and his Ph.D. in 1974 at the University of Tokyo under the direction of Professor Shun-ichi Yamada. From 1974–1977, he did postdoctoral studies with Professor E. J. Corey at Harvard University and in 1986, he took the professorship at Hokkaido University, before returning to the University of Tokyo as a professor in 1991. He was appointed as the Dean of Graduate School of Pharmaceutical Sciences, the University of Tokyo (2006.4– 2008.3). After retiring from the University of Tokyo (2010.3), he took the directorship at Institute of Microbial Chemistry, Tokyo (2010.4–).

His awards and honors include The Pharmaceutical Society of Japan Award for Young Scientists, 1981 (Japan); Inoue Prize for Science, 1994 (Japan); Fluka Prize (Reagent of the Year 1996), 1996 (Switzerland); The Elsevier Award for Inventiveness in Organic Chemistry (Tetrahedron Chair), 1998 (Belgium); The Pharmaceutical Society of Japan Award, 1999 (Japan); Molecular Chirality Award, 1999 (Japan); The Naito Foundation Research Prize for 2002 (Japan); ACS Award: Arthur C. Cope Senior Scholar Award, 2002 (USA); Medal with Purple Ribbon, 2003 (Japan); The Toray Science Award, 2004 (Japan), The Japan Academy Prize, 2005 (Japan); Takamine Memorial Sankyo Award, 2006 (Japan); The Rare Earth Society of Japan Award, 2007 (Japan); ACS Award: Creative Work in Synthetic Organic Chemistry, 2008 (USA); Centenary Medal and Lectureship (Royal Society of Chemistry), 2008 (UK); Prelog Medal, 2008 (ETH, Switzerland), Special Award of Synthetic Organic Chemistry of Japan, 2010 (Japan) and Ryoji Noyori Prize 2012 (Japan).

Recent Progress in Cooperative Asymmetric Catalysis

Masakatsu Shibasaki

Institute of Microbial Chemistry, Tokyo (BIKAKEN)
3-14-23 Kamiosaki, Shinagawa-ku, Tokyo 141-0021, Japan e-mail:
mshibasaki@bikaken.or.jp

Our research focuses on the development of catalytic asymmetric C-C bond-forming reactions with particular emphasis on high atom economy and their application to the synthesis of biologically significant compounds. Thus, the concept of cooperative asymmetric catalysis such as Lewis acid-Brønsted base catalysis [1,2] and Lewis acid-Lewis base catalysis [3] plays the key role in our research paradigm. In this lecture, we report our recent progress in asymmetric Lewis acid-Brønsted base cooperative catalysis. In 1995, we developed the first example of a *syn*-selective catalytic asymmetric nitroaldol reaction using LLB (La-Li-BONOL) as catalyst. At this time the *anti*-selective reaction remained a longstanding problem. Finally, by changing the catalyst design to a Nd/Na heterobimetallic catalyst possessing a chiral amide ligand, we succeeded in developing an efficient and practical *anti*-selective catalytic asymmetric nitroaldol. In addition, the development of direct catalytic asymmetric aldol-type reaction of thioamides with aldehydes such as RCH₂CHO was also considered to be impossible due to the low acidity of the α -proton. Recently we could overcome this inherent problem by identifying an asymmetric soft Lewis acid- hard Brønsted base cooperative catalyst. How to overcome this problem as well as application to an efficient and practical catalytic asymmetric synthesis of atorvastatin as well as memprenone B will also be discussed.

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- [3] M. Kanai, N. Kato, E. Ichikawa, and M. Shibasaki, "Power of Cooperativity: Lewis Acid-Lewis Base Bifunctional Asymmetric Catalysis", *Synlett*, 10, 1491-1508 (2005).

**CAT International Symposium in Madrid:
Asymmetric C-C Bond Formation & Organometallics**



Name: Hisashi Yamamoto

Organization: Chubu University, Molecular Catalyst Research Center, The University of Chicago, Department of Chemistry

Profile Weblink <http://yamamotogroup.uchicago.edu/main.html>

Short Biography:

He received his Bachelor's degree from Kyoto University (Professors H. Nozaki and R. Noyori) and his Ph. D. from Harvard University (Professor E. J. Corey). He became assistant professor at Kyoto University, and in 1977 was appointed associate professor at the University of Hawaii. In 1980 he moved to Nagoya University as professor. In 2002, he moved to the United States as professor at the University of Chicago then in 2012 moved back to Japan as professor and director of Homogeneous Catalyst Research Center at Chubu University.

During his research career of over three decades, Yamamoto's research group has developed a wide range of new reagents and reactions. In particular, his research laid the foundation for modern designer Lewis and Brønsted acid chemistry. His group has invented many methods of carbon-carbon bond formation by controlling stereochemistry, and in the early 1980's developed the first chiral Lewis acid catalyst for asymmetric synthesis. His current interests are primarily the development of new synthetic reactions in the field of acid catalysis including designer Lewis and Brønsted acids, and combination of these two acid systems targeting more versatile, more selective, and more reactive catalysts, aiming at environmentally benign systems. He has over 600 publications (30,000 citations; h-index of 86). He has been invited to present plenary or keynote lectures at international conferences (>180 times) and honorary lectureships (>60 times) and is editor or advisory board member of over 20 international journals.

He has been honored as recipient of: the Chemical Society of Japan Award for Young Chemist in 1977, IBM Science Award in 1988, Houkou Award in 1991, Chunichi Press Award, 1992, Prelog Medal in 1993, the Chemical Society of Japan Award in 1995, Toray Science and Technology Award in 1997, the Max-Tishler Prize in 1998, Tetrahedron Chair in 2002, Le Grand Prix de la Fondation Maison de la Chimie in 2002, National Prize of the Purple Medal (Japan) in 2002, Molecular Chirality Award in 2003, Yamada Prize in 2004, and Tetrahedron Prize in 2006, The Karl-Ziegler Professorship Award in 2006, The Japan Academy Prize in 2007, Honorary Member of the Chemical Society of Japan in 2008, ACS Award for Creative Work in Synthetic Organic Chemistry in 2009, and Grand Prize of Synthetic Organic Chemistry in 2009, Fellow of the American Academy of Arts and Sciences in 2011, the Noyori Prize in 2012, and the Fujiwara Prize in 2012.

Combined Acid Catalysis - History and Future

Hisashi Yamamoto

Chubu University, Molecular Catalysis Research Center, 1200 Matsumoto, Kasugai, Japan
The University of Chicago, Department of Chemistry 5735 South Ellis Avenue, Chicago, IL
USA

Email: yamamoto@uchicago.edu

In the early 1980's, we first introduced binaphthol as a key ligand for chiral Lewis acid catalysts. This work was the forerunner of a vast quantity of present-day research on the C-2 symmetry based chiral Lewis acid catalyst, now known as one of the privileged ligands for carbon-carbon bond construction. Later his 3,3'-disilyl or diaryl substituted binaphthol derived catalysts were developed for various metal catalysts, which were not only used broadly for essential ligands for asymmetric transformations but also are proving to be a very popular catalyst design for organocatalysis.

Our discovery of tartaric acid based catalyst (CAB catalyst) and amino acid based catalyst (oxaborolidine-type catalyst) led to the first and the most general enantioselective Diels-Alder reaction of a broad range of dienes and dienophiles. The same catalyst was shown to be the first one efficient for asymmetric aldol, ene, and Sakurai-allylation reactions. More importantly, the concept of CAB catalyst grew to be used in the design of Brønsted acid-Lewis acid co-catalyst, "the combined acid catalyst", which offered numerous asymmetric syntheses including the most efficient asymmetric Lewis acid catalyst for Diels-Alder reaction. We proposed a combined acid catalyst between Lewis acid/Lewis acid, Lewis acid/Brønsted acid, Brønsted acid/Lewis acid, and Brønsted acid/Brønsted acid catalysis both intermolecularly and intramolecularly, which has now become one of the general concepts for designing an asymmetric acid catalyst. This concept was employed for our catalytic asymmetric protonation under acidic conditions, which is capable of creating a long sought proton induced asymmetric and biomimetic polyene cyclization. Our discovered metal catalyzed aldol and allylation process have provided a new entry to the creation of a tertiary and quaternary carbon stereogenic center for asymmetric synthesis.

Review:

Ten years of research in Chicago, Hisashi Yamamoto, *Tetrahedron*, **69**, 4503-4515 (2013).

New reaction and new catalyst - A personal perspective, Hisashi Yamamoto, *Tetrahedron*, **63**, 8377-8412(2007)

"Designer Acids": Combined Acid Catalysis for Asymmetric Synthesis, Hisashi Yamamoto and Kentaro Futatsugi. *Angew. Chem. Int. Ed. Engl*, **117**, 4463-4465 (2005)

ICAT International Symposium in Madrid: Asymmetric C-C Bond Formation & Organometallics



Carmen Nájera obtained her B.Sc. at the University of Saragossa in 1973 and her PhD at the University of Oviedo under the supervision of J. Barluenga and M. Yus in 1979. She performed postdoctoral work at the ETH (Zurich) with D. Seebach, at the Dyson Perrins Laboratory (Oxford) with J. E. Baldwin, at Harvard University with E. J. Corey, and at Uppsala University with J.-E. Bäckvall. She was promoted to Associate Professor in 1985 at the University of Oviedo and Full Professor in 1993 at the University of Alicante.

She has held visiting Professorships at the University of Arizona in Tucson (USA), Universidad Nacional del Sur in Bahía Blanca (Argentina), Louis Pasteur University in Strasbourg (France), Ecole Nationale Supérieure de Chimie de Paris (France) and Federal University of Rio de Janeiro (Brazil).

She is coauthor of more than 350 papers, form them 40 review articles and 33 book chapters and has supervised the work of 42 PhD Thesis. She has delivered more than 160 lectures in Congresses and Research Institutions.

Member of the Advisory Board of ChemCatChem, Synthesis, Synlett, European Journal of Organic Chemistry, Tetrahedron, Tetrahedron Letters, Tetrahedron: Asymmetry, Reports in Organic Chemistry and Letters in Organic Chemistry.

Awards: “2006 Organic Chemistry Prize” from the Spanish Royal Chemical Society of Chemistry, “2006 Rosalind Franklin International Lectureship” from the English Royal Society, SCF 2010 French-Spanish Prize from the Société Chimique de France and the IUPAC 2015 Distinguished Women in Chemistry award. In October 2010 was named Correspondent Member and in April 2012 Full Member of the Royal Spanish Academy of Sciences (www.rac.es) and in 2012 she was named member of the European Academy of Sciences and Arts (www.euro-acad.eu).

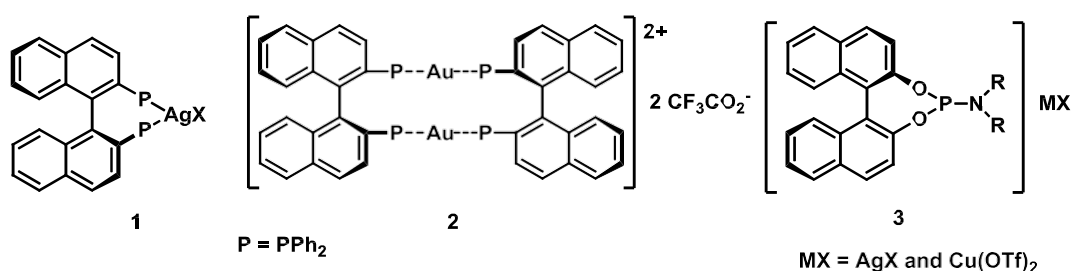
Her scientific contributions are focused on synthetic organic chemistry such as sulfone chemistry, new peptide coupling reagents, asymmetric synthesis of alpha-amino acids, oxime-derived palladacycles as precursor of palladium nanoparticles, asymmetric metallo catalysis and organocatalysis. In the last decade she has been working on the development of efficient metal catalysts for cross-coupling reactions and chiral metal complexes and organocatalysts and for asymmetric synthesis focused on sustainable processes using low catalyst loading, water as reaction medium or solvent-free conditions with the aim of recovering and reusing the catalyst.

Coinage Metal Complexes as Chiral Catalysts for Asymmetric 1,3-Dipolar Cycloadditions

Carmen Nájera

Department of Organic Chemistry, Faculty of Sciences and Centro de Innovación en Química Avanzada (ORFEO-CINQA), University of Alicante, Apdo. 99, E-03080 Alicante, Spain,
E-mail: cnajera@ua.es

Metal-catalyzed 1,3-dipolar cycloadditions (1,3-DC) of azomethine ylides and dipolarophiles allowed the simultaneous formation of two carbon-carbon to give the corresponding pyrrolidines. The use of different chiral catalysts derived from binap and phosphoramidites as privileged ligands and silver, gold(I) and copper(II) salts for the enantioselective synthesis of highly substituted prolines by 1,3-DC of azomethine ylides with dipolarophiles is presented. The 1,3-DC using bidentate binap complexes gave good enantioselectivities for azomethine ylides when silver salts monomeric complexes **1** [1] and dimeric gold **2** trifluoroacetates [2] are used yielding endo-cycloadducts. In the case of monodentate ligands such as phosphoramidites, metal complexes **3** derived from silver salts have been used for the general 1,3-DC of different imino esters and dipolarophiles to afford endo-cycloadducts [3]. In the case of using nitroalkenes as dipolarophiles copper(II) triflate and also silver benzoate and triflate complexes **3** were the most appropriate catalysts affording exo-cycloadducts [4]. In addition, computational studies have also been carried out in order to explain the high enantioselection exhibited by these chiral complexes. This methodology has been applied to the synthesis of hepatitis C virus inhibitors blocking the viral RNA-dependent RNA-polymerase [5] and for the preparation of exo-4-nitroprolines, which are excellent chiral organocatalysts [6][7].



- [1] C. Nájera, M. de G. Retamosa, J. M. Sansano, *Org. Lett.* **2007**, 9, 4025.
[2] M. Martín-Rodríguez, C. Nájera, J. M. Sansano, A. de Cózar, F. P. Cossío, *Chem. Eur. J.* **2011**, 17, 14224.
[3] C. Nájera, M. de Gracia Retamosa, J. M. Sansano, *Angew. Chem. Int. Ed.* **2008**, 47, 6055; *Eur. J. Org. Chem.* **2009**, 5622.
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[6] M. de G. Retamosa, A. De Cózar, M. Sánchez, J. I. Miranda, J. M. Sansano, L.M. Castelló, C. Nájera, A. I. Jiménez, F. J. Sayago, C. Cativiela, F. P. Cossío, *Eur. J. Org. Chem.* **2015**, 2503.
[7] This work has been supported by the Spanish Ministerio de Ciencia e Innovación (MICINN) (Consolider INGENIO 2010 CSD2007-00006 and CTQ2010-20387), the Spanish Ministerio de Economía y Competitividad (MINECO) (projects CTQ2013-43446-P and CTQ2014-51912-REDC), FEDER, the GeneralitatValenciana (PROMETEO 2009/039 and PROMETEOII/2014/017), and by the University of Alicante.

ICAT International Symposium in Madrid: Asymmetric C-C Bond Formation & Organometallics



Armin de Meijere

| | | |
|--|---------------|--|
| Education and Experience | 1939 | Born in Homberg (Niederrhein), Germany, May 18 |
| | 1958-61 | Universität Freiburg i. Br., B. S. Vordiplom (corr. to B.S.) |
| | 1961-63 | Universität Göttingen, M. S. Diplom (corr. to M.S.) |
| | 1963-67 | Universität Göttingen, Dr. rer. nat. 1966 (mentor: W. Lüttke) |
| | 1967-69 | Yale University, New Haven, Postdoctoral Fellow (K. B. Wiberg) |
| | 1969-77 | Universität Göttingen 1971 Venia legendi for Organic Chemistry, 1972 |
| | | Universitätsdozent, 1974 (Adjunct Prof.) Apl. Professor |
| | 1977-89 | Universität Hamburg, Full Professor (Ordentlicher Professor) |
| | 1989-2006 | Universität Göttingen, Full Professor of Organic Chemistry |
| | 2006- current | Universität Göttingen, Professor emeritus, Organic Chemistry |
| Visiting Professorships | | University of Wisconsin, Madison, Wisconsin, USA, Jan / May 1973 (Visiting Associate Professor) |
| | | IBM Research Laboratories, San José, CA, USA, Aug / Oct 1978 (IBM Visiting Scientist) |
| | | Technion – Israel Institute of Technology, Haifa, Israel, March / April 1984 |
| | | Princeton University, Princeton, New Jersey, USA, Sep / Dec 1985 |
| | | Université d'Aix-Marseille III, St. Jérôme, Marseille, France, Feb / March 1990 |
| | | Università degli Studi di Firenze, Florence, Italy, Oct 1995 |
| | | Ecole Normale Supérieure, Paris, France, Oct 1996 |
| | | University of Colorado, Boulder, Colorado, USA, Aug 1999 |
| | | Indian Institute of Science, Bangalore, India, Nov 2003 |
| | | Université de Bordeaux, Bordeaux, France, Feb / March 2004 |
| | | Università degli Studi di Milano, Milano, Italy, March 2006 |
| | | Universidad de Santiago de Compostela, Santiago d. C., Spain, June 2006 |
| | | Distinguished Visiting Professorship, Taiwan National University, March 2007 |
| Fellowships, Honors, and Awards | | German National Merit Foundation 1961-1963 |
| | | Carl-Duisberg-Stipendium 1964 |
| | | Fonds der Chemischen Industrie, "Dozenten-Stipendium," 1972 |
| | | Elected Member Norwegian Academy of Science and Letters, 1992 |
| | | French "Alexander von Humboldt-Gay-Lussac Award," 1996 |
| | | St. Petersburg State University, St. Petersburg, Russia, 1997, Honorary Professor |
| | | Elected Member Braunschweigische Wissenschaftliche Gesellschaft, 1997 |
| | | Fellow Japan Society for the Promotion of Science, 1997 |
| | | University of Florida, Gainesville, FL, USA, Jan 2000 |
| | | Novartis Chemistry Lectureship, Novartis Pharma AG, Basel, Schweiz, 2000 |
| | | Lady Davis Distinguished Lecturer at the Technion in Haifa, Israel, 2001 |
| | | SFC Merck-Lectureship, Société Française de Chimie, Talence, Frankreich, 2002 |
| | | Society of German Chemists "Adolf von Baeyer Medal" 2005 |
| | | Novartis Lecturer in Central Europe, Novartis Pharma AG, Basel, Schweiz, 2006 |

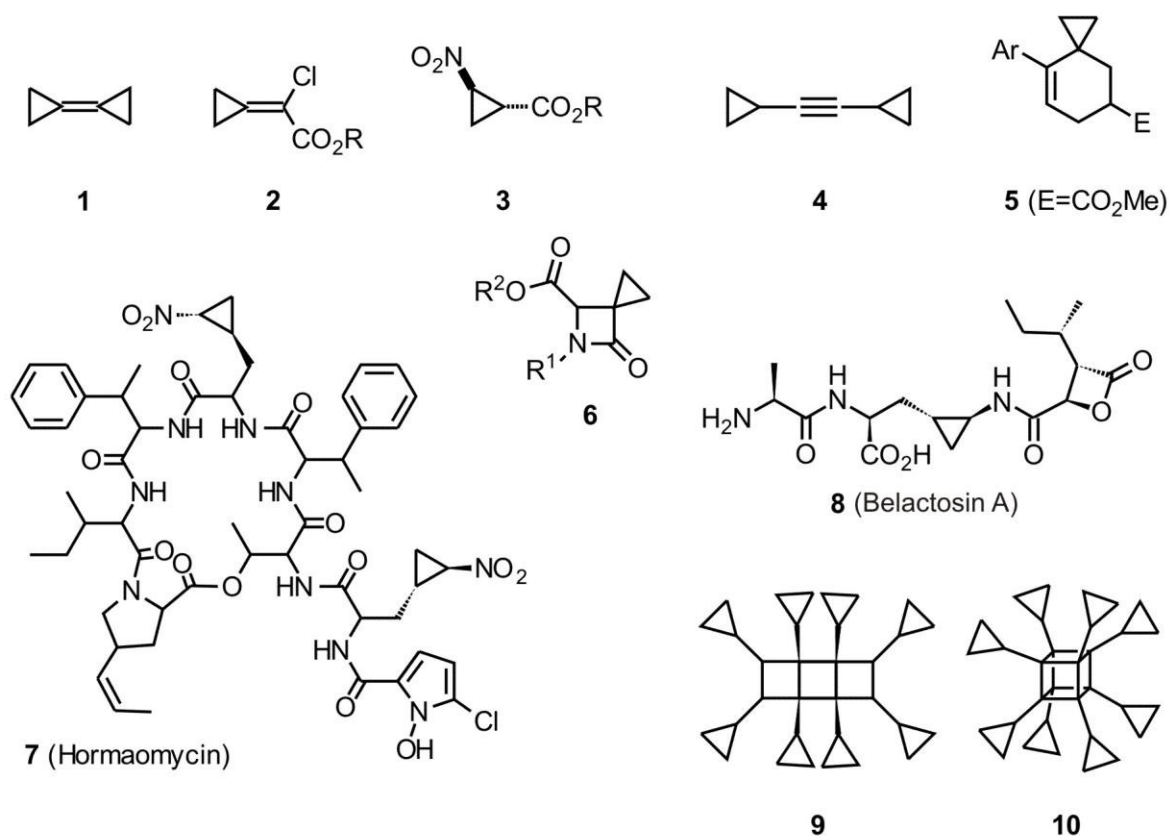
Recent Achievements Concerning Cyclopropanes, Natural Products and Metal Catalysis

Armin de Meijere

*Institut für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen,
Tammannstrasse 2, D-37077 Göttingen, Germany*

e-mail: Armin.deMeijere@chemie.uni-goettingen.de

Reliable and easily scalable syntheses of a number of multifunctional cyclopropane derivatives like bicyclopropylidene (**1**), 2-chloro-2-cyclopropylideneacetate (**2**), *trans*-2-nitrocyclopropanecarboxylate (**3**) and others will be presented. Their applications towards efficient syntheses of potentially biologically active compounds like the biaryl mimetics **5**, spirocyclopropanated β -lactams **6** as well as the highly active natural products hormaomycin (**7**) and belactosin (**8**) will be discussed. The review will be rounded off with the two-step synthesis of the high-energy molecule octacyclopropylcubane (**10**) from dicyclopropylacetylene (**4**) via the tricyclooctadiene **9**.



For literature references concerning all this chemistry and more, see the homepage at <http://www.adm.chemie.uni-goettingen.de>

ICAT International Symposium in Madrid: Asymmetric C-C Bond Formation & Organometallics



Eduardo Peris graduated in Chemistry in 1988 in the University of Valencia. He received his Ph.D. Degree in Chemistry (1991) in the Universidad de Valencia, under the supervision of Prof. Pascual Lahuerta. In 1994 he joined Prof. Robert Crabtree's group at Yale University, where he stayed for two years, working on a research project regarding the determination of hydrogen bonding to metal hydrides (dihydrogen bond). In October 1995 he moved to the Universitat Jaume I (Castellón-Spain) as profesor ayudante (1995-1997), then profesor titular (1997-2007) and finally catedrático (Full Professor) of Inorganic Chemistry. At the Universitat Jaume I he started a research project related to the use of organometallic push-pull compounds with non-linear-optical properties. During the last decade, Eduardo Peris developed an intense research activity on the chemistry and catalytic applications of N-heterocyclic-carbene-based organotransition metal catalysts. Most of his activity was devoted to the preparation of new catalysts for the activation of small molecules, paying special attention to processes implying the activation of C-H bonds, carbon dioxide, and reactions implying borrowing-hydrogen methodologies. During the last five years, the group has also devoted great attention to the design of catalysts for tandem catalytic reactions. Several homo- and heterodimetallic complexes have been obtained for this purpose.

The use of heterodimetallic complexes of Ir/Rh and Ir/Pd, allowed for studying their activity in catalytic tandem processes in which each metal mediated a mechanistically distinct reaction.

The current interest of his group is the design of new polytopic rigid In 2012 he was awarded the 'Spanish Royal Society of Chemistry' award in the field of Inorganic Chemistry Research. In the period 2007-2010 Eduardo Peris was member of the Advisory Board of Organometallics. Some other relevant features of his academic career are: IRTG 2015 Distinguished Scientist Visitor, at the Wesfalische Milheims-Universitat; President of the Organometallic Chemistry Division of the RSEQ (since 2014); and Vice-Director of the Institute of Advanced Materials-UJI (INAM).

Polyaromatic n-heterocyclic carbenes and Π -stacking. Catalytic consequences

Eduardo Peris

Institute of Advanced Materials (INAM), Universitat Jaume I, Castellón, Spain

The choice of a ligand to build a metal complex is often considered to be restricted to its well-defined stereoelectronic properties, and this is why great attention has been paid to the study of the steric and electronic properties of the ubiquitous N-heterocyclic carbenes (NHCs).¹ However, little has been made in order to design homogeneous catalysts with multifunctional NHC-based ligands. Exploring the addition of organic additives that may enhance the reactivity is also important, because some organic molecules added to the homogeneously catalysed reaction may facilitate the stabilization of transition states or modify the reactivity pattern of the substrates.

The use of NHC ligands with extended polyaromatic systems has given rise to families of metal complexes whose properties are influenced by the Π -stacking affinities of the substrates with the ligands.^{2a,2b} We tried to rationalize the effects of Π -stacking on the catalytic properties of a series of catalysts decorated with extended polyaromatic systems, and proved that the addition of Π -stacking additives, such as pyrene, had important influences on their catalytic performances.³

In this presentation we will try to unveil the reasons governing the influence of Π -stacking in some homogeneous and heterogeneously catalysed reactions, and will demonstrate that Π -stacking should be taken into account when using catalysts with extended polyaromatic systems.

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**ICAT International Symposium in Madrid:
Asymmetric C-C Bond Formation & Organometallics**



Name: Tamio Hayashi

Organization: Institute of Materials Research and Engineering (IMRE), A*STAR, Singapore and Department of Chemistry, National University of Singapore Profile Weblink:

<http://www.imre.a-star.edu.sg/researcher.php?startlet=H&rid=&id=P534G532S533>

Short Biography:

Tamio Hayashi graduated from Kyoto University in 1970. He received his Ph.D. degree in 1975 from Kyoto University under the direction of Professor Makoto Kumada, and then he was appointed as a Research Associate in Faculty of Engineering, Kyoto University. He spent the year 1976-1977 as a postdoctoral fellow at Colorado State University with Professor Louis S. Hegeudus. He was promoted to Full Professor in 1989 in the Catalysis Research Center, Hokkaido University. In 1994 he moved to Faculty of Science, Kyoto University. Since 2012, he has been in a joint appointment in Institute of Materials Research and Engineering (IMRE), A*STAR, and in National University of Singapore. His awards include the Award for Young Chemists of the Society of Synthetic Organic Chemistry, Japan in 1983, IBM Japan Prize in 1991, The Chemical Society of Japan Award in 2003, Thomson Scientific Research Front Award in 2004, The Ryoji Noyori Prize, Author C. Cope Scholar Award in 2008, and The Medal with Purple Ribbon in 2010. Tamio Hayashi has published more than 400 original papers and the total citation number is around 32,000 (H-index 92). He has been interested in the development of new reactions catalyzed by transition metal complexes, especially in catalytic asymmetric reactions.

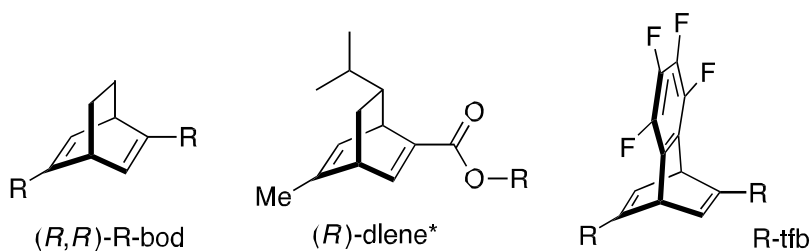
Recent Advances in Chiral Diene Ligands

Tamio Hayashi

Institute of Materials Research and Engineering, 2 Fusionopolis Way, Singapore
138634: Department of Chemistry, National University of Singapore, 3 Science Drive
3, Singapore 117543

Email: tamioh@imre.a-star.edu.sg; chmtamh@nus.edu.sg

As conceptually new chiral ligands, we have been developing enantiomerically pure C_2 -symmetric chiral dienes, whose basic diene skeleton is bicyclo[2.2.1]hepta-2,5-diene (nbd) or bicyclo[2.2.2]octa-2,5-diene (bod). They have two alkyl or aryl substituents on the double bonds, one on each of the two double bonds. The chiral diene ligands were found to be better than the conventional chiral ligands represented by chiral bisphosphines in terms of both catalytic activity and enantioselectivity in some of the catalytic asymmetric reactions. Their high performance was observed in rhodium-catalyzed asymmetric addition of organoboron reagents to α,β -unsaturated ketones, N -sulfonylimines, and so on.¹ Recently, we have developed two new chiral diene ligands: One is (*R*)-diene* readily obtained through [4+2] cycloaddition of (*R*)- α -phellandrene with 2-naphthyl acetylenecarboxylate. The other is that based on tetrafluorobenzobarrelene (tfb) skeleton. They were found to be excellent chiral ligands for the rhodium-catalyzed asymmetric arylation reactions² including the conjugate addition to β,β -disubstituted α,β -unsaturated ketones and ketimines forming quaternary carbon centers with high enantioselectivity.



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