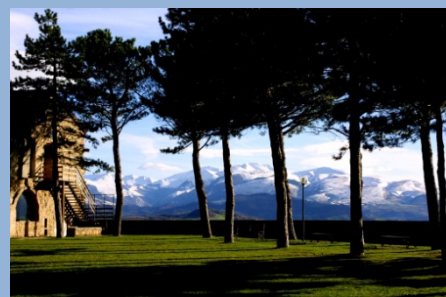


XV International School of Organometallic Chemistry

Camerino, Italy

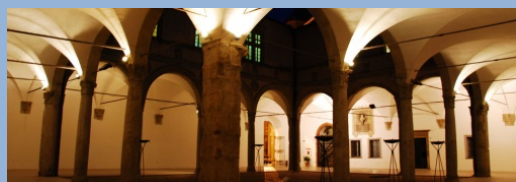
4-8 September 2025

<http://d7.unicam.it/isoc/>



University of Camerino

School of Pharmacy and School of Science and Technology



Organometallic Chemistry

Interdivisional Group of Organometallic Chemistry

Title Organometallic Chemistry
ISBN 9788867680733

e-printed by
University of Camerino – e-mail: isoc@unicam.it
03 August 2025

Organometallic Chemistry beyond the future

The ISOC series is the most important school on organometallic chemistry at the European level, organized by Camerino University under the auspices of the Interdivisional Group of Organometallic chemistry of the Italian Chemical Society. The aim is to encourage the presence of young researchers and Ph.D students both from University and Industry, including those not directly involved in organometallic research projects, in order to bring together young researchers and distinguished European scientists as a contribution to the important goal of increasing the transfer of knowledge at a high level between different European countries and different generation of scientists.

Organometallic compounds continue to have a tremendous impact on modern organic synthesis and are nowadays commonly employed as catalysts for the production of fine chemicals, pharmaceuticals and advanced materials. The XV edition of ISOC will deal not with fundamental principles and their use in novel applications, but also with the role of organometallic chemistry in finding solutions to many of the major societal challenges in the 21st century: from the development of sustainable energy solutions to the mitigation of climate change, from the synthesis of effective therapeutics to the production of new materials ranging from novel polymers to nanomaterials, from the generation of industrial feedstocks to the remediation of the environment.

The scientific community is increasingly being stimulated to tackle problems of practical interest and the society will undoubtedly rely on advances made in the field of organometallic chemistry in the development of improved sustainable chemical transformations.



ELSEVIER

CHIMICA  CENTRO
Soluzioni per laboratori scientifici



Timetable ISOC 2025

Thursday 4 September	Friday 5 September	Saturday 6 September	Sunday 7 September
	7:45-8:45 Breakfast	7:45-8:45 Breakfast	7:45-8:45 Breakfast
9:00-14:40 Registration	9:00-10:20 (PL3) Joseph Dyson <i>Catalytic transformation of natural and synthetic waste into value-added chemicals</i>	9:00-10:20 (PL7) Luca Pignataro <i>Two strategies for exploiting base metals in homogeneous catalysis</i>	9:00-10:20 (PL11) Elena Fernandez-Gutierrez <i>Catalytic activation of organoboron compounds for strategic and selective construction of target compounds</i>
	10:20-10:40 Coffee Break	10:20-10:40 Coffee Break	10:20-10:40 Coffee Break
	10:40-12:00 (PL4) Alessandro Bismuto <i>Exploring Heavy Pnictogens: From low-valent compounds to luminescence</i>	10:40-12:00 (PL8) Antonio Zanotti -Gerosa <i>Homogeneous hydrogenation catalysis in the fine chemicals industry: how to develop industrially viable and sustainable processes?</i>	10:40-12:00 (PL12) Matthias Driess <i>Cooperative Low-Valent Silicon Atoms in Small Molecule Activation</i>
	12:00-12:30 Elsevier Presentation	12:00-13:00 Panel discussion <i>Is there a future for organometallic chemistry?</i>	12:00-12:30 Flash-presentations
	12:30-14:40 Lunch		12:30-14:40 Lunch
	14:40-16:00 (PL5) Jeanne Crassous <i>Organometallic Chemistry of Helicenes</i>	14:40-16:00 (PL9) Didier Bourissou <i>Expanding the Chemical Space of Gold thanks to Ligand Design</i>	14:40-16:00 (PL13) Christopher Teskey <i>Cobalt hydride catalysis under the spotlight</i>
15:00 -15:30 Opening Ceremony			
15:30-16:50 (PL1) Holger Braunschweig <i>Turning Boron Chemistry on its Head: The Unusual Reactivity of Boron in Low Oxidation States</i>	16:00-17:20 (PL6) Sonja Herres-Pawlis <i>Tailored catalyst design for the synthesis and the recycling of bioplastics</i>	16:00-17:20 (PL10) Christian Hartinger <i>Bioorganometallic Chemistry: Organometallic Drugs and Drug Candidates</i>	16:00 -16:30 Closing Ceremony
16:50-17:10 Coffee Break			17:10-19:40 Guided visit to the University Botanical Garden and the Church of San Venanzio
17:10-18:30 (PL2) Cristina Nevado <i>A journey towards mechanistic understanding in organometallic chemistry</i>			
	17:30-19:40 Poster Session	17:30-18:20 Flash-presentations	
		18:20-19:40 Poster Session	
20:00 Welcome Cocktail	20:00 Dinner	20:00 Dinner	20.00 Social Dinner

ORGANIZING COMMITTEE



Prof. Augusto Cingolani
Honorary President of ISOC



Prof. Claudio Pettinari
Chair



Prof. Fabio Marchetti
Co-chair



Prof. Riccardo Pettinari



Prof. Corrado Di Nicola



Prof. Marino Petrini



Prof. Enrico Marcantoni



Prof. Alessandro Palmieri



Prof.ssa Serena Gabrielli



Dott.ssa Alessia Tombesi



Dott.ssa Sonila Khafa



Dott.ssa Noemi Pagliaricci

Advisory Board

Lidia Armelao – University of Padova, Italy – CNR
Marco Bandini – University of Bologna, Italy
Andrea Biffis - University of Padova, Italy
Pierre Braunstein - University of Strasbourg, France
Angela Casini - TUM, Germany
Emma Gallo - University of Milan, Italy
Roberto Gobetto - University of Torino, Italy
Hansjörg Grützmaker - ETH Zurich, Switzerland
Stephen K. Hashmi – University of Heidelberg
Jerome Lacour - University of Geneva, Switzerland
Alceo Macchioni - University of Perugia, Italy
Jacques Maddaluno - CNRS Paris, France
Robin A. Perutz - University of York, United Kingdom
Maurizio Peruzzini - ICCOM CNR Firenze, Italy
Claudio Pettinari - University of Camerino, Italy
Rinaldo Poli - LCC-CNRS Toulouse, France
Armando Pombeiro - University of Lisbon, Portugal
Gianna Reginato - ICCOM CNR Firenze, Italy
Emmanuelle Schultz - University of Paris-Saclay, France
Anna M. Trzeciak – University of Wrocław

Scientific Committee

Prof. Alessandro Abboto
Prof. Marco Bandini
Prof. Andrea Biffis
Prof. Vito Capriati
Prof. Mario Chiesa
Prof. Emma Gallo
Prof. Enrico Marcantoni
Prof. Matteo Mauro
Prof. Mina Mazzeo
Prof. Elena Petricci
Prof. Claudio Pettinari
Prof. Francesco Ruffo

Prof. Alessandro Bismuto



University of Bonn, Bonn, Germany

“Exploring Heavy Pnictogens: From low-valent compounds to luminescence”



Biography: Alessandro was born and grew up in Southern Italy (Naples). He obtained his Bachelor and Master degree at the University of Naples (Federico II) working under the Supervision of Prof. Francesco Ruffo. In 2014, he moved to Scotland (United Kingdom) where he started his doctorate studies on the CRITICAT CDT (Doctoral Training in Critical Resources) programme. During that time, he worked under the supervision of Dr Stephen Thomas and Dr Michael Cowley on main group catalysis at the direct interface between inorganic and organic chemistry. In 2017, he was awarded a Research Mobility grant

from Royal Society of Chemistry to undertake a research placement at the University of California, Berkeley, with Prof. John Hartwig, to study the mechanism in Ir-catalysed borylation reactions. In 2018, he moved to Switzerland to join the group of Prof. Bill Morandi as post-doctoral researcher at ETH Zürich. During the time in Switzerland he has worked on transition-metal chemistry, developing novel catalytic cycles, and studying their mechanism. After starting an independent career at the Institute of Organic and Biomolecular Chemistry (University of Göttingen), Alessandro was appointed Junior Professor (tenure track) at the Institute of Inorganic Chemistry (University of Bonn) in May 2023.

Email: bismuto@uni-bonn.de

Website: <https://www.bismutolab.com/>

Prof. Didier Bourissou



University of Toulouse III, Toulouse, France

"Expanding the Chemical Space of Gold thanks to Ligand Design"



Biography: Didier Bourissou studied chemistry at the Ecole Normale Supérieure in Paris and obtained a PhD degree from Paul Sabatier University in 1998 under the supervision of G. Bertrand. He then worked with F. Mathey and P. Le Floch at the Ecole Polytechnique in Palaiseau as a research associate. He was appointed as a CNRS junior researcher in 1998. Since 2006, he holds a senior scientist position (Directeur de Recherche) at the CNRS and from 2006 to 2018, he has been Associate Professor at the Ecole Polytechnique in Palaiseau. He is Director of the Laboratory of Fundamental and Applied Heterochemistry at the University Paul Sabatier in Toulouse since 2011. His research interests

concern new bonding situations and reactivity patterns arising from the main group elements, the transition metals and their interplay. He has pioneered ambiphilic ligands in the mid 2000's and developed the concept of acceptor ligands. Part of his research also deals with non-innocent pincer complexes and unusual behavior of the coinage metals, in particular gold. He is also interested in biodegradable polymers (ring-opening polymerization, organic and dual catalysis, drug delivery systems).

Email: didier.bourissou@univ-tlse3.fr

SPEAKERS

Website: <https://lhfa.cnrs.fr/index.php/en/teams/lbpb-en>

Prof. Holger Braunschweig



University of Wuerzburg, Wuerzburg, Germany

“Turning Boron Chemistry on its Head: The Unusual Reactivity of Boron in Low Oxidation States”



Biography: Braunschweig is head and chair of Inorganic Chemistry at the University of Würzburg, as well as managing head and founding director of our newly established research center ICB - institute of sustainable chemistry & catalysis with boron. He obtained his PhD and Habilitation with Prof. P. Paetzold (RWTH Aachen). He was post-doc with Prof. M. F. Lappert at Sussex and held a position as Reader at Imperial College, London. He carried out seminal work on metal boron complexes, boron heterocycles, and boron-boron multiple bonds. His work was published in over 720 publications, the majority of which

appeared in first ranking journals. His discoveries have been highlighted in a wide range of outlets, including New Scientist, The Times of London, Science, Nature, Nature Chemistry, Chemical and Engineering News, Chemistry World, Spektrum, Chemie in unserer Zeit, and Angewandte Chemie. He was awarded the Gottfried Wilhelm Leibniz award (2009), the RSC Main Group Chemistry Award (2014), and received the Arduengo, Steinhöfer, Bruker, and ScotCHEM named visiting lectureships. He is a member of the Bavarian Academy of Sciences, the German National Academy of Sciences (Leopoldina), the North Rhine-Westphalian Academy of Sciences, and the DFG advisory panel for molecular inorganic chemistry.

Email: holger.braunschweig@uni-wuerzburg.de

Website: <https://www.braunschweiggroup.de/>

Prof. Jeanne Crassous



CNRS-University of Rennes, Rennes, France

“Organometallic Chemistry of Helicenes”



Biography: She received her PhD in 1996 from the Ecole Normale Supérieure de Lyon (ENS Lyon) on ‘The Absolute Configuration of Bromochlorofluoromethane (CHFCIBr)’ under the supervision of Prof. André Collet. After a one-year postdoctoral period studying ‘The Chirality of Fullerenes’ in Prof. François Diederich’s group (ETH Zurich, Switzerland), she received a CNRS researcher position at the ENS Lyon in 1998 and then she joined the ISCR in 2005. She is currently coordinating a French national network (GDR CHIRAFUN, Chirality and multifunctionality) and a European ITN Project (HEL4CHIROLED, Helical molecules for Chiral OLEDs). She is member of the Editorial Board of Chirality and ChemPhysChem journals (Wiley). In 2020, she

received the National Prize of the Organic Chemistry Division of the French Chemical Society (DCO-SCF). In 2023, she was awarded the CNRS Silver Medal. She is also a Member of the European Academy of Science (EurASc) and a Chemistry Europe Fellow. She is dealing with many fields of chirality (heteroatomic and organometallic helicenes, chiral π -conjugated systems and assemblies, fundamental aspects of chirality). She is studying chiroptics (electronic and vibrational circular dichroism, circularly polarized luminescence) for potential applications in optoelectronics and spintronics. Jeanne Crassous is a CNRS Research Director at the ‘Institut des Sciences Chimiques de Rennes’ (ISCR). She is currently active for the French Chemical Society as an elected member of the DCO-SCF executive board (2021-2024).

Email: jeanne.crassous@univ-rennes.fr

Website: <https://iscr.univ-rennes.fr/jeanne-crassous>

SPEAKERS

Prof. Joseph Dyson



EPFL-Lausanne, Lausanne, Switzerland

“Catalytic transformation of natural and synthetic waste into value-added chemicals”



Biography: Paul Dyson joined the Institute of Chemical Sciences and Engineering at the EPFL in 2002 where he heads the Laboratory of Organometallic and Medicinal Chemistry and between 2008 and 2016 chaired the Institute. He has won several prizes including the Werner Prize of the Swiss Chemical Society in 2004, the Award for Outstanding Achievements in Bioorganometallic Chemistry in 2010, the Centennial Luigi Sacconi Medal of the Italian Chemical Society in 2011, the Bioinorganic Chemistry Award of the Royal Society of Chemistry in 2015, the European Sustainable Chemistry Award of the European Chemical Society in 2018 and the Green Chemistry Award from the Royal Society of Chemistry in 2020. He is also a Clarivate Highly Cited

Researcher and has an H-index >110 (web of science and google scholar). He was elected a Fellow of the Royal Society of Chemistry in 2010, a Fellow of the European Academy of Science in 2019 and a life-long fellow of the American Association for the Advancement of Science in 2020. Over the years he has held visiting professorships at the University of Bourgogne, University of Pierre et Marie Curie, University of Vienna, University of Rome Tor Vergara, Chimie Paristech and Shanghai Jiao Tong University. Since 2016 he has been Member of the Council of the Division of Mathematics, Natural and Engineering Sciences at the Swiss National Science Foundation. Between 2016-2021 he has been Member of the Council of the Division of Mathematics, Natural and Engineering Sciences at the Swiss National Science Foundation. In 2021 he was appointed Dean of the Faculty of Basic Sciences.

Email: paul.dyson@epfl.ch

Website: <https://people.epfl.ch/paul.dyson?lang=en>

Prof Matthias Driess



Technical University of Berlin, Berlin, Germany

“Cooperative Low-Valent Silicon Atoms in Small Molecule Activation”



Biography: Matthias Driess was born in 1961 in Eisenach, Thuringia. He received his Diplom in chemistry in 1985 and completed his PhD in 1988 at Heidelberg University. While at Heidelberg, he also studied philosophy and wrote his final thesis on "Über den logischen Empirismus von Rudolf Carnap und die Einheit der Wissenschaften" (On the logical empiricism of Rudolf Carnap and the unity of the sciences). After working as a postdoctoral fellow with Professor Robert West in Madison, Wisconsin, U.S.A., for a year, he returned to Heidelberg in 1989, completing his Habilitation in inorganic chemistry there in 1993 with a thesis about silicon and phosphorus in unusual coordination. After three more intellectually stimulating years in Heidelberg, he was appointed professor for inorganic chemistry at Ruhr

University Bochum in 1996. In 2004, Matthias Driess moved to Technische Universität Berlin, where he heads the Chair of Inorganic Chemistry / Metalorganic Chemistry and Inorganic Materials at the Institute of Chemistry. He was spokesperson for the UniCat Cluster of Excellence from 2007 to 2018. Since 2019, he has been co-spokesperson of the successor Cluster of Excellence Unifying systems in Catalysis, UniSysCat. Professor Driess was made a member of the German National Academy of Sciences Leopoldina in 2012 and has been an Ordinary Member of the Berlin-Brandenburg Academy of Sciences and Humanities BBAW since 2014. He has been a member of the European Academy of Sciences since 2020.

Email: matthias.driess@tu-berlin.de

Website: <https://www.tu.berlin/en/metallorganik/about-us/head-of-chair>

Prof. Elena Fernandez-Gutierrez



University of Rovira i Virgili, Tarragona, Spain

“Catalytic activation of organoboron compounds for strategic and selective construction of target compounds”



Biography: Elena Fernández received her degree in chemistry at the University of Barcelona in 1991. She did PhD studies in catalytic hydroformylation of sugars with Prof. S. Castellón and Prof. A. Ruiz (1991-1995) and she moved to Oxford University (UK) (1995-1997) for a postdoctoral position with Prof. John M. Brown where her studies culminated with an approach towards the first catalytic asymmetric hydroboration-amination reaction. Elena accepted in 1997 a lecturer position at the University Rovira i Virgili, becoming part of the permanent staff in 2000 and Full Professor in 2019. She received the

Award on Excellence of Research in Organometallic Chemistry 2014 and the Award on Excellence of Research in Chemistry 2017, both from the Spanish Royal Society of Chemistry. She is Distinguished Professor at the URV from 2018. Her current scientific campaign is aimed to generate knowledge and awareness about activation modes of borane reagents to be used in selective organic synthesis of multifunctional compounds. She has contributed to several seminal articles, reviews and book's chapters, highlighting the edition of two books on Synthesis and Applications of Organoboron Compounds for Springer (2015) and Advances in Organoboron Chemistry toward Organic Synthesis for Science of Synthesis-Thieme (2019).

Email: mariaelena.fernandez@urv.cat

Website: <https://www.catborchem.recerca.urv.cat/en/>

Prof. Christian Hartinger



University of Auckland, Auckland, New Zealand

“Bioorganometallic Chemistry: Organometallic Drugs and Drug Candidates”



Biography: I received my PhD in Chemistry in 2001 under the supervision of Bernhard Keppler at the University of Vienna. After a period at the University of Vienna, I joined Paul Dyson's group at the EPFL in Switzerland in 2006 as a Schrödinger Fellow. I returned to Vienna in 2009 to finish my habilitation. In 2011, I accepted a position as Associate Professor at the University of Auckland and was promoted to Professor in 2016.

I have received national and international recognition with the Society of Biological Inorganic Chemistry Early Career Award 2016, the NZ Institute of Chemistry's premier award, the Maurice Wilkins Centre Prize for Chemical Science, in 2016, the NZAS Hill Tinsley Medal in 2017, the Morrison Medal of the Australian and New Zealand Society for Mass Spectrometry in 2019, and I was elected a Fellow of the Royal Society of New Zealand in 2021, among others.

Email: c.hartinger@auckland.ac.nz

Website: <https://hartinger.wordpress.fos.auckland.ac.nz/>

Prof. Sonja Herres-Pawlis



University of Aachen, Aachen, Germany

“Tailored catalyst design for the synthesis and the recycling of bioplastics”



Biography: Franc Meyer earned his Ph.D. with Peter Paetzold at RWTH Aachen (1993, boron chemistry) and was a postdoc with Peter Armentrout at the University of Utah (gas phase guided ion beam studies). On returning to Germany, he completed his Habilitation at the University of Heidelberg in 2000 and became Professor of Inorganic Chemistry at the University of Göttingen in 2001. He is a member of the Göttingen Academy of Sciences, the Royal Physiographic Society in Lund, and the German National Academy of Sciences Leopoldina. His group's research focuses on the activation of small molecules and on

cooperative effects in bimetallic and multimetallic complexes, with particular interests in bioinorganic chemistry, bioinspired catalysis and magnetic nanoswitches.

Email: sek.bioac@ac.rwth-aachen.de

Website: <https://www.bioac.ac.rwth-aachen.de/go/id/ictk/?lidx=1>

Prof. Cristina Nevado



University of
Zurich^{UZH}

University of Zurich, Zurich, Switzerland

“A journey towards mechanistic understanding in organometallic chemistry”



Biography: Cristina Nevado was born in Madrid, where she graduated in chemistry at the Autónoma University in 2000. In October 2004 she received her PhD from the same university working with Prof. Antonio M. Echavarren thereafter joining the group of Prof. Alois Fürstner at the Max-Planck-Institut für Kohlenforschung (Germany) as a post doctoral associate. In May 2007 she started her independent career as an Assistant Professor of Organic Chemistry at the University of Zürich. In 2011, Cristina was awarded the Chemical Society Reviews Emerging Investigator Award and the Thieme Chemistry Journal Award in recognition of her contributions in the field of synthetic organic chemistry. In 2012 she received an ERC Junior Investigator grant and in 2013 was awarded the Werner Prize of the Swiss Chemical Society and was directly promoted to Full Professor. In 2019, she received the Royal Society of Chemistry Award in Organometallic Chemistry and in 2020 the Excellence Research Trajectory Award of the Royal Spanish Chemical Society (RSEQ) as well as the Margaret Faul Women in Chemistry Award. Among her many contributing roles to the community, Cristina is currently Senior Associate Editor for ACS Central Science, Organic Syntheses and Science of Synthesis. Rooted in the wide area of organic chemistry, her research program is focused on complex chemical synthesis and new organometallic reactions.

Email: cristina.nevado@chem.uzh.ch

Website: <https://www.nevadogroup.com/>

Prof. Luca Pignataro



UNIVERSITÀ
DEGLI STUDI
DI MILANO

University Of Milano, Milano, Italy

“Two strategies for exploiting base metals in homogeneous catalysis”



Biography: Luca Pignataro completed his PhD at the University of Milan with Prof. Franco Cozzi in 2006. After postdoc periods in the group of Prof. David Leigh (University of Edinburgh) and Prof. Cesare Gennari (University of Milan), he became Researcher (2012) and then Associate Professor (2019) at the University of Milan. His current research interests are in the fields of homogeneous catalysis (base metal catalysis, supramolecular catalysis, enantioselective catalysis, light-driven reactions), and targeted delivery of drugs (small molecule-drug conjugates for anti-tumor therapy).

Email: luca.pignataro@unimi.it

Website: <https://sites.unimi.it/apos.lab/luca-pignataro/>

Prof. Christopher Teskey



Technical University of Braunschweig, Braunschweig, Germany

“Cobalt hydride catalysis under the spotlight”



Biography: Christopher J. Teskey carried out his undergraduate studies in Natural Sciences at the University of Cambridge and then, in 2012, began his PhD with Prof. Michael F. Greaney at the University of Manchester. After graduating in 2016, he was awarded an EPSRC Doctoral Prize Fellowship to stay at the University of Manchester for a further year. Following this, in 2017 he moved to the University of Vienna, Austria to take up a postdoctoral researcher position in the group of Prof. Nuno Maulide as a Lise Meitner Research Fellow of the FWF (Austrian Science Fund). From March 2019 to October 2023, he led a Junior Research Group at the Institute of Organic Chemistry at RWTH Aachen, Germany funded by a Liebig Fellowship from the Fonds der Chemischen Industrie. From November 2023, he has been a Professor of Organic Chemistry at the TU Braunschweig where he holds a Niedersachsen-Impuls-Professorship.

Email: christopher.teskey@tu-braunschweig.de

Website: <https://www.teskeygroup.com/christopher-teskey>

Prof. Antonio Zanotti -Gerosa



Johnson-Matthey, United Kingdom

“Homogeneous hydrogenation catalysis in the fine chemicals industry: how to develop industrially viable and sustainable processes?”



Biography: Antonio Zanotti-Gerosa studied in Milano, Italy, completing his PhD in organometallic chemistry in 1994 (Prof. S. Maiorana). His academic experience includes secondments to Imperial College (Professor S.V.Ley), University of Bonn (Prof K.H. Doetz) and Nagoya University (Professor R. Noyori) and post-doctoral research at the University of Lausanne (Professor C. Floriani). Since 1997 he has been working on industrial applications of homogeneous catalysis. In 2003 he joined Johnson Matthey and, as R&D Director, he is now leading the JM chemocatalysis group in the Cambridge laboratories.

Email: Antonio.Zanotti-Gerosa@matthey.com

Website: <https://contactout.com/Antonio-ZanottiGerosa-85605>

SPONSORS



SHERWIN-WILLIAMS®



ELSEVIER

CHIMICA  **CENTRO**
Soluzioni per laboratori scientifici



PL 1, September 4, 15:30 - 16:20

Turning Boron Chemistry on its Head: The Unusual Reactivity of Boron in Low Oxidation States

Holger Braunschweig

^a ICGM, Université Montpellier, CNRS, ENSCM, Montpellier, France. ^b Department of Chemistry and Hylleraas Centre for Quantum Molecular Sciences, University of Oslo, 0315 Oslo, Norway.

odile.eisenstein@umontpellier.fr

In 1900, a PhD student, named Victor Grignard, in the laboratory headed by Philippe Barbier in Lyon, discovered the reagent and the reaction that have now his name.¹ Twelve years later, Grignard was awarded the Nobel prize “for the discovery of the so-called Grignard reagent, which in recent years has greatly advanced the progress of organic chemistry”. Despite more than 100 years of extensive studies, the mechanism of this reaction has remained elusive, with little quantitative information and missing consensus. Difficulties in elucidating this mechanism are prominently related to the fact that the ethereal solutions of Grignard reagents contain a variety of chemical species that are strongly dependent on the nature of each chemical partner, the organic solvent and the experimental conditions. As written by Dietmar Seyferth, “Generally written as RMgX, the Grignard reagents in ethereal solution are more complicated than this simple formula indicates”.²

In this lecture, the Grignard reagent and reaction will be described. The computational study adapted to the case (ab-initio molecular dynamics) and its impact on chemistry will be briefly summarized.

This will be followed by a description of the study of the Grignard reagent and reaction with this method.

- 1) A study of the fast exchange process between CH_3MgCl , $\text{Mg}(\text{CH}_3)_2$ and MgCl_2 , known as Schlenk equilibrium, to determine the nature of the species in THF solution and their relative concentration.³
- 2) A study of the Grignard reaction addressing the following points i) Which of the magnesium species are the most reactive (model acetaldehyde), ii) when is a radical based reaction preferred over a nucleophilic addition, (observation SET reaction with aromatic carbonyl reagents)?⁴
- 3) With a goal to study further the variants of the Grignard reaction, notably that known as the turbo-Grignard (reagents are RMgX plus LiX), preliminary results on the nature of species of this mixed system will be presented.⁵

[1] Grignard, V. C. Compt. Rend. Hebd. Séances Acad. Sci. 1900, 130, 1322.

[2] Seyferth, D. *Organometallics* **2009**, 28, 1598.

[3] Peltzer, R. M.; Eisenstein, O.; Nova, A.; Cascella, M. *J. Phys. Chem. B* **2017**, 121, 4226.

[4] Peltzer, R. M.; Gauss, J.; Eisenstein, O.; Cascella, M. *J. Am. Chem. Soc.* **2020**, 142, 2984.

[5] de Giovanetti, M.; Hopen Eliasson, S. H; Castro, A. C. Eisenstein, O. Cascella, M. *J. Am. Chem. Soc.* **2023**, DOI: 10.1021/jacs.3c04238

PL 2, September 4, 17:10 - 18:30

A journey towards mechanistic understanding in organometallic chemistry

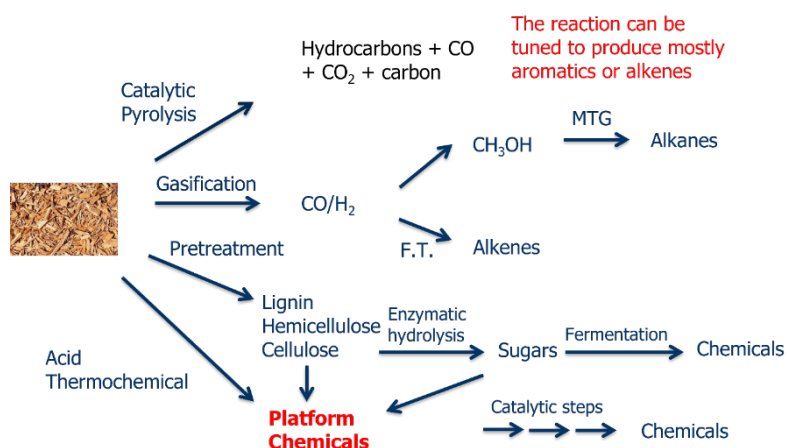
Cristina Nevado

Leibniz Institut für Katalyse, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany

Johannes.devries@catalysis.de

In order to reduce global warming, the use of fossil resources needs to be curbed as much as possible. Although the largest part of these resources is used for fuel, the chemicals our daily lives depend on are also made from fossil fuels, and thus there is a dire need to develop new production routes based on renewable resources. Lignocellulose in the form of wood or agro waste is the most abundantly available renewable resource, thus this material as well as its constituents: cellulose, hemicellulose as well as the constituent sugars and lignin are the raw materials of the future. In addition, fats, oils terpenes and CO₂ may also be considered.

There are a number of different methods to convert lignocellulose into chemicals that are depicted in the figure below. In the lecture we will concentrate on the methodology that is based on the use of platform chemicals that are easily prepared in a single step from renewable resources.



Levulinic acid is a C-5 platform chemical that can be made directly from lignocellulose by treatment with dilute acid at high temperatures. A range of products have been made from levulinic acid. We will outline our method to produce the nylon intermediates caprolactam and adipic acid from levulinic acid.¹ A second platform chemical is 5-hydroxymethyl-furfural

(HMF), which is made by dehydration of fructose.² HMF is rather unstable and thus it is currently produced on rather small scale. More stable variants will be produced in plants that are currently under construction.³ In the chemistry we have performed with HMF its reduction to 1-hydroxy-2,5-hexanedione takes a central role.⁴ This compound can be converted into a range of different products. Most recently we have accomplished the synthesis of aromatic compounds from this intermediate.^{5,6} The second half of the lecture will mostly concentrate on how to prepare aromatic compounds from renewables.

[1] J. G. de Vries, *Chem. Rec.* **2016**, *16*, 2787–2800.

[2] R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, Hero J. Heeres, J. G. de Vries, *Chem. Rev.* **2013**, *113*, 1499–1597.

[3] J. G. de Vries, *Curr. Opin. Green Sustain. Chem.* **2023**, *39*, 100715.

[4] B. Wozniak, S. Tin and J. G. de Vries, *Chem. Sci.*, **2019**, *10*, 6024–6034.

[5] S. Zheng, S. Chakraborty, E. Baráth, S. Tin, and J. G. de Vries, *ACS Sustainable Chem. Eng.* **2022**, *10*, 15642–15647.

[6] S. Zheng, Z. Wei, B. Wozniak, F. Kallmeier, E. Baráth, H. Jiao, S. Tin, J. G. de Vries, *Nat. Sust.* **2023**, accepted for publication. (DOI : 10.1038/s41893-023-01190-w).

PL 3, September 5, 9:00 - 10:20

Catalytic transformation of natural and synthetic waste into value-added chemicals

Joseph Dyson

^aIstituto di Chimica dei Composti Organometallici, Dipartimento di Chimica "U. Schiff", via della Lastruccia 13, 50019, Sesto Fiorentino, Firenze
alessandro.mordini@unifi.it

Organic conjugated aromatic and heteroaromatic compounds have found broad application as active components in optoelectronic and photovoltaic devices, either as light-harvesting or charge carrier-transporting materials, and for the photocatalytic production of hydrogen.¹ Due to their importance, many efforts have been made to establish easy, efficient and sustainable procedures to access donor-acceptor conjugated organic compounds endowed with a large structural diversity and thus able to be employed in various solar energy conversion technologies, such as dye-sensitized and perovskite solar cells,² photocatalytic systems for hydrogen production³ and luminescent solar concentrators⁴ (Figure 1).

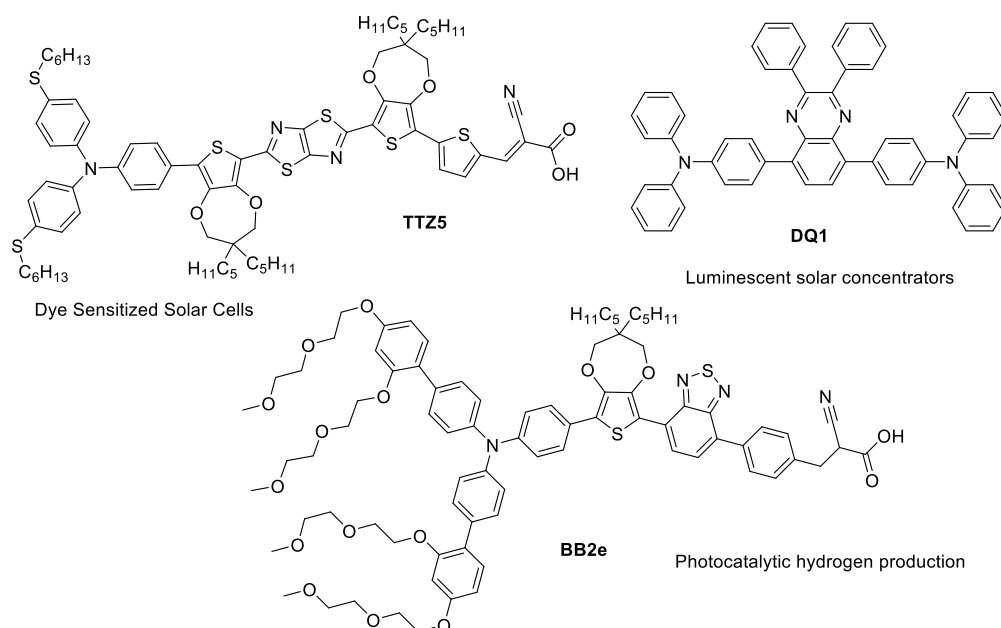


Figure 1: Structures of selected organic compounds recently applied in solar energy conversion devices

In this talk, some selected examples will be presented, illustrating the rational design and the synthesis of the compounds and discussing the relationship between their spectroscopic and electrochemical properties and the performances of the corresponding solar-powered devices.

[1] A. Mordini *et al.*, *Coord. Chem. Rev.* **2019**, 392, 177.

[2] L.A. Castriota *et al.*, *Energy & Environmental Materials*, 2022, doi:10.1002/eeem2; A. Dessì *et al.*, *Sust. Energy Fuels* **2021**, 5, 1171.

[3] M. Bartolini *et al.*, *ACS Appl. Energy Mater.* **2020**, 3, 8912.

[4] C. Papucci *et al.*, *J. Mater. Chem. C*, **2021**, 9, 15608.

PL 4, September 5, 10:40 - 12:00

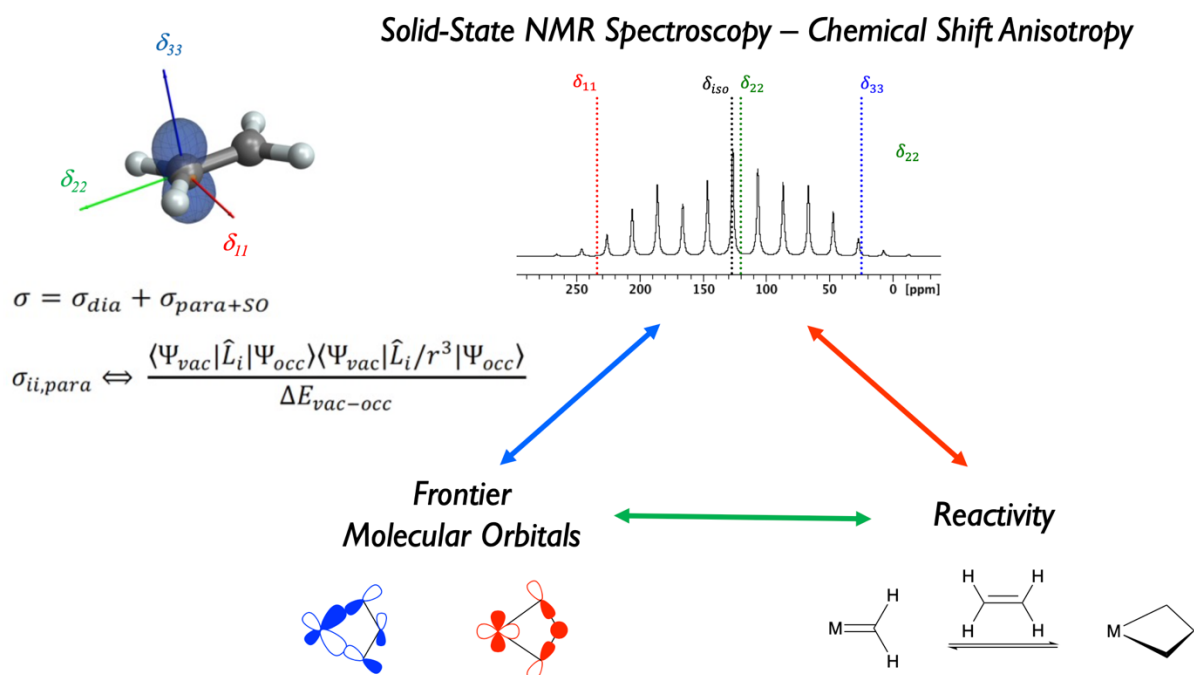
Exploring Heavy Pnictogens: From low-valent compounds to luminescence

Alessandro Bismuto

Department of Chemistry and Applied Biosciences – ETH Zürich, Switzerland

ccoperet@inorg.chem.ethz.ch

Chemical shift has been successfully used since the beginning of NMR to identify the signature of molecules (and materials) making NMR an invaluable tool of characterizations. Because of its power to elucidate molecular structure, NMR interpretation is taught at early stage, often in laboratory courses, even before one understand the fundamentals of spectroscopy and their selection rules. We all remember solving organic and inorganic puzzles based on 1D and 2D NMR spectra during our undergraduate (and graduate...) times.¹ This lecture, targeted for all aficionados of NMR (and those who want to become one), will concentrate on developing a detailed understanding of the origin of NMR chemical shift, and how it can be used to reconstruct the electronic structure of molecules, in particular organometallic intermediates. This lecture will also aim to show that the angular momentum operator has an “ideal” symmetry, that makes NMR a privilege spectroscopic descriptor of reactivity.



[1] Spectral identification of organic compounds, Eds. Silverstein, Webster and Kiemle, Wiley&Sons, **2005**.

[2] a) Metal Olefin Complexes: Revisiting the Dewar-Chatt-Duncanson Model and Deriving Reactivity Patterns from Carbon-13 NMR Chemical Shift. C. P. Gordon, R. A. Andersen, C. Copéret *Helvetica Chim Acta* **2019**, *102*, e1900151. b) Carbon-13 NMR Chemical Shift: A Descriptor for Electronic Structure and Reactivity of Organometallic Compounds C.P. Gordon, C. Raynaud, R.A. Andersen, C. Copéret, O. Eisenstein, *Acc. Chem. Res.* **2019**, *52*, 2278-2289. c) Nuclear Magnetic Resonance: A Spectroscopic Probe to Understand the Electronic Structure and Reactivity of Molecules and Materials. C. P. Gordon, L. Lätsch, C. Copéret *J. Phys. Chem. Lett.* **2021**, *12*, 2072- 2085. d) Classifying and understanding the reactivities of Mo-based alkyne metathesis catalysts from ⁹⁵Mo NMR chemical shift descriptors. Z. Berkson, L. Lätsch, J. Hillenbrand, A. Fürstner, C. Copéret, *J. Am. Chem. Soc.* **2022**, *144*, 15020–15025.

PL 5, September 5, 10:40 - 12:00

Organometallic Chemistry of Helicenes

Jeanne Crassous

Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland

morandib@ethz.ch

In this presentation, recent developments in synthetic methodology from our group will be discussed. This will include e.g. new developments in the area of shuttle catalysis, including applications to feedstock and waste valorization. This will be completed by a discussion on further methods recently developed in our group, as well as accompanying mechanistic studies.

PL 6, September 5, 16:00 - 17:20

Tailored catalyst design for the synthesis and the recycling of bioplastics

Sonja Herres-Pawlis

University of Göttingen, Institute of Inorganic Chemistry, Tammannstr. 4, 37077 Göttingen, Germany.

franc.meyer@chemie.uni-goettingen.de

N-heterocyclic carbenes (NHCs) have become textbook examples of strong σ -donor supporting ligands in organometallic chemistry and catalysis.¹ In recent years, their beneficial properties for stabilizing 3d metals in unusual oxidation states² have been increasingly exploited in bioinspired chemistry. Using NHCs as surrogates of ubiquitous imidazole ligands, or using tetra-NHC macrocycles in place of common porphyrins, can impart unusual electronic structures to reactive bioinorganic species and allow for their isolation and/or beneficial application in biorelevant catalytic transformations.

This lecture will discuss some fundamentals of NHC ligands in organometallic chemistry and will then present recent examples from our group for the use of macrocyclic NHC platforms in bioinspired Fe and Cu chemistry, focusing on (a) high-valent oxoiron intermediates for H atom abstraction reactions,³ (b) the stabilization of organometallic Cu in multiple oxidation states⁴ and (c) models for key features of the unique Cu_A and Cu_Z sites relevant for N₂O reduction by the metalloenzyme nitrous oxide reductase (N₂OR).^{5,6} In all cases, the combination of structural, spectroscopic, kinetic and computational investigations has revealed important electronic structure contributions to the complexes' properties and reactivities.

[1] (a) Nahra, F.; Nelson, D. J.; Nolan, S. P. *Trends in Chem.* **2020**, 2, 1096; (b) D. Munz, *Organometallics* **2018**, 37, 275.

[2] (a) Cheng, J.; Wang, L.; Wang, P.; Deng, L. *Chem. Rev.* **2018**, 118, 9930; (b) Zámbo, G. G.; Schlagintweit, J. F.; Reich, R. M.; Kühn, F. E. *Catal. Sci. Technol.* **2022**, 12, 4940.

[3] (a) Meyer, S.; Klawitter, I.; Demeshko, S.; Bill, E.; Meyer, F. *Angew. Chem. Int. Ed.* **2013**, 52, 901; (b) Ye, S.; Kupper, C.; Meyer, S.; Andris, E.; Navrátil, R.; Krahe, O.; Mondal, B.; Atanasov, M.; Bill, E.; Roithová, J.; Meyer, F.; Neese, F. *J. Am. Chem. Soc.* **2016**, 138, 14312; (c) Kupper, C.; Mondal, B.; Serrano-Plana, J.; Klawitter, I.; Neese, F.; Costas, M.; Ye, S.; Meyer, F. *J. Am. Chem. Soc.* **2017**, 139, 8939; (d) Cordes, C.; Morganti, M.; Klawitter, I.; Schremmer, C.; Dechert, S.; Meyer, F. *Angew. Chem. Int. Ed.* **2019**, 58, 10855.

[4] (a) Liu, Y.; Resch, S. G.; Klawitter, I.; Cutsail III, G. E.; Demeshko, S.; Dechert, S.; Kühn, F. E.; DeBeer, S.; Meyer, F. *Angew. Chem. Int. Ed.* **2020**, 59, 5745; (b) Geoghegan, B. L.; Liu, Y.; Peredkov, S.; Dechert, S.; Meyer, F.; DeBeer, S.; Cutsail III, G. E. *J. Am. Chem. Soc.* **2022**, 144, 2520.

[5] Liu, Y.; Resch, S. G.; Chen, H.; Dechert, S.; Demeshko, S.; Bill, E.; Ye, S.; Meyer, F. *Angew. Chem. Int. Ed.* **2023**, 62, e202215840

[6] Liu, Y.; Chatterjee, S.; Cutsail III, G. E.; Peredkov, S.; Gupta, S. K.; Dechert, S.; DeBeer, S.; Meyer, F. *J. Am. Chem. Soc.* **2023**, 145, doi.org/10.1021/jacs.3c04893.

PL 7, September 6, 09:00 - 10:20

Two strategies for exploiting base metals in homogeneous catalysis

Luca Pignataro

ITQB NOVA, Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Avenida da
República, 2780-157 Oeiras, Portugal.

brovo@itqb.unl.pt

Hydrosilylation is one of the most significant homogeneous processes for the reduction of diverse functional groups. It represents a useful alternative process for hydrogenation. Notably, hydrosilylation operates under mild reaction conditions, consequently over-reduced products are rarely detected, and does not involve the use of highly flammable hydrogen gas or pressure reactors.¹ Depending on the type of unsaturated systems, e.g. carbonyls (ketones, aldehydes, esters), imines, or nitriles, a variety of silyl ethers are obtained, which can be easily hydrolyzed to give alcohols or amines. Moreover, hydrosilylation of unsaturated C-C bonds leads to valuable organosilicon compounds. Traditionally, late transition metals (e.g. Pd, Pt, Ru, Rh) have been applied as hydrosilylation catalysts, but more recently, Earth-abundant 3d transition metals (e.g. Fe, Mn) have received increasing attention.² In this lecture, an overview of the Mn-based catalysts that have developed so far as powerful alternatives for the hydrosilylation of unsaturated organic groups will be presented. Evolution of the ligand design in Mn-catalyzed hydrosilylations, from highly sensitive Mn(II) catalysts bearing bidentate and polydentate N- and P-based ligands to air-stable Mn(I) complexes with bidentate N-heterocyclic carbenes will be discussed. Special emphasis will be given to the influence of the ligand design on the catalytic activity and selectivity of the catalysts and the mechanistic aspects.

[1] Schlichter, P.; Werlé, C. *Synthesis*. **2022**, 54, 517.

[2] Royo, B. *Advances in Organometallic Chemistry*. **2019**, Vol. 70

PL 8, September 6, 10:40 - 12:00

Homogeneous hydrogenation catalysis in the fine chemicals industry: how to develop industrially viable and sustainable processes?

Antonio Zanotti -Gerosa

Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany.

matthias.beller@catalysis.de

The sufficient and sustainable supply of energy remains one if not the most important challenge for our future. In the coming years it will be vital to develop efficient processes to interconvert renewable energy sources to chemical energy. In this respect, the talk will present different technological concepts to achieve this goal with the help of new catalysts. Specifically, the role of carbon dioxide in a sustainable chemical industry will be discussed. Furthermore, several examples for the cost-effective and waste-free synthesis of industrially relevant materials, life science goods and other kinds of organic products using innovative catalysts will be presented. Here, it will be shown how new and improved homogeneous and heterogeneous catalysts can be developed by learning from each other. Specifically, the phenomenon of cooperative catalysis will be addressed in the context of non-noble metal-based catalysts. In detail, it will be demonstrated that recently developed molecular-defined as well as nano-structured cobalt and iron catalysts enable catalytic (de)hydrogenation processes with high yields and unprecedented selectivity. Examples which demonstrate the potential of such catalytic processes with bio-relevant metal complexes compared to more traditional catalytic reactions will also include reactions for energy technologies.

Furthermore, if time permits the development of novel catalysts for carbonylation reactions will be shown. Here specifically, the role of ligands in carbonylations of olefins will be addressed. By rational design novel ligands and complexes have been synthesized, which allow for unprecedented efficiency in such transformations by following the principles of cooperative catalysis. Apart from industrially relevant processes, interesting carbonylation reactions for modern organic synthesis are presented.

LECTURES

PL 9, September 9, 14:40 - 16:00

Expanding the Chemical Space of Gold thanks to Ligand Design

Didier Bourissou

Institute of Organic Chemistry Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.

dorota.gryko@icho.edu.pl

“Look deep into nature, and then you will understand everything better.”

Albert Einstein

Porphyrinoids, also known as *the pigments of life*, are a class of naturally occurring organic dyes. They play key roles in crucial processes that support life - oxygen transport (hem), electron transport (cytochrome c), photosynthesis (chlorophyll a), and synthesis of DNA (vitamin B₁₂). Vitamin B₁₂ - a co-factor in many catalytic processes.¹ Following nature, this unique Co-complex has been exploited in sustainable catalysis.²⁻⁴ Along this line, we have developed new vitamin B₁₂- catalyzed reactions involving reduction of Co(III) to Co(I) or Co(II) and subsequent reactions with electrophiles or radicals. Vitamin B₁₂ derivative catalyzes an unusual new sp² C-H alkylation reaction with diazo reagents as a carbene source,⁵ acylation of activated olefins,⁴ alkylation of strained molecules.⁵⁻⁸ These key findings emphasize the unique feature of vitamin B₁₂ as a catalyst to achieve something unachievable with other methodologies or to find a greener approach.

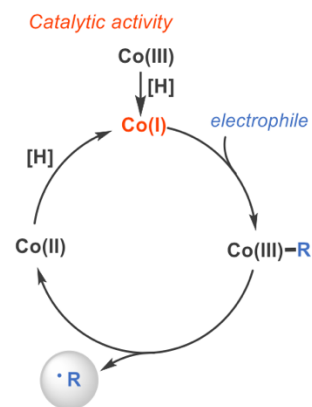
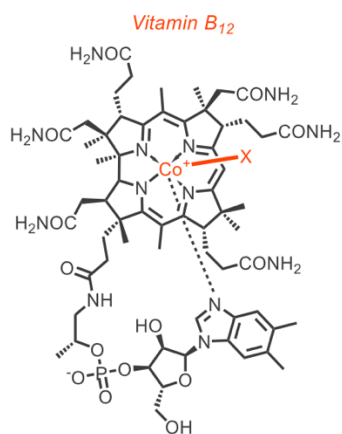


Figure 1. Vitamin B₁₂ not only a medicine

- [1] Banerjee, R. *Chemistry and Biochemistry of B₁₂*, John Wiley & Sons, Inc, 1999
- [2] Giedyk, M., Golsizewska, K., Gryko, D. *Chem. Soc. Rev.* **2015**, *44*, 3391.
- [3] Wdowik, T., Gryko, D. *ACS Catal.* **2022**, *12*, 6517.
- [4] Giedyk, M.; Gryko, D.; *Chem Cat.* **2022**, *2*, 1534.
- [5] Giedyk, M.; Fedosov, S.; Gryko, D. *Chem. Commun.* **2014**, *50*, 4674.
- [6] Ociepa, M., Baka, O., Narodowicz, J., Gryko, D. *Adv. Syn. Cat.* **2017**, *359*, 3560.
- [7] M. Ociepa, A. J. Wierzba, J. Turkowska, D. Gryko, *J. Am. Chem. Soc.* **2020**, *142*, 5355.
- [8] Potrząsaj, A.; Musiejuk, M.; Chaładaj, W.; Giedyk, M.; Gryko, D *J. Am. Chem. Soc.*, **2021**, *143*, 9368.
- [9] Turkowska, J.; Durka, J.; Ociepa, M.; Gryko, D. *Chem. Commun.*, **2022**, 58, 509.
- [10] Potrząsaj, A.; Ociepa, M.; Chaładaj, W.; Gryko, D. *Org. Lett.* **2022**, *24*, 2469.
- [11] Potrząsaj, A.; Musiejuk, M.; Chaładaj, W.; Giedyk, M.; Gryko, D. *J. Am. Chem. Soc.* **2021**, *143*, 9368.

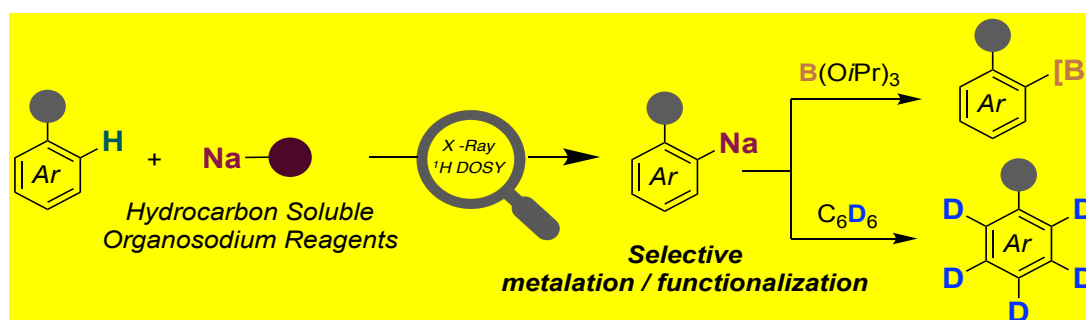
PL 10, September 6, 16:00-17:20

Bioorganometallic Chemistry: Organometallic Drugs and Drug Candidates

Christian Hartinger

Department of Chemistry, Biochemistry and Pharmacy, University of Bern. Freiestrasse 3, 3012 Bern (Switzerland).

Organosodium compounds have attracted the attention of the scientific community in recent years as an alternative to widely used organolithium reagents.^[1] Lithium alkyls and amides reside at the front of organometallic synthesis as key players in countless transformations, owing to their availability, substantial stability and solubility in hydrocarbon solvents.^[2] However, these desirable traits are often pitfalls of heavier alkali-metal organometallics, meaning that their applications have remained underexplored. While recent reports have hinted at the untapped potential of these reagents,^[3] the constitution of the organometallic intermediates that operate in these reactions has been overlooked, missing an opportunity to tackle their high reactivity and improve their poor solubility. Filling this gap in the knowledge, the preparation of organosodium compounds soluble in hydrocarbon solvents and the isolation and characterization of reactive sodium organometallic intermediates in the solid state and in solution by X-Ray crystallography and ¹H DOSY (Diffusion Ordered Spectroscopy) have allowed the development of new protocols for the functionalisation of organic molecules. Our efforts have been focused on selective deprotonative metalation reactions of synthetically attractive arenes, providing access to the selective functionalization of these scaffolds, including the borylation^[5] and the perdeuteration of aromatic scaffolds,^[6] and the arylation of toluene derivatives via selective benzylic metalation.^[7] The reactivity and/or selectivity obtained with organosodium compounds was different to the one with its lithium analogues, opening new vistas in the use of polar organometallic reagents for the functionalization of organic molecules.



[1] De, P. B.; Asako, S.; Ilies, L.; *Synthesis* **2021**, 53, 3180–3192.

[2] Lithium Compounds in Organic Synthesis – From Fundamentals to Applications, (Eds.: Luisi, R. and Capriati, V.), Wiley-VCH, Weinheim 2014.

[3] Asako, S.; Nakajima, H.; Takai, K.; *Nat. Catal.* **2019**, 2, 297–303.

[4] Reich, H. J.; *Chem. Rev.* **2013**, 113, 7130–7178.

[5] Bole, L. J.; Tortajada, A.; Hevia, E.; *Angew. Chem. Int. Ed.* **2022**, 61, e202204262.

[6] Tortajada, A.; Hevia, E.; *J. Am. Chem. Soc.* **2022**, 144, 20237–20242.

[7] Anderson, D. E.; Tortajada, A.; Hevia, E.; *Angew. Chem. Int. Ed.* **2023**, 62, e202218498.

PL 11, September 7, 09:00 – 10:40

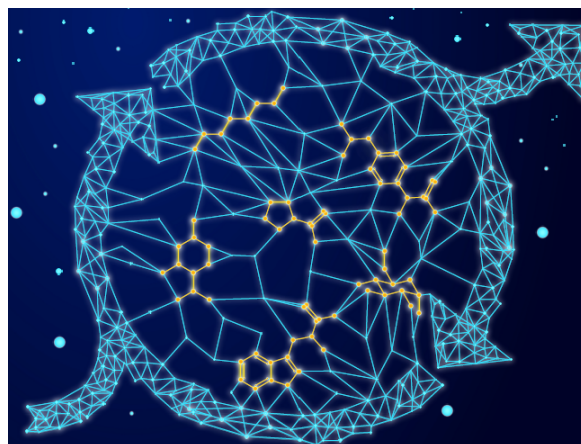
Catalytic activation of organoboron compounds for strategic and selective construction of target compounds

Elena Fernandez-Gutierrez

University of Manchester, Department of Chemistry, Oxford Road, Manchester, M13 9PL, United Kingdom

In The development of greener and more efficient synthetic methodologies is essential for organic chemistry to reach its full potential in its application to many applied and fundamental scientific problems. Over the last two decades C-H activation has emerged as a powerful tool to streamline syntheses, functionalize complex scaffolds, while massively improving atom and step economy. However, several challenges are still to be addressed before C-H functionalization can be widely applied: 1) the development of mild reaction conditions with a broad scope, including late-stage functionalization, 2) the control of the regioselectivity of C-H activation, 3) the control of the selectivity of homo- versus cross-coupling, and 4) the development of conditions that can be safely used in industry.

Mechanistic understanding is a cornerstone for progress in organic chemistry. In this talk I will present some of our group's approaches in applying the knowledge derived from mechanistic studies into the design of more efficient processes and of novel catalysts and catalytic systems, such as the use of bimetallic Pd/Ag,¹ Pd/Cr² and Au/Ag³ synergistic systems, and Ru-catalysts for late stage functionalization.^{4,5} Additionally, recent developments in the application of machine learning to mechanism elucidation will be discussed.⁶



[1] Chiara Colletto, Adyasha Panigrahi, Jaime Fernandez-Casado and Igor Larrosa *J. Am. Chem. Soc.* **2018**, *140*, 9638-9643.

[2] Maria Batuecas, Junfei Luo, Ivana Gergelitsová, Katrina Krämer, Daniel Whitaker, Iñigo J. Vitorica-Yrezabal and Igor Larrosa *ACS Catal.* **2019**, *9*, 5268.

[3] Xacobe C. Cambeiro, Nanna Ahlsten and Igor Larrosa *J. Am. Chem. Soc.* **2015**, *137*, 15636.

[4] Marco Simonetti, Diego M. Cannas, Xavier Just-Baringo, Iñigo J. Vitorica-Yrezabal and Igor Larrosa *Nature Chem.* **2018**, *10*, 724.

[5] Matthew Wheatley, Michael T. Findlay, Rocio Lopez-Rodriguez, Diego M. Cannas, Marco Simonetti and Igor Larrosa *Chem Catal.* **2021**, *1*, 691.

[6] Jordi Bures and Igor Larrosa *Nature* **2023**, 10.1038/s41586-022-05639-4.

LECTURES

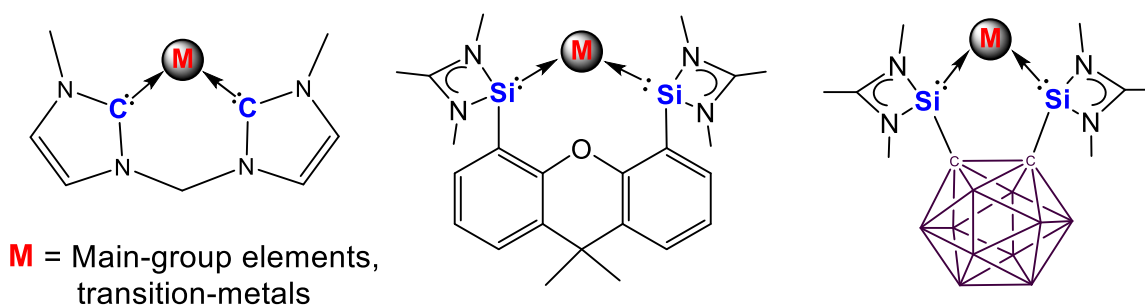
PL 12, September 7, 10:40 – 12:00

Cooperative Low-Valent Silicon Atoms in Small Molecule Activation

Matthias Driess

Technical University of Berlin, Department of Chemistry: Metalorganics and Inorganic Materials, Secr C2,
Strasse des 17. Juni 135, E-mail: Matthias.driess@tu-berlin.de

Replacement for noble metals by earth abundant non-metals is a longstanding challenge in small molecule activation and catalysis. In my talk I will address the research question how to tame a single subvalent silicon to serve as an active site in small molecule activation, homogeneous catalysis and stabilizing unusual low oxidation states of heavy main group metals. In fact, silicon, the second most abundant element of the earth crust, provides unexpected opportunities to mimic transition-metals in small molecule activation if it is in a low oxidation state (+2, +1 and 0). Notably, silylenes, the congener of carbenes bearing divalent silicon, show a precious metal-like reactivity and are competent in selective carbon-heteroatom bond activation of organic substrates and even pave the way to organosilicon triplet diradicals.^[1] Over the last few years, we have demonstrated that the reactivity of silylenes can be significantly enhanced towards very stable small molecules such as carbon monoxide if two silylene moieties are placed in close proximity in the same molecular entity, giving rise to metal-free cooperative bond activation. Additionally, silylenes are much stronger donor ligands towards transition-metals than phosphines and carbenes that pave the way to more efficient chemoselective metal-mediated catalysis and stabilizing unusual oxidation states.^[2-7] Some of these intriguing features of bis-silylenes will be discussed as well.



[1] Xiong, Y., Dong, S., Yao S., Lorent, C., Krause, K., Vijakumer G., Zhu, J., Limberg, C. Driess, M., *Nat. Synthesis* **2023**, DOI: <https://doi.org/10.1038/s44160-023-00279-6>.

[2] Shan, C., Yao, S., Driess, M. *Chem. Soc. Rev.* **2020**, 49, 6733-6754.

[3] Yao, S., Xiong, Y., Seddington, A., Driess, M. *Chem. Commun.* **2021**, 57, 10130-10152.

LECTURES

[1] Xu, J.; Yao S.; Fossum, V.; Maultz, E.; Lorent, C.; *Chem. Sci.*, **2023**, 10, 10620–10632.

PL 13, September 7, 14:40 – 16:00

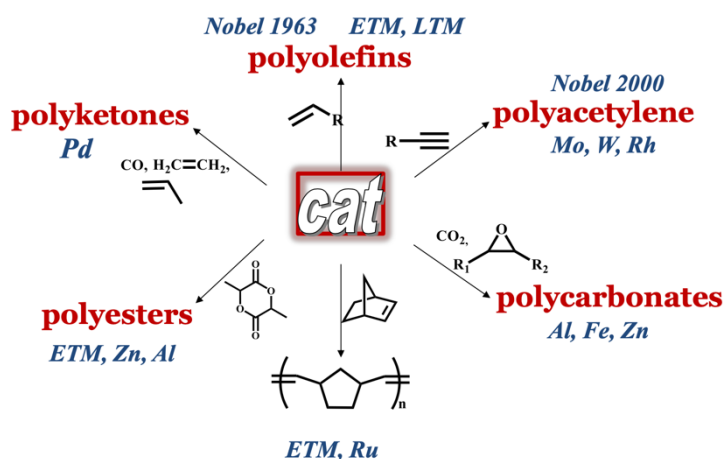
Cobalt hydride catalysis under the spotlight

Christopher Teskey

Our modern life relies on synthetic polymers that find application to make cars, aeroplanes, clothes, houses, food packaging, electronics, medicine, just to mention a few. This is possible thanks to the development of suitable, highly efficient catalysts for polymerization reactions. The starting point of catalysis for polymerization reactions dates back to the beginning of the fifties of last century when Karl Ziegler and Giulio Natta introduced the first catalysts for the synthesis of polyolefins. The huge impact of this discovery on our Society was immediately clear and this year we celebrate the 60th anniversary of the award of the Noble Prize in Chemistry to these two scientists.

The impressive evolution of the research in the field has witnessed the development of catalysts spanning from the initial ones, based on Early Transition Metals (ETM), to the most recent ones, based on Late Transition Metals (LTM) and this lecture is focused on the latter. Moreover, inside the wide number of catalytic polymerization reactions (some examples in the Figure) only a few will be presented, e.g. the Ring Opening Polymerization of cyclic esters to yield linear aliphatic polyesters, the Ring Opening CoPolymerization of CO₂ with epoxides to yield polycarbonates, the homopolymerization of ethylene to yield polyolefins and the copolymerization of ethylene with polar vinyl monomers to obtain functionalized polyolefins.

In addition to give an overview of the studied catalysts, particular attention will be addressed to the mechanism of the catalytic cycle. Finally, in the last part a brief discussion about the current challenges in the field, like the recycling of waste materials and the use of monomers from renewable resources, will be presented.



Poster 1

Photooxygenation of p xylene catalyzed by Fe(III) pyclen complexes: an insight into the magnetic and spectroscopical properties of the catalysts.

Matteo Alberti,^{a*} Djihed Boucherabine,^a Fausto Cargnoni,^b Mario Italo Trioni,^b Dominika Zakutna,^c Andrea Sartorel,^d Alessandro Caselli.^{a, b}

^a Department of Chemistry, Università degli Studi di Milano, Via Golgi, 19, 20133 Milano, Italy.

*matteo.alberti@unimi.it

^b Istituto di Scienze e Tecnologie Chimiche “G. Natta” CNR-SCITEC, via Golgi 19, 20133 Milano, Italy.

^c Department of Inorganic Chemistry, Charles University, Hlavova 2030/8, 128 40, Prague 2, Czech Republic.

^d Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova, Italy.

Iron complexes have long been studied in oxidative transformations as biomimetic models of enzyme active sites. In this context, while many examples of iron-mediated oxidation of organic compounds under thermal activation have been reported, the photochemical activation of iron complexes is a less explored field.¹ We report herein the synthesis and detailed characterization of a series of [Fe(III)(X₂)pyclen]X complexes (X = Cl, Br, OTf; pyclen = 3,6,9-triaza-1(2,6)-pyridinacyclodecaphane, complexes 1–3, Figure 1), relevant to the selective photocatalytic oxidation. Structural analysis, Mössbauer spectroscopy, magnetization studies, and UV-vis absorption spectroscopy combined with DFT calculations were employed to investigate their properties. Notably, the complexes display extended absorption into the visible range, attributed to ligand-to-metal charge transfer transitions involving the pyclen and halide/triflate ligands. Evidence suggests that light absorption can promote homolytic cleavage of the Fe–X bond, particularly for X = Cl and Br. Inspired by these findings, the photochemical behavior of the complexes under visible light irradiation (up to 415 nm) was explored for the aerobic oxidation of p-xylene. The nature of the halide ligand was found to influence the reactivity: the bromide complex (2) promoted the selective formation of p-tolualdehyde via a hydrogen atom transfer (HAT) mechanism, while the chloride (1) and triflate (3) analogs showed negligible activity. These results not only demonstrate the catalytic potential of photochemically activated iron complexes but also provide a foundation for future studies aimed at developing sustainable, light-driven oxidation processes.

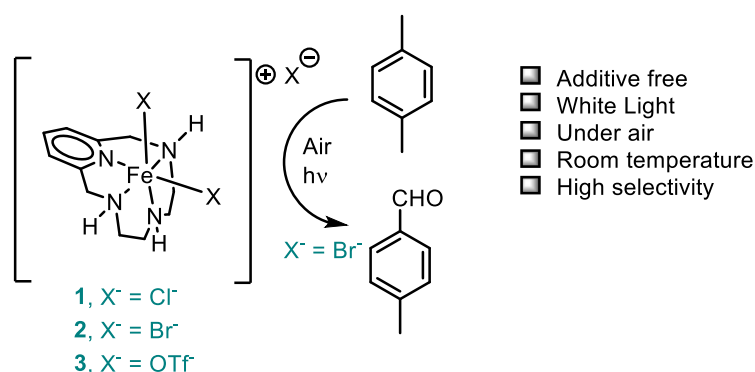


Figure 1

[1] W.-J. Zhou, X.-D. Wu, M. Miao, Z.-H. Wang, L. Chen, S.-Y. Shan, G.-M. Cao, D.-G. Yu, *Chemistry – A European Journal* **2020**, *26*, 15052–15064.

Poster 2

Cyclometalated C[^]N Diphosphine Ruthenium Catalysts for Oppenauer-Type Oxidation / Transfer Hydrogenation Reactions and Cytotoxic Activity

Dario Alessi,^{a*} Pierfrancesco del Mestre,^b Eleonora Aneggi,^a Maurizio Ballico,^a Antonio P. Beltrami,^b Marta Busato,^a Daniela Cesselli,^b Alexandra A. Heidecker,^c Daniele Zuccaccia,^a and Walter Baratta^{a*}

^a Dipartimento di Scienze Agroalimentari, Ambientali e Animali, Università di Udine, Via Cotonificio 108, I-33100 Udine, Italy; *alessi.dario@spes.uniud.it. ^b Dipartimento di Area Medica, Università di Udine, Via Colugna 50, I-33100 Udine, Italy. ^c Inorganic Chemistry/Molecular Catalysis, Department of Chemistry & Catalysis Research Center, TUM, Lichtenbergstraße 4, 85747 Garching b. München, Germany.

Cyclometalated ruthenium complexes have been demonstrated to be highly attractive for a wide range of catalytic reactions.¹ [Ru(η^2 -OAc)₂(dppb)] easily reacts with phenyl substituted *N*-heterocycles in methanol to afford the corresponding cyclometalated acetate derivatives [Ru(C[^]N)(η^2 -OAc)(dppb)] (dppb = 1,4-bis(diphenylphosphino)butane; HC[^]N = 2-phenylpyridine **1**, benzo[*h*]quinoline **2**, 1-phenylpyrazole **3**, 2-phenyl-2-oxazoline **4**). All complexes have been characterized by SC-XRD and multinuclear NMR spectroscopy. The derivatives **1-4** display catalytic activity in the *Oppenauer*-type oxidation of secondary alcohols to ketones at S/C = 1000, using acetone or cyclohexanone as hydrogen acceptor and KO^tBu as base in toluene, with TOF up to 12000 h⁻¹. Complexes **1-4** are also active in the TH of carbonyl compounds to alcohols in 2-propanol and in the presence of NaOⁱPr, with TOF up to 14300 h⁻¹. Protonation of the OAc ligand with HCOOH gives the formate [Ru(C[^]N)(η^2 -HCOO)(dppb)] (**5**). The cytotoxic activity of **1-4** against U87 glioblastoma cell line was established by MTT assay affording IC₅₀ values ranging from 1.4 to 4.1 μ M.

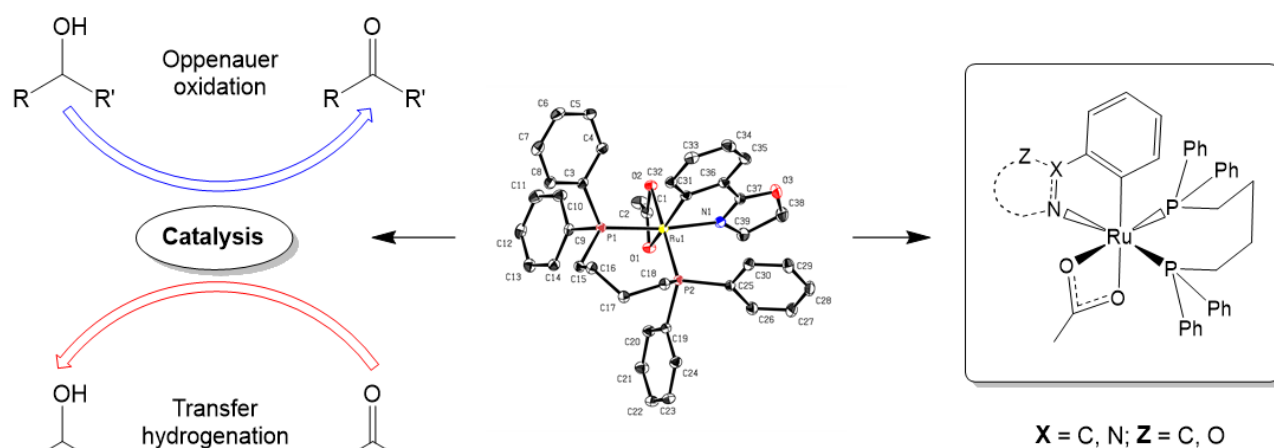


Figure 1

[1] Findlay, M. T.; Domingo-Legarda, P.; McArthur, G.; Yen, A. and Larrosa I. *Chem. Sci.*, **2022**, *13*, 3335-3362.

Poster 3

Synthesis, Characterization, and Evaluation of Anticancer Activity of New Organometallic Pt(II) Complexes With Imidazole Ligands

Asjad Ali,^{a*} Federica De Castro,^a Erika Stefàno,^a Michele Benedetti,^a Francesco Paolo Fanizzi.^a

^a Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Prov.le Lecce-Monteroni, Centro Ecotekne, 73100 Lecce, Italy. *asjad.ali@unisalento.it

Platinum complexes have been studied for years and a few of them (e.g., cisplatin, carboplatin, oxaliplatin) are serving globally as anticancer agents in clinics. Conversely, the obstacles generally related to these traditional drugs in cancer therapy are low water solubility, toxicity, adverse side effects, and cancer recurrence of certain tumors.¹ Thus, progress in the synthesis of new Pt(II) complexes specifically targeting cancer cells is considered a high priority. Therefore, we previously reported the synthesis and cytotoxicity evaluation of some $[\text{Pt}(\eta^1\text{-C}_2\text{H}_4\text{OR})(\text{DMSO})(\text{phen})]\text{Cl}$ complexes ($\text{R} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$),² finding higher cytotoxicity for the Et derivative. In this work, we focused our attention on water-soluble products derived from the $[\text{PtCl}(\eta^1\text{-C}_2\text{H}_4\text{OEt})(\text{phen})]$ complex, after chloride substitution with *N*-donor ligands. We studied the $[\text{Pt}(\eta^1\text{-C}_2\text{H}_4\text{OEt})(\text{NH}_3)(\text{phen})]\text{Cl}$ (**1**),³ $[\text{Pt}(\eta^1\text{-C}_2\text{H}_4\text{OEt})(1\text{-hexyl-1H-imidazole})(\text{phen})]\text{Cl}$ (**2**), and $[\text{Pt}(\eta^1\text{-C}_2\text{H}_4\text{OEt})(1\text{-hexyl-1H-benzo[d]imidazole})(\text{phen})]\text{Cl}$ (**3**), complexes (Figure 1A). These Pt(II) derivatives were characterized by nuclear magnetic resonance spectroscopy (NMR), and cytotoxic activity was evaluated by sulforhodamine B (SRB) assay on healthy and cancerous cell lines (Figure 1B). Complexes **1-3** cytotoxicity seem to be related to the inert $\eta^1\text{-C}_2\text{H}_4\text{OEt}$ moiety (stable in the absence of water), producing EtOH and labile $\eta^2\text{-C}_2\text{H}_4$ easily giving reactive aquo species upon hydrolysis. Interestingly, complex **3** demonstrated the higher cytotoxic activity observed in the series of **1-3** complexes and cisplatin, against selected cancer cell lines (Figure 1B). In conclusion, platinum-bonded biocompatible imidazole moieties⁴ could drastically increase the cytotoxicity and possible related anticancer potential of these type of complexes.

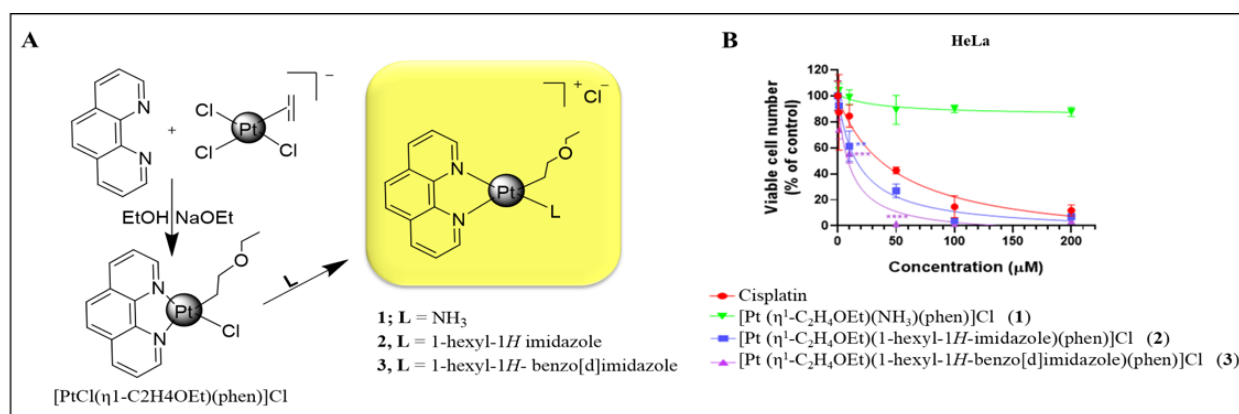


Figure 1: Showing the synthesis and cytotoxic activity of newly synthesized platinum(II) complexes

[1] Qi-Pin Q.; Shu-Long W.; Ming-Xiong T.; Yan-Cheng L.; Ting M.; Bi-Qun Z.; Hong L.; *European Journal of Med. Chem.*, **2019**, 161, 334-342.

[2] Erika S.; Federica D. C.; Erik D. L.; Antonella M.; Santo M.; Michele B.; Francesco P.F. *Inorg. Chim. Act.*, **2023**, 546, 121321.

[3] Federica D. C.; Erika S.; Erik D. L.; Michele B.; Francesco P.F. *Pharmaceutics*, **2021**, 13, 642.

[4] Monika G.; Chander M.; *Med. Chem. Research*. **2016**, 25, 173-210.

Poster 4

Expanding the Scope of Allylic C–H Alkynylations via Copper-Photocatalyzed Cross-Dehydrogenative Coupling

Gustavo Álvarez,* and Esteban Mejía.

Leibniz Institute for Catalysis (LIKAT), Albert-Einstein-Str. 29a, 18059 Rostock, Germany.

*Gustavo.Alvarez@catalysis.de

Photocatalytic functionalization of C–H bonds in a chemo-, regio-, or stereo-selective way using coordination compounds is one of the biggest challenges in photoredox catalysis, where copper photocatalysts are among the few alternatives.^[1] One of these was reported recently by our group for the alkynylation of allylic substrates under oxidative conditions.^[2] However, this methodology relies on the use of unstable organic peroxides and their parallel decomposition forces the use of high excess, which can affect the selectivity of the reaction and promote the further decomposition of the desired products. In the light of recent experimental results, we have suggested the formation of a reactive Cu–OH complex able to perform a hydrogen atom transfer (HAT) as the key step.^[3] However, the formation of further Cu–oxygen species cannot be neglected.^[4]

Herein we report how the use of N and P-containing additives (A in Scheme 1) have provided a better understanding of the Cu species involved in the reaction. Control experiments and isolation (crystallization) of side products and intermediates have given us further insights on the reaction mechanism. On the other hand, it has allowed us to expand the scope of this transformation, from mainly cyclic unactivated alkenes to more challenging linear and/or allyl-substituted substrates containing heteroatoms.

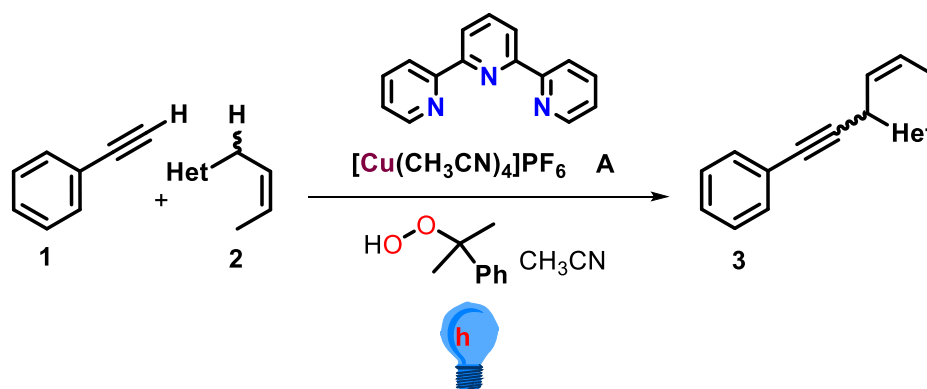


Figure 1

[1] I. Bosque, R. Chinchilla, J. C. Gonzalez-Gomez, D. Guijarro, F. Alonso, *Org. Chem. Front.* **2020**, 7, 1717-1742.

[2] a) A. A. Almasalma, E. Mejía, *Chem. - Eur. J.* **2018**, 24, 12269-12273; b) A. A. Almasalma, E. Mejía, *Synthesis* **2020**, 52, 529-536.

[3] D. Dhar, W. B. Tolman, *J. Am. Chem. Soc.* **2015**, 137, 1322-1329.

[4] C. E. Elwell, N. L. Gagnon, B. D. Neisen, D. Dhar, A. D. Spaeth, G. M. Yee, W. B. Tolman, *Chem Rev* **2017**, 117, 2059-2107.

Poster 5

Synthesis of Nylon 6,6 With Pyrene Chain-End for Compati-Bilization with Graphite and Improvement of Thermal and Mechanical Properties

Veronica Balzano^{a*}, Annalisa Mariconda^b, Maria Rosaria Acocella^a, Marialuigia Raimondo^c, Assunta D'Amato^a, Pasquale Longo^a, Liberata Guadagno^c, and Raffaele Longo^c

^a Department of Chemistry and Biology "A. Zambelli", University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano, Italy. *vbalzano@unisa.it. ^b Department of Basic and Applied Sciences, University of Basilicata, Via Dell'Ateneo Lucano 10, 85100 Potenza, Italy. ^c Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano, Italy.

Nylon 6,6 (PA66) is valued for its mechanical strength, chemical resistance, and thermal stability. To enhance its performance in applications such as automotive and aerospace, it is commonly reinforced with graphite, which provides a high strength-to-weight ratio and excellent thermal conductivity¹⁻³. However, poor adhesion between graphite and the PA66 matrix limits composite effectiveness. In order to tackle this drawback, in this work pyrene-functionalized PA66 (PA66py) was synthesized via interfacial polycondensation (Scheme 1)⁴⁻⁶. The pyrene end group promotes π - π stacking interactions with graphite, improving filler dispersion and matrix compatibility. Composites were prepared by ball milling, facilitating graphite exfoliation and uniform distribution. X-ray diffraction (XRD) showed a slight increase in graphite interlayer spacing (from 0.340 to 0.343 nm), indicating polymer intercalation. Thermogravimetric analysis (TGA) revealed enhanced thermal stability, while differential scanning calorimetry (DSC) showed increased crystallinity in PA66py composites, unlike standard PA66, which exhibited disrupted crystal structures. Atomic Force Microscopy (AFM) confirmed more uniform mechanical properties and better interfacial adhesion in PA66py composites, attributed to π - π interactions. Overall, pyrene functionalization significantly improves PA66-graphite compatibility, enhancing thermal, structural, and mechanical performance. This approach is promising for developing high-performance, lightweight composites and can be extended to other polymers and carbon fillers such as graphene and carbon nanotubes.

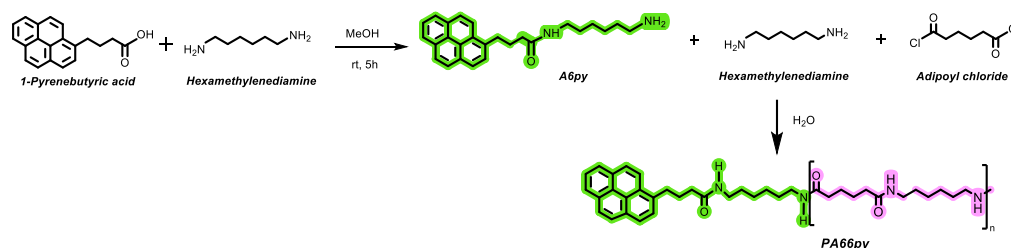


Figure 1: Synthesis of PA66py.

- [1] Chacón, J.M.; Caminero, M.A.; Núñez P.J.; García-Plaza, E.; García-Moreno, I.; Reverte, J.M. *Compos. Sci. Technol.* **2019**, *181*, 107688.
- [2] Chavarria, F.; Paul, D.R. *Polymer* **2004**, *45*, 8501–8515.
- [3] Das, A.; Etemadi, M.; Davis, B.A.; McKnight, S.H.; Williams, C.B.; Case, S.W.; Bortner, M.J. *Polym. Compos.* **2021**, *42*, 6010–6024.
- [4] Botelho, E.C.; Scherbakoff, N.; Rezende, M.C.; Kawamoto, A.M.; Sciamareli, J. *Macromolecules* **2001**, *34*, 3367–3375.
- [5] Weissmehl, K.; Arpe, H.J. *Industrial Organic Chemistry* John Wiley & Sons, **2003**, ISBN 978-3-527-30578-0.
- [6] Mark, J.E. *Polymer Data Handbook*; Oxford University Press, **1999**, ISBN 978-0-19-510789-0.

Poster 6

Synthesis and Characterization of Manganese- and Iridium-Pincer Complexes

Sadhna,^{a*} Ola F. Wendt,^a

^a Centre for Analysis and Synthesis, Department of Chemistry, Lund University, 22100 Lund, Sweden

*sadhna.sadhna@chem.lu.se

Manganese and iridium *NNN*-pincer based non-innocent complexes were designed and developed. These complexes are synthesized and characterized by NMR, FT-IR and XRD-crystallography (Figure 1). The Mn- and Ir-complexes show metal-ligand cooperation (MLC) as they consist the non-innocent ligand backbone which could undergo aromatization-dearomatization during the catalysis. Similar manganese and iridium complexes are generally employed in various catalysis such as hydrogenation, dehydrogenation, C–H activation, CO₂ insertions reactions etc.¹ We have previously reported the ruthenium complexes using the same *NNN*-ligand and utilized for the dehydrogenative coupling reactions.² The activity of current Mn- and Ir-based pincer complexes are currently been explored in various catalysis.

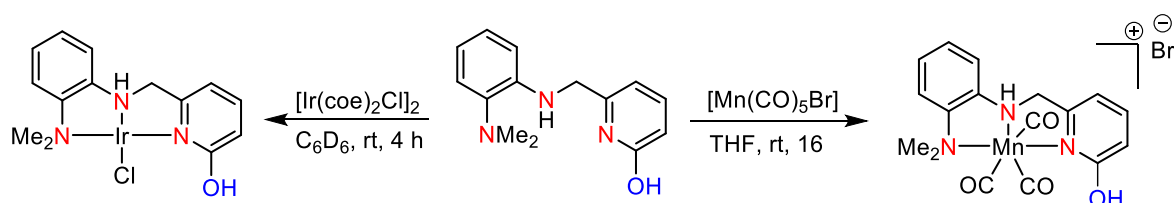


Figure 1. Synthesis of Mn- and Ir-*NNN* pincer complexes.

[1] a) Bisarya, A., Jasra, R. V., & Kumar, A. *Organometallics*, **2023**, 42, 1818–1831; b) Bisarya, A., Dhole, S., & Kumar, A. *Dalton Transactions*, **2024**, 53, 12698–12709; c) Völker, M.; Schreyer, M.; Burger, P. *Chemistry* **2024**, 6, 1230-1245.

[2] Garg, N. K., Goriya, Y., Manojveer, S., Wendt, O. F., & Johnson, M. T. *ChemCatChem*, **2024**, 16, e202301601.

Poster 7

Improving the selective synthesis of 2,5-bishydroxymethylfuran: scale up and sustainable solutions

Stefano Baratti,^{*a-b} Andrea Piazza,^{a-b} Chiara Lenzi,^{a-b} Tommaso Tabanelli,^{a-b} Stefania Albonetti,^{a-b} Rita Mazzoni.^{a-b}

^a Department of Industrial Chemistry “Toso Montanari” University of Bologna, V. Gobetti 85, 40129 Bologna, Italy.

^b Center for Chemical Catalysis – C3, University of Bologna, V. Gobetti 85, 40129 Bologna, Italy.

*stefano.baratti3@unibo.it

The biorefinery approach aims to sustainably produce key chemical building blocks from biomass rather than relying on fossil-based resources. Due to the complex nature of biomass feedstocks, a wide variety of valuable chemicals can be obtained. Among these, 5-hydroxymethylfurfural (HMF) has emerged as a crucial platform molecule. One of its most valuable derivatives, 2,5-bis(hydroxymethyl)furan (BHMF), is gaining attention for its versatility in applications such as biodiesel additives, non-ionic surfactants, polymer precursors, and flavoring agents. The catalytic conversion of HMF to BHMF was successfully carried out under mild conditions using Shvo’s catalyst in a hydrogen atmosphere, yielding over 99% in both conversion and selectivity. Additionally, a new iron-based catalyst demonstrated rapid and complete HMF conversion within 20 minutes at moderate conditions (toluene, 90 °C, 5 bar H₂). Building upon these advancements, we have established a scalable and efficient process for producing BHMF, notable for its excellent catalyst recyclability and use of greener solvents like anisole.

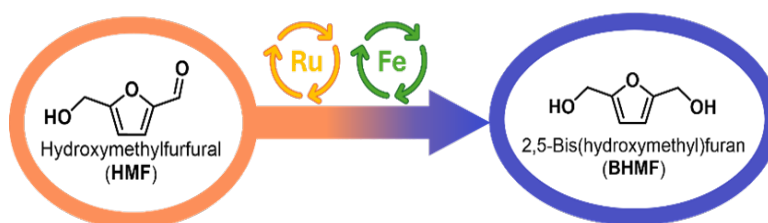


Figure 1: HMF conversion to BHMF

- [1] A. Messori, A. Fasolini, and R. Mazzoni, *ChemSusChem*, **2022**, vol. 15, no. 13.
- [2] T. Pasini, G. Solinas, V. Zanotti, S. Albonetti, F. Cavani, A. Vaccari, A. Mazzanti, S. Ranieri and R. Mazzoni, *Dalton Trans.*, **2014**, vol. 43, no. 26, pp. 10224–10234.
- [3] R. Mazzoni, A. Messori, A. Piazza, N. Santarelli, G. Martelli, M. Curcio, S. Albonetti, T. Tabanelli, **2023**, Patent n. 102023000023637.
- [4] P. P. Upare, Y. K. Hwang, D. W. Hwang, *Green Chemistry*, **2018**, 20, 879–885.

Poster 8

Synthesis and Characterization of new Potential TADF Photocatalysts

J. Barbieri,^{*a} F. Vasile,^a A. Bossi,^b M. Penconi,^b L. Pignataro^a

^a Università degli Studi di Milano, Dipartimento di Chimica, Via C. Golgi 19, 20133 Milano. ^b Istituto di Scienze e Tecnologie Chimiche “Giulio Natta” (SCITEC) del Consiglio Nazionale delle Ricerche (CNR), via Fantoli 16/15, 20138 Milano. *jacopo.barbieri@unimi.it

The use of organic dyes in photoredox catalysis represents one of the fields in which photocatalysis must still unfold its potential. In the last 10 years, thanks to the pioneering work of Zeitler¹ and Zhang,² donor-acceptor cyanoarenes have emerged as an asset for photoredox catalysis, due to their modular structure which allows the easy tuning of their photoredox properties. In a study on a Ni-catalytic, visible light-promoted C-N cross-coupling,³ we found that one of the best performing photocatalyst, commercially available 3DPA2FBN, was also producing two by-products, identified by HPLC-MS analysis as deriving, respectively, from loss of one and two HF molecules.

In this work, we successfully isolated the two products (**1** and **2** in Figure 1) as new potential visible light-absorbing photocatalysts and managed to assess an optimized method to synthesize them. NMR and XRD studies showed that each of these products is obtained as a single regioisomer, whose structure was fully elucidated. The photophysical properties of **1** and **2** were determined by electrochemical and spectroscopic techniques. Their catalytic activity was preliminarily assessed in several types of reactivity.

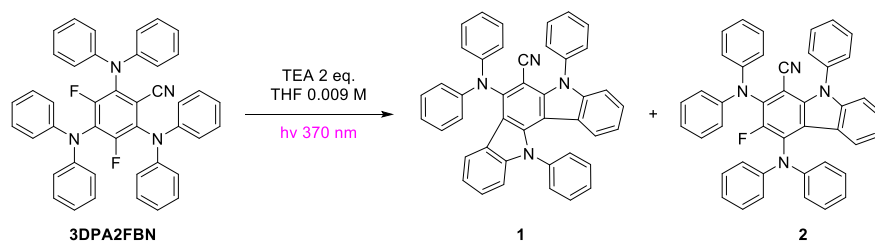


Figure 1. Synthesis of new potential TADF photocatalysts.

[1] E. Speckmeier, T. G. Fischer, K. Zeitler, *J Am Chem Soc*, **2018**, *140*, 15353-15365

[2] J. Luo, J. Zhang, *ACS Catal*, **2016**, *6*, 873-877.

[3] T. Gandini, L. Dolcini, L. Di Leo, M. Fornara, A. Bossi, M. Penconi, A. Dal Corso, C. Gennari, L. Pignataro, *ChemCatChem* **2022**, *14*, e202200990.

Poster 9

Synthesis of Copper(II) β -Diketonate Complexes and their Catalytic Applications in Ullmann-Type Coupling Reactions

Luca Barigelli,^{*a} Dario Gentili,^a Gabriele Lupidi,^a Francesca Stella,^a Jo' Del Gobbo,^a Miriam Caviglia,^a Maura Pellei,^a Carlo Santini,^a H. V. Rasika Dias,^b Enrico Marcantoni,^a Cristina Cimarrelli,^a Serena Gabrielli^a

^aSchool of Science and Technology - Chemistry Division, University of Camerino, Italy. ^bDepartment of Chemistry and Biochemistry, The University of Texas at Arlington, United States.

The Ullmann reaction has attracted considerable interest due to its broad applicability in the formation of new aryl C–C and C–heteroatom bonds, including C–N, C–O, C–S, C–P, and C–Se.¹ Conventional Ullmann protocols typically employ copper catalysts, either in their commercially available forms or as newly synthesized complexes; however, these reactions often require harsh conditions to proceed efficiently. Consequently, there is ongoing interest in developing new copper-based catalytic systems that can operate under milder conditions. Among the various ligands investigated, β -diketones have gained considerable interest due to their strong chelating ability and their effectiveness in stabilizing metals in various oxidation states. In this study, we present the synthesis of a series of Cu(II) complexes supported by different β -diketonate ligands (Figure 1).

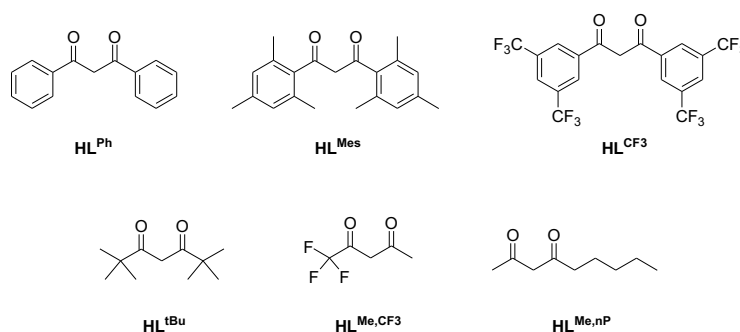


Figure 1. Molecular structures of β -diketone ligands.

All copper complexes were fully characterized in both solution and solid state and subsequently evaluated as catalysts in Ullmann-type C–O coupling reactions for the synthesis of diaryl ethers, using bromobenzene and 2-naphthol as starting materials. Various reaction conditions were explored, including variations in solvent, base, and reaction time. Additionally, microwave irradiation was employed to improve reaction efficiency. All copper(II) β -diketonate complexes exhibited good catalytic activity, with the complex bearing the L^{Ph} ligand emerging as the most effective, achieving a yield of 88%. In addition, various phenol and aryl bromide derivatives were tested using [Cu(L^{Ph})₂] as the catalyst, resulting in moderate to good yields.²

Acknowledgements: *Unione Europea – NextGenerationEU (NGEU PNRR, D.M. n. 630/2024 M4C2 I3.3)*

[1] Ley, S. V.; Thomas, A. W. *Angew. Chem. Int. Ed.* **2003** *42*, 5400-5449.

[2] Gentili, D.; Lupidi, G.; Stella, F.; Del Gobbo, J.; Caviglia, M.; Barigelli, L.; Pellei, M.; Santini, C.; Rasika Dias, H. V.; Marcantoni, E.; Cimarrelli, C.; Gabrielli, S. *Adv. Synth. Catal.* **2025**, submitted.

Poster 10

Monocarbonyl Ruthenium Catalysts for Aldehyde and Ketone Reduction in Water

Marta Busato,^{a*} Giulia Mannoni,^a Maurizio Ballico,^a Antonio Zanutti-Gerosa,^b Daniele Zuccaccia,^a Walter Baratta^a

^a DI4A, University of Udine, Via Cotonificio 108, 33100, Udine, Italy. *busato.marta@spes.uniud.it. ^b Johnson Matthey plc, 28 Cambridge Science Park, Milton Road, Cambridge, CB4 0FP, United Kingdom.

Water represents the ideal solvent, as it is non-toxic, non-flammable, inexpensive, and abundant, contrary to most organic solvents employed in homogeneous catalytic processes, which pose significant environmental, health, and safety concerns. Since the introduction of water-soluble phosphines in the 70's as ligands, water attracted a great deal of interest and begun to be studied for many important catalytic reactions, such as hydrogenation (HY) and transfer hydrogenation (TH), mainly mediated by Rh(III), Ir(III), and Ru(II) catalysts.¹⁻³ Monocarbonyl diphosphine ruthenium(II) catalysts have proven to be efficient in the reduction of aldehydes and ketones in both HY and TH reactions in ethanol and 2-propanol, respectively.⁴ Herein, we present a study of the catalytic activity in water or water-modified media (e.g., H₂O/2-propanol) of [Ru(OAc)(CO)(NN)(PP)]OAc (NN=ampy, en; PP=dppe, dppb) complexes in HY, as well as in TH using formate and formic acid as hydrogen sources (Figure 1).

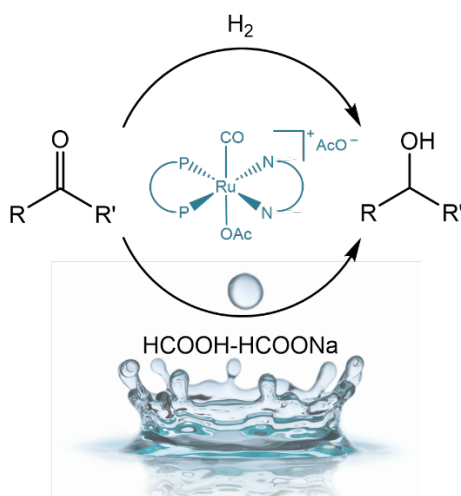


Figure 1

- [1] Deshmukh, G.; Rana, T. R. K.; Rajaraman, G.; and Murugavel, R. *Chem Asian J.*, **2025**, 20, e20240116.
- [2] Wang, R.; Yue, Y.; Qi, J.; Liu, S.; Song, A.; Zhuo, S.; Xing, L. *J. Catal.*, **2021**, 399, 1–7.
- [3] Wu, X.; Xiao, J.; Metal-Catalyzed Reactions in Water, *Wiley-VCH 2013*, Weinheim, 173-242.
- [4] Giboulot, S.; Comuzzi, C.; Del Zotto, A.; Figliolia, R.; Lippe, G.; Lovison, D.; Strazzolini, P.; Susmel, S.; Zangrando, E.; Zuccaccia, D.; Baldino, S.; Ballico, M.; and Baratta, W. *Dalton Trans.*, **2019**, 48, 12560-12576.

Poster 11

Highly Active and Recyclable Rhenium Catalysts: A New Heterogeneous Platform for Polyol Deoxydehydration

M. E. Casacchia,^{a*} A. Di Giuseppe,^a M. Crucianelli,^a N. d'Alessandro,^b L. Tonucci,^b A. Mascitti,^b E. Rombi,^c M.G. Cutrufello,^c F. J. Platero,^c A. Ruggiu,^c S. Piccinin,^d C. F. Pauletti^{d,e}

^a Dipartimento di Scienze Fisiche e Chimiche, Università degli Studi dell'Aquila, Via Vetoio, L'Aquila, Italy.

^b Department of Engineering and Geology, University of Chieti-Pescara, Viale Pindaro, 42, Pescara, Italy.

^c Dipartimento di Scienze chimiche e geologiche, Università di Cagliari, S.S. 554, Monserrato (CA), Italy. ^d CNR-IOM Trieste, Strada Statale 14, km 163,5, Basovizza (TS), Italy. ^e Department of Physics, University of Trieste, Via Alfonso Valerio, 2, Trieste, Italy. *mariaedith.casacchia@univaq.it

The transition from petrochemical-based resources to renewable biomass is a key objective in sustainable chemical production. Biomass-derived polyols are promising feedstocks for light olefins, essential intermediates in the polymer and fuel industries. However, their selective deoxygenation remains challenging due to the hydrophilicity of polyols, the reliance of deoxydehydration (DODH) reactions on expensive rhenium-based catalysts, and the harsh reaction conditions typically required. ^[1–3] This research, arising from a national research project (PRIN) collaboration, focuses on the design of cost-effective, environmentally benign, and industrially scalable heterogeneous rhenium-based catalysts for DODH. Rhenium was supported on a range of metal oxides—including SiO₂, Nb₂O₅, CeO₂, ZrO₂, and mixed oxides such as SiO₂–Nb₂O₅ and CeO₂–ZrO₂—prepared via soft-template (ST), hydrothermal (HT), and alcoholthermal (AT) methods. Extensive catalytic screening using diethyl tartrate as a model substrate enabled the identification of the most efficient materials. Through systematic optimization of temperature, reaction time, and solvent choice, the Re/SiO₂–Nb₂O₅ ST catalyst emerged as the most active and robust system, delivering high yields under significantly milder conditions (130–170 °C). The optimized protocol also ensured excellent recyclability across multiple cycles and proved effective with structurally diverse diol substrates. These findings underscore the critical role of support composition and synthesis methodology in tuning catalytic performance. Overall, this work delivers a practical and scalable DODH protocol, offering a valuable step forward in the catalytic conversion of renewable feedstocks into high-value-added chemicals within a circular economy framework.



Figure 1: General description of the project

[1] N.N. Tshibalonza, J.C.M. Monbaliu, *Green Chem.* **2020**, 22, 4801.

[2] G. Scioli, L. Tonucci, P. Di Profio, A. Proto, R. Cucciniello, N. d'Alessandro, *Sust. Chem. Pharm.*, **2020**, 17, 100273.

[3] L.J. Donnelly, S. P. Thomas, J. B. Love, *Chem. Asian J.* **2019**, 14, 3782 – 3790.

Poster 12

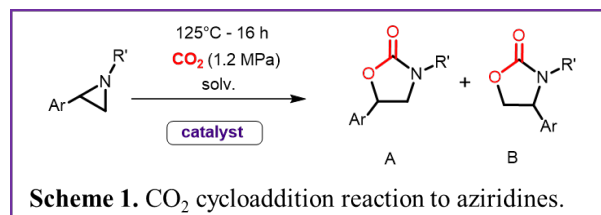
Hematin@ColorCatcher®: a Sustainable Catalyst for Oxazolidinones Synthesis

Caterina Damiano, Matteo Cavalleri,* and Emma Gallo.

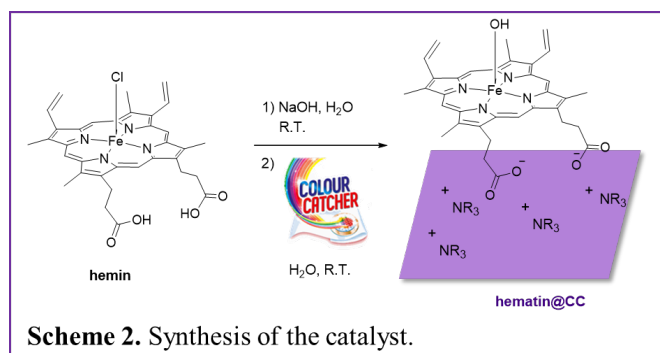
Department of Chemistry, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy.

*matteo.cavalleri@unimi.it

Oxazolidinones play a significant role as intermediates and chiral auxiliaries in organic synthesis¹ and they also belong to a class of active antibacterial and antibiotic compounds². An intriguing approach for synthesizing oxazolidinones involves the CO₂ cycloaddition reaction to aziridines, utilizing this greenhouse gas as a renewable C1 synthon rather than other carbon sources derived from the oil-based feedstock. Our research has extensively focused on promoting this reaction by using catalytic systems based on porphyrin metal complexes³ or metal free porphyrins,⁴ in combination with ammonium salts. Additionally, we successfully demonstrated the possibility to graft these catalytic systems onto silica supports⁵ and, more recently, we developed an innovative supporting method to easily immobilize anionic porphyrins onto a commercially available laundry product, called ColorCatcher®. This approach provides a sustainable and convenient strategy for obtaining newly supported porphyrins suitable for various applications across different fields, such as sensing⁶ and catalysis⁷. Within this work, we investigated the catalytic activity of hemin (or hematin)/tetrabutyl ammonium chloride



homogeneous binary systems to promote the cycloaddition reaction of carbon dioxide to aziridines. Then we successfully immobilized hematin onto ColorCatcher® to synthesize a sustainable heterogeneous catalyst. The



so-obtained material was effective in synthesizing several *N*-alkyl and *N*-aryl oxazolidin-2-ones in yields up to 91% and a good regioselectivity, with an A/B ratio as high as 99:1. Here, we present the hematin synthesis, the grafting method employed, the optimization of reaction conditions and the study of the reaction scope.

[1] Zadsirjan, V., Heravi, M. M. *Curr. Org. Synth.* **2018**, 15, 3–20.

[2] Roger, C., Roberts, J. A., Muller, L. *Clin. Pharmacokinet.* **2018**, 57, 559–575.

[3] Carminati, D., Gallo, E., Damiano, C., Caselli, A., Intriery, D. *Eur. J. Inorg. Chem.* **2018**, 5258–5262.

[4] Sonzini, P., Damiano, C., Intriery, D., Manca, G., Gallo, E. *Adv. Synth. Catal.* **2020**, 362, 2961–2969.

[5] Sonzini, P., Berthet, N., Damiano, C., Dufaud, V., Gallo, E. *J. Catal.* **2022**, 414, 143–154.

[6] Caroleo, F., Magna, G., Damiano C., Cavalleri M., Gallo E., Di Natale C., Paolesse R. *Sensors Actuators B Chem.*

2022, 364.

[7] Damiano, C., Cavalleri, M., Di Natale, C., Paolesse, R., Gallo, E. *ChemistryEurope* **2023**, e202300020.

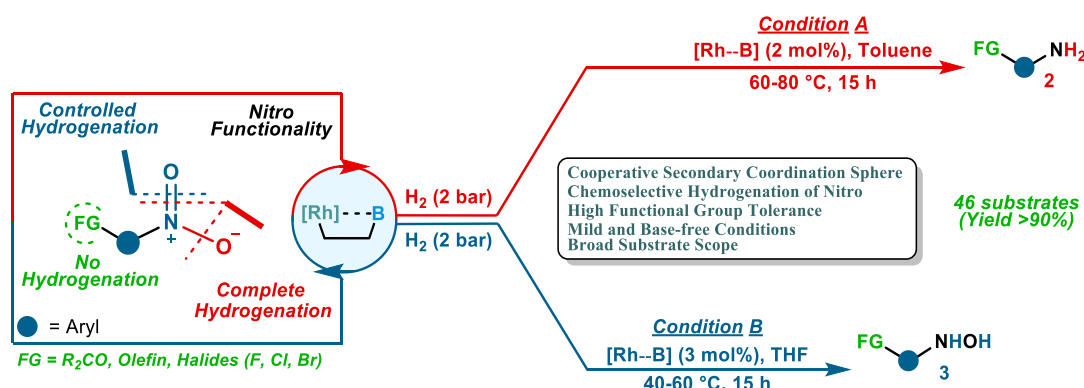
Poster 13

An Adaptive Rhodium Catalyst to Control the Hydrogenation Network of Nitroarenes

V. Chugh,^{a,b} B. Chatterjee,^{a,b} W.C. Chang,^{a,b} H. H. Cramer,^a H. Randel,^{a,b} C. Hindemith,^{a,b}
T. Weyhermüller,^a C. Farès,³ and C. Werlé^{a,b*}

^a Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany. ^b Ruhr University Bochum, Universitätsstr. 150, 44801 Bochum, Germany. ^c Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim/Ruhr, Germany.

Catalysts and catalytic systems are typically used to transform substrates selectively into a single product.¹ Alternatively, one could imagine dynamic catalytic systems that adapt to the reaction conditions—allowing precise control over bond activation processes and catalytic sequences—to yield distinct products.² In this context, the reduction of nitro compounds on the way to fully reduced aniline might lead to other potentially useful platforms, provided selectivity can be controlled.³



Scheme 1: Development of a rhodium-based catalyst system for the chemoselective hydrogenation of nitro functionalities to anilines and N-hydroxyl amines.

Recently, we designed an adaptive rhodium-based catalytic system for the controlled hydrogenation of nitro-containing substrates to anilines and hydroxylamines (**Scheme 1**). The system employs a rhodium(III) center with a Lewis acidic boron arm in the secondary coordination sphere to control the catalytic network.⁴

- [1] Cornils, B.; Herrmann, W. A.; Beller, M.; Paciello, R., *Applied homogeneous catalysis with organometallic compounds a comprehensive handbook in four volumes*. Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim: **2018**.
[2] Cramer, H. H.; Chatterjee, B.; Weyhermüller, T.; Werlé, C.; Leitner, W., Controlling the Product Platform of Carbon Dioxide Reduction: Adaptive Catalytic Hydrosilylation of CO₂ Using a Molecular Cobalt(II) Triazine Complex. *Angew. Chem., Int. Ed.* **2020**, 59 (36), 15674-15681.
[3] Formenti, D.; Ferretti, F.; Scharnagl, F. K.; Beller, M.. Reduction of Nitro Compounds Using 3d-non-noble Metal Catalysts. *Chemical Reviews* **2019**, 119 (4), 2611-2680.
[4] Chugh, V.; Chatterjee, B.; Chang, W. C.; Cramer, H. H.; Hindemith, C.; Randel, H.; Weyhermüller, T.; Farès, C.; Werlé, C., An Adaptive Rhodium Catalyst to Control the Hydrogenation Network of Nitroarenes. *Angew. Chem. Int. Ed.* **2022**, 61 (36), e202205515.

Poster 14

New findings on $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ toward the development of potential electrocatalysts for H_2 production

Alessia Cinci,* Tiziana Funaioli, Gianluca Ciancaleoni, Lorenzo Biancalana, Fabio Marchetti

Department of Chemistry and Industrial Chemistry, University of Pisa, Via G. Moruzzi 13, 56124 Pisa (PI), Italy.

*alessia.cinci@phd.unipi.it

The sustainable generation of molecular hydrogen (H_2) plays a fundamental role in achieving a carbon-neutral economy, and the electrochemical H_2 generation represents an efficient strategy for storing renewable energy.¹ Although platinum remains the benchmark catalyst, its rarity and high cost have driven the search for earth-abundant alternatives.² Nature's $[\text{FeFe}]$ -hydrogenases (Figure 1A), found in anaerobic microorganisms, efficiently catalyze H_2 formation³ and have inspired the development of synthetic mimics.⁴ A promising starting material is $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (**Fp₂**, Cp = $\eta^5\text{-C}_5\text{H}_5$), a commercially available and cost-effective compound. Recently, the **Fp₂**-derived complex $[\text{Fe}_2\text{Cp}_2(\text{CN})(\text{CO})_2(\mu\text{-CNMe}_2)]$ (**FeCN**) has demonstrated catalytic activity for H_2 evolution starting from acetic acid in acetonitrile,⁵ encouraging further screening of related complexes. With a view to air-stable and sufficiently water-soluble catalysts, various cationic complexes bearing a bridging thiocarbonyl ligand have been developed (Figure 1C).⁶ In this work, recent findings on both known and newly synthesized complexes based on the Fe_2Cp_2 core will be discussed in the context of theoretical investigations and spectroelectrochemical studies.

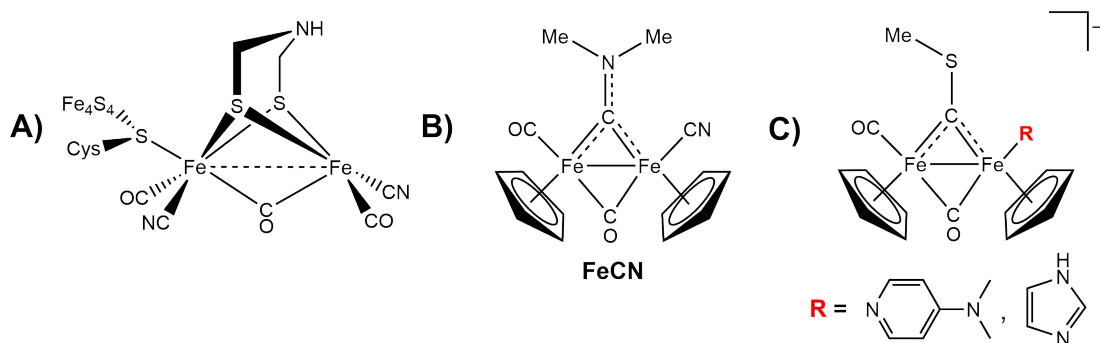


Figure 1: Structures of the active site of $[\text{FeFe}]$ -Hydrogenase (A), diiron aminocarbonyl cyanide complex (B), electrocatalytically-active cationic thiocarbonyl complexes (C).

- [1] X. Li, L. Zhao, J. Yu, X. Liu, X. Zhang, H. Liu, W. Zhou, *Nano-Micro Lett.*, **2020**, *12*, 131.
- [2] V. Sara Thoi, Y. Sun, J. R. Long, C. J. Chang, *Chem. Soc. Rev.*, **2013**, *42*, 2388.
- [3] W. Lubitz, H. Ogata, O. Rüdiger, E. Reijerse, *Chem. Rev.*, **2014**, *114*, 4081.
- [4] J. T. Kleinhaus, F. Wittkamp, S. Yadav, D. Siegmund, U.-P. Apfel, *Chem. Soc. Rev.*, **2021**, *50*, 1668.
- [5] R. Mazzoni, A. Gabiccini, C. Cesari, V. Zanotti, I. Gualandi, D. Tonelli, *Organometallics*, **2015**, *34*, 3228.
- [6] L. Biancalana, I. Gualandi, S. Zacchini, G. Martelli, E. Scavetta, V. Zanotti, R. Mazzoni, F. Marchetti, *Inorg. Chem. Front.*, **2025**, *12*, 1156.

Poster 15

Tri- and Di-Nuclear Palladium Complexes Stabilized by Bridging η^2 -C=N Coordination of Ar-Bian Ligands

Andrea Dariol,^{*a} Francesco Ferretti,^a Fabio Ragaini,^a Piero Macchi^b

^a Università degli Studi di Milano, Dipartimento di Chimica, via C. Golgi 19, 20133, Milano, Italy.

^b Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, V. Mancinelli 7, Milano, Italy.

Ar-BIAN (bis(arylimino)acenaphthene) Schiff bases are well-known ligands for both transition and main group metals due to their rigid structure, which ensures optimal geometry for chelation and enhances compound stability against hydrolysis and central C–C bond cleavage. In the absence of other ligands, the treatment of the $\text{Pd}_2(\text{dba})_3$ with Ar-BIAN type ligands results in the unprecedented isolation of a trinuclear palladium complex which represents the first example of a structurally characterized Pd(0) compound stabilized solely by nitrogen ligands. X-ray crystallography reveals that each palladium atom is coordinated in a standard κ^2 -N,N chelating mode to an Ar-BIAN ligand and in an η^2 coordination to the C=N double bond of a neighboring Ar-BIAN ligand. This unique bonding motif links three Pd(Ar-BIAN) units into a cyclic trimeric structure (Figure1, left).

Additionally, a mixed-valence dinuclear Pd complex was isolated, featuring a $[\text{Pd}(\text{Ar-BIAN})]^0$ fragment bridged to a $[\text{Pd}^{\text{II}}(\text{Ar-BIAN})\text{X}_2]$ unit via a similar η^2 coordination of the iminic bond (Figure1, right).

These findings highlight an unusual mode of palladium stabilization via $\eta^2(\text{C}=\text{N})$ bridging in both trimeric and dinuclear complexes supported exclusively by Ar-BIAN ligands.

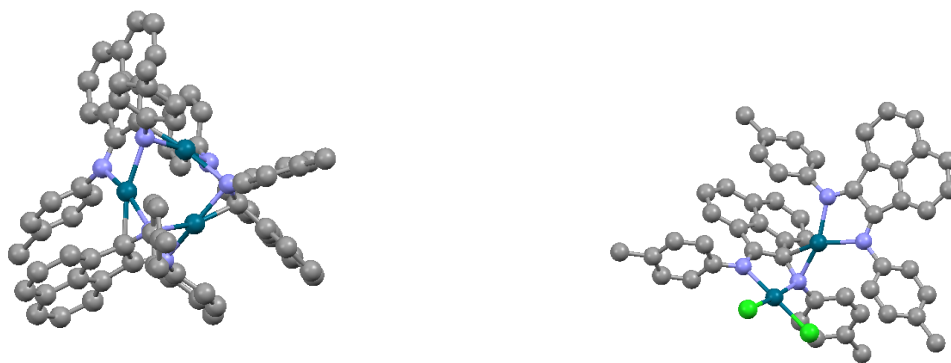


Figure 1: X-ray structure of $[\text{Pd}(\text{Tol-BIAN})]_3$ (left) and $[\text{Pd}(\text{Tol-BIAN})]_2\text{Cl}_2$ (right)

Overall, the trinuclear complex has a propeller shape, with the six aryl rings divided into two inequivalent groups. Other complexes have also been obtained showing unusual structures and their synthesis will be described.

Poster 16

Conjugation of iridium(III) complexes to peptide nucleic acids through solid phase synthesis

Rosa Maria Dell'Acqua,^{a*} Veronica Schifano,^a Maria Vittoria Dozzi,^a Monica Panigati,^a Daniela Maggioni,^a Silvia Cauteruccio^a

^aDipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, I- 20133, Milan, Italy.

*rosa.dellacqua@unimi.it

Peptide nucleic acids (PNAs) are mimics of natural nucleic acids in which the sugar phosphate backbone present in oligonucleotides is replaced by a pseudopeptide backbone formed by *N*-(2-aminoethyl)glycine units, on which nucleobases are attached.¹ PNAs are able to bind complementary DNA or RNA strands with high sequence specificity and affinity. Moreover, the high chemical and enzymatic stability towards nucleases make these systems excellent candidates in molecular biology, diagnostics and as therapeutics. However, unmodified PNAs often exhibit low cell penetration and this feature constitutes one of the most important drawbacks towards their effective use in therapy. One of the strategies to overcome this problem is the conjugation of PNA to metal complexes that can modify their intrinsic physico-chemical and spectroscopic properties.² Currently, our group is working on the development of novel bioorganometallic iridium-PNA conjugates that can be employed as dual activity agents for the synergic treatment of cancer, combining antisense therapy based on PNAs and photodynamic therapy (PDT) related to the use of the Ir(III) complex as the photosensitizer³, which is able to generate cytotoxic singlet oxygen (¹O₂) under appropriate excitation light. This complex is also able to penetrate cell membrane, thus it could act as a carrier for the intracellular delivery of PNAs.

In this communication we will report our studies on the synthesis of the Ir(III)-PNA conjugate (PNA-Ir, **Figure 1**), in which a PNA tetramer containing all the four nucleobases was selected as model PNA sequence. The PNA tetramers PNA-COOH and PNA-NH₂ (**Figure 1**) were synthesized on solid phase using Fmoc/Bhoc strategy and their conjugation to Ir(III) complexes Ir-NH₂ and Ir-COOH (**Figure 1**), respectively, was investigated through a coupling reaction on solid phase to form the amide bond. The acid-promoted cleavage of the oligomer from the resin followed by the reverse-phase HPLC purification allowed us to obtain the required conjugate PNA-Ir, which was characterized by HR-ESI mass spectrometry.

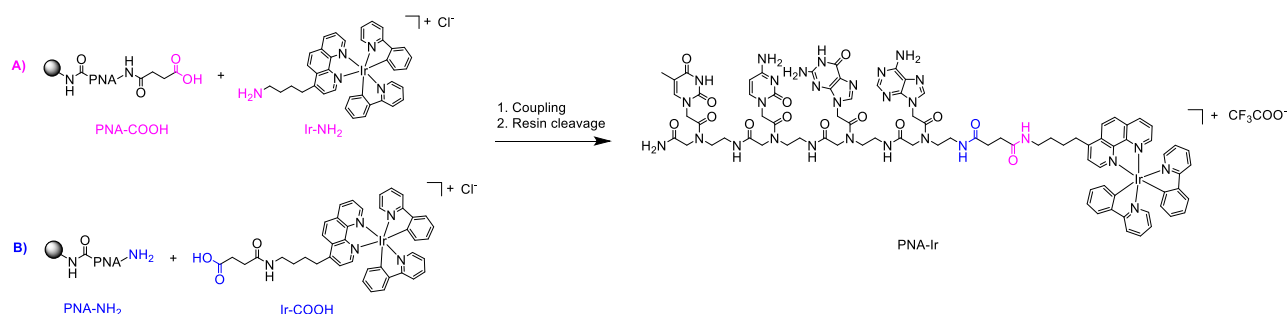


Figure 1: Conjugation of Ir(III) complexes to PNAs.

[1] P. E. Nielsen, M. Egholm, R. H. Berg, O. Buchardt. *Science*, **1991**, 254, 1497–1500.

[2] S. Cauteruccio, M. Panigati, L. Veronese, N. Zaffaroni, M. Folini, E. Licandro, *J. Organomet. Chem.* **2019**, 887, 32–39.

[3] D. Maggioni, M. Galli, L. D'Alfonso, D. Inverso, M. V. Dozzi, L. Sironi, M. Iannacone, M. Collini, P. Ferruti, E. Ranucci, G. D'Alfonso. *Inorg Chem.* **2015**, 54, 544–553.

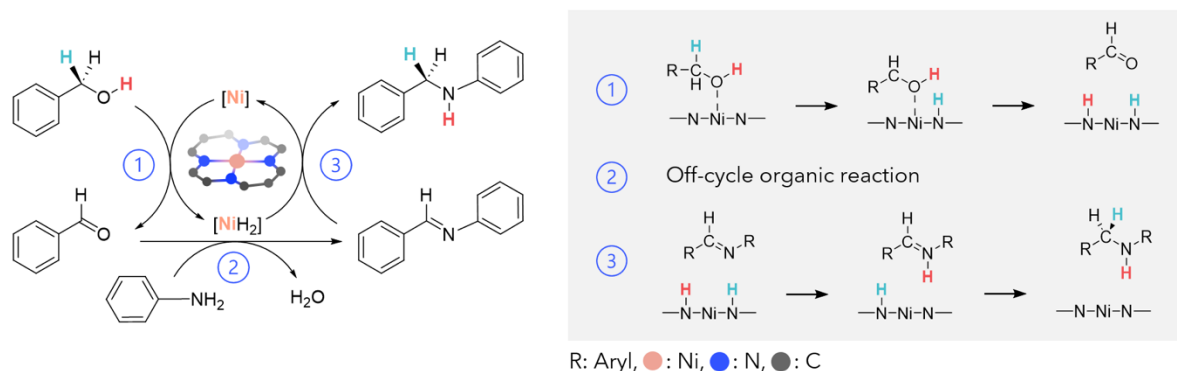
Poster 17

N-doped Graphene-based Nickel(II) Single-Atom Catalyst for Hydrogen Borrowing: a DFT computational study

Aurore Denjean,* Ainara Nova, David Balcells

Department of Chemistry, Hylleraas Centre for Quantum Molecular Sciences University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway

Graphene-based single atoms catalysts (SACs), which are expected to provide robust catalysts with well-defined reactive centers, are primarily used in electrochemistry.^{1,2} Yet, thermal organic reactions like hydrogen borrowing (HB) are highly valuable for numerous synthetic processes. Examples of graphene-based SACs for HB are scarce, with only a few examples reported in the literature. Furthermore, the lack of computational studies has contributed to an insufficient understanding of the reactivity of these systems. To gain more insight into SACs for HB, a first study on a reported nickel N-doped graphene-based material converting aniline and benzyl alcohol into N-benzylaniline has been carried out at the DFT level, using cluster models.³



Our calculations revealed that, unlike typical homogeneous systems, and for all tested models, the H₂ dissociation step results in the formation of two protons, while the remaining electrons are transferred to the surface. The Ni-atom only acts as a spectator, challenging common expectations. Interestingly, the mechanism of the HB reaction is significantly different from that postulated for homogeneous catalysts, involving first the transfer of the carbon's hydrogen to the surface. Finally, our findings highlight the influence of the system charge on the reactivity and feasibility of the reaction. We believe that these results will contribute to the further development of more efficient catalysts.

[1] Wang, A.; Li, J.; Zhang, T. *Nat. Rev. Chem.* **2018**, 2, 65-81.

[2] Zhuo, H. Y.; Zhang, X.; Liang, J. X.; Yu, Q.; Xiao, H.; Li, J. *Chem. Rev.* **2020**, 120, 12315-12341.

[3] Su, H.; Gao, P.; Wang, M. Y.; Zhai, G. Y.; Zhang, J. J.; Zhao, T. J.; Su, J.; Antonietti, M.; Li, X. H.; Chen, J. S. *Angew. Chem.* **2018**, 130, 15414-15418.

Poster 18

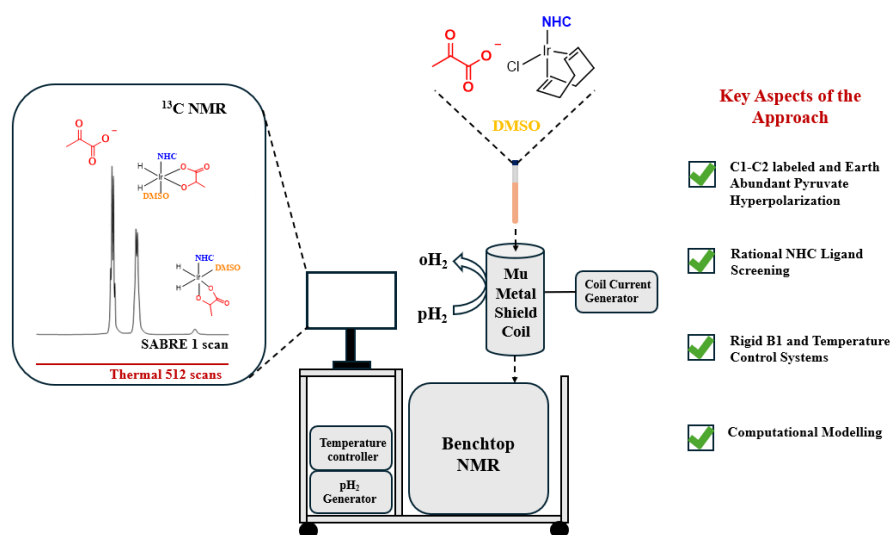
SABRE of [1-¹³C]Pyruvate: Ligand design for better hyperpolarization and catalyst separation

Federico Floreani,^{*a} Salvatore Mamone,^b Ahmed Mohammed Faramawy,^a Lorenzo Franco,^a Marco Ruzzi,^a Cristina Tubaro^a and Gabriele Stevanato^a

^aDipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131, Padova, Italy. ^bDept. MESVA (Life, Health & Environmental Sciences), Università dell'Aquila, Via Vetoio SNC, Località Coppito, 67100, L'Aquila, Italy.

SABRE (Signal Amplification By Reversible Exchange) enhances NMR sensitivity by transferring polarization from parahydrogen to target molecules via their reversible coordination to an iridium catalyst. Among all the candidate molecules, [1-¹³C]pyruvate stands out as a key probe for metabolic imaging, enabling real-time monitoring of cellular metabolism.

We present a systematic investigation of SABRE hyperpolarization of [1-¹³C]pyruvate-_{h3} using a series of Ir–NHC catalysts. In addition to the benchmark IMes ligand,^{1,2} we explore sterically and electronically diverse ligands. Furthermore, we introduce novel fluorinated NHCs bearing mono- and difluorinated alkyl chains, designed to preserve hyperpolarization efficiency while enabling more effective post-polarization catalyst removal. Carbon polarization levels exceeding 3% are achieved using 50% parahydrogen, corresponding to over 10% under full enrichment. Experimental results indicate that polarization efficiency is primarily governed by exchange kinetics rather than spin–spin couplings. This observation is corroborated by a reduced-dimension Liouville-space kinetic model, which accurately reproduces the experimental temperature dependence.



- [1] Tickner, B.J.; Semenova, I. W.; Rayner, P. J.; Whitwood, A.; Duckett, S.B. *Catal. Sci. Technol.*, **2020**, *10*, 1343
 [2] Rayner, P. J.; Gillions, J.P.; Hannibal, V.D.; John, R.O.; Duckett, S.B. *Dalton Trans.*, **2019**, *48*, 15198.

Poster 19

Synthesis of Organobismuth(III) Bis(arylselenolates) from Bismuth(I) Precursors: Toward Luminescent Main-Group Compounds

Raffaele Fontana,* Darius Dumitras, Alexandra M. Pop, Anca Silvestru, Cristian Silvestru

Supramolecular Organic and Organometallic Chemistry Centre, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, 11 Arany Janos Street, RO-400028, Cluj-Napoca, Romania. *raffaele.fontana@ubbcluj.ro

Luminescent compounds, especially phosphorescent ones, are of great interest due to their various applications. Transition metal complexes with strong spin–orbit coupling (SOC), such as those of platinum, iridium, and gold, have shown promising luminescent properties but suffer from high cost and low abundance. Bismuth, by contrast, is earth-abundant, low in toxicity, and possesses the highest SOC among non-radioactive elements, yet its luminescent complexes often display only weak, ligand-centered emission. Starting from this background and from recent studies reporting some phosphorescent organobismuth(III) bis(arylthiolates)¹ we decided to synthesize some novel organobismuth(III) bis(arylselenolates) through the oxidative addition of diselenides to organobismuth(I) species generated *in situ* (Figure 1), and to test their optical properties.

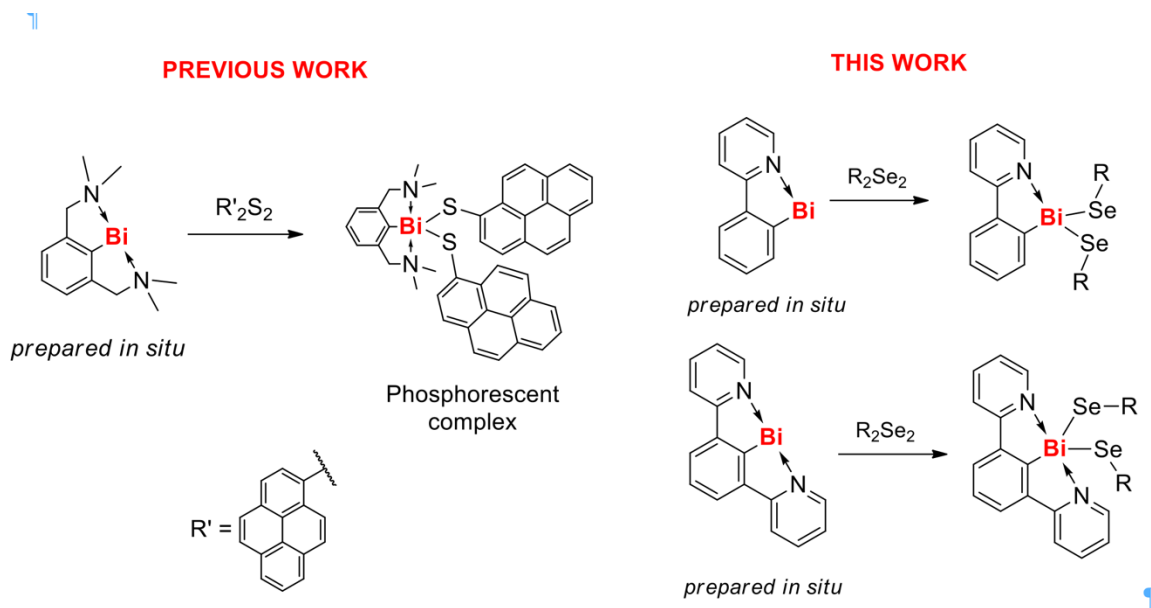


Figure 1

[1] Geppert M.; Jellinek K.; Linseis M.; Bodensteiner M.; Geppert J.; Unterlass M. M.; Winter R. F.; *Inorg. Chem.* **2024**, 63, 14876–14888.

Poster 20

Polymerization of 1-vinylcyclohexene (VCH) and (*S*)-4-isopropenyl-1-vinyl-1-cyclohexene (IVC) and its copolymerization with linear terpenes mediated by titanium complexes with [OSSO]-type ligands

Mariarosaria C. Gambardella,^{a,b*} Ilaria Grimaldi,^a Assunta D'Amato,^a Antonio Buonerba,^a Raffaele Marzocchi,^c Finizia Auriemma,^c Carmine Capacchione^a

^a University of Salerno, Department of Chemistry and Biology "A. Zambelli", Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy. ^b University of Perugia, Department of Chemistry, Biology and Biotechnology, Via Elce di Sotto 8, 06123, Perugia, Italy. ^c University of Naples Federico II, Department of Chemical Sciences, Via Cintia, 80126, Naples, Italy. *mgambardella@unisa.it

The production of plastics from renewable resources to reduce reliance on fossil fuels is particularly appealing.¹ Among natural substances, terpenes include a wide family of compounds characterized by a common isoprenoid unit, and their structural variety contributes to their potential as monomers.² This study investigates the versatility of two titanium complexes with [OSSO]-type ligands (catalysts **1-2**), activated by methylalumoxane (MAO), in the polymerization of the 1-vinylcyclohexene (VCH), chosen as a model monomer. Complex **2**, characterized by cumyl substituents, provided a regio- and stereo-regular homopolymer. Furthermore, the stereoselective polymerization was extended to the (*S*)-4-isopropenyl-1-vinyl-1-cyclohexene (IVC),³ a bio-based monomer synthesized from the perillaldehyde,⁴ that differs from the VCH only for the presence of an additional isopropenyl group. Finally, the copolymerization of IVC with two linear terpenes, β -myrcene and β -ocimene, was accomplished, obtaining notable copolymers from sustainable sources.

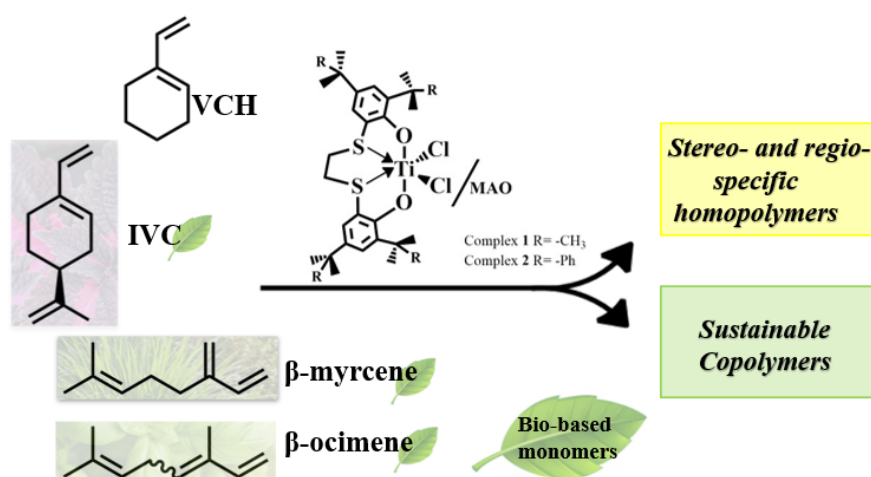


Figure 1. (Co)polymerization of conjugated dienes promoted by [OSSO]-type catalysts.

[1] Zhu, Y.; Romain, C.; Williams, C.K. *Nature* **2016**, 540, 354.

[2] Mosquera, M. E. G.; Jiménez, G.; Tabernero, V.; Vinuesa-Vaca, J.; García-Estrada, C.; Kosalková, K.; Sola-Landa, A.; Monje, B.; Acosta, C.; Alonso, R.; Valera, M. *Sustain. Chem.* **2021**, 2, 467.

[3] Grimaldi, I.; D'Amato, A.; Gambardella, M.C.; Buonerba, A.; Marzocchi, R.; Auriemma, F.; Capacchione, C. *Macromol. Rapid Commun.*, **2025**, 46, 2400834.

[4] Liu, H.; You, F.; Shi, W.; Hu, X.; So, Y.; Shi, X. *Polym. Chem.*, **2023**, 14, 447.

Poster 21

Bifunctional nickel-photoredox catalysts for C-O cross coupling reactions

Iacopo Gamberoni,^{a*} Andres M. Hidalgo-Núñez,^a Daniele Lavelli,^a Alberto Dal Corso,^a
Luca Pignataro^a

^a Università degli Studi di Milano, Via Festa del Perdono 7, Milano, Italy

*iacopo.gamberoni@unimi.it

Our research group recently reported a bifunctional approach to Ni-photoredox catalytic C-O cross-coupling. Connecting a donor-acceptor cyanoarene photocatalyst to a bipyridine ligand leads to photocatalysts **1a-b** (Figure 1), featuring an improved catalytic activity compared to the corresponding dual systems, as a crucial step of the catalytic cycle is turned from intermolecular to intramolecular.^[1]

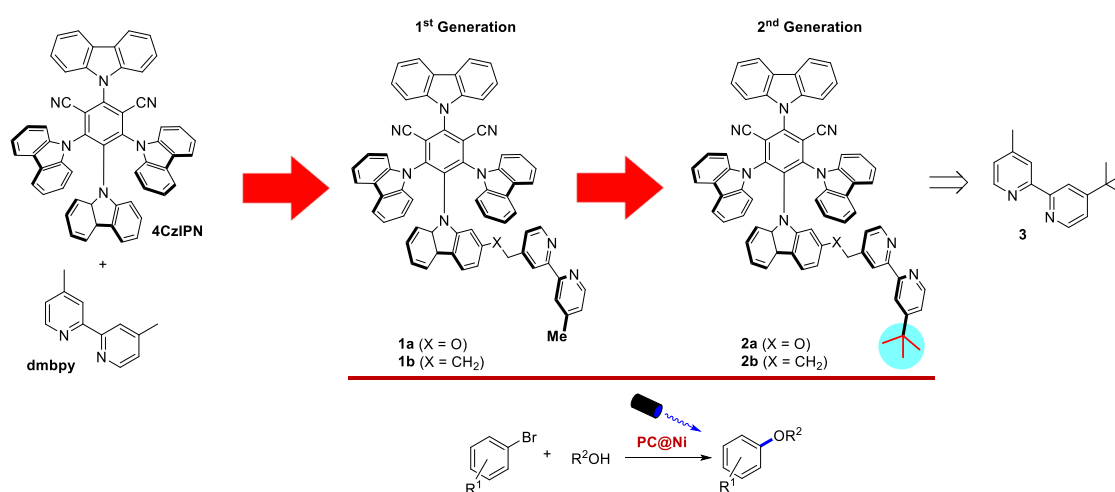


Figure 1. First- and second-generation bifunctional photocatalysts for C-O cross-coupling reactions.

In the dual catalytic system, 4,4'-bis-*tert*-butyl bipyridine is the ligand giving the best results (in combination with 4CzIPN), and for this reason we decided to introduce a *tert*-butyl substituent on the bipy moiety of our bifunctional system, expecting a beneficial effect on catalytic activity. The synthesis of the 2nd generation bifunctional photocatalysts **2a-b** involved 4-*tert*-butyl-4'-methyl-2,2'-bipyridine (**3**) as key intermediate – a previously unreported compound whose preparation turned out to be challenging. Several attempts to forge the pyridine-pyridine bond by cross-coupling were made, but bipyridine **3** was obtained in very low yield at best. For this reason, we opted for a different approach consisting in the construction of one of the pyridine ring according to the methodology reported by Ciufolini and co-workers.^[2] Preliminary tests in Ni-photoredox C-O cross-coupling at low catalyst loading confirm that the second-generation systems **2a-b** display the expected improvement in terms of activity.

[1] L. Dolcini, A. Solida, D. Lavelli, A. M. Hidalgo-Núñez, T. Gandini, M. Fornara, A. Colella, A. Bossi, M. Penconi, D. Fiorito, C. Gennari, A. Dal Corso, L. Pignataro, *ACS Catal.* **2024**, *14*, 18651

[2] a) M. A. Ciufolini, F. Roschangar, *Tetrahedron* **1997**, *53*, 11049; b) J. G. Cordaro, J. K. McCusker, R. G. Bergman, *Chem. Comm.* **2002**, *2*, 1496.

Poster 22

Combined Spectroscopic Approach for Studying Protein Recognition by *trans*-Pd(II)-based Complexes

Claudia Ghelarducci,^{a*} Ester Giorgi,^a Francesca Binacchi,^a Michele Mannelli,^b Andrea Cesari,^a
Tania Gamberi,^b Chiara Gabbiani,^a Alessandro Pratesi^a

^a Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, 56124 Pisa, Italy.

^b Department of Experimental and Clinical Biomedical Sciences, Viale G.B. Morgagni 50, 50134 Firenze, Italy.

*claudia.ghelarducci@phd.unipi.it

Despite their widespread clinical use, Pt(II)-based anticancer drugs suffer from several limitations, including severe side effects, resistance phenomena, and the need for intravenous administration.¹ A promising strategy to overcome these drawbacks involves the development of metal-based complexes incorporating alternatives to platinum. In this context, Pd(II) compounds have gained increasing attention as potential anticancer agents due to their structural similarity to Pt(II) analogues and improved water solubility.² Although the mechanisms underlying their biological activity are not yet fully elucidated, several *trans*-Pd(II) complexes have demonstrated cytotoxicity comparable to or exceeding that of cisplatin against various cancer cell lines.³ However, their higher kinetic lability and reduced thermodynamic stability often result in rapid ligand exchange reactions, potentially hindering effective cellular targeting.⁴ To tackle this challenge, we established a reproducible methodology to investigate square-planar *trans*-Pd(II) complexes, aiming to lay the groundwork for broader mechanistic studies of metal-based therapeutics.⁵ A series of compounds with the general formula *trans*-PdL₂X₂ (where L = pyridine or piperidine, X = Cl, Br, I) was synthesized and characterized (Figure 1). This rational combination of monodentate labile and spectator ligands was designed to enhance the stability of the final molecules during circulation inside the body. The interactions of these complexes with model proteins were explored by a combined UV-Vis/NMR approach, and the *in vitro* activity was evaluated against selected cancer cell lines.

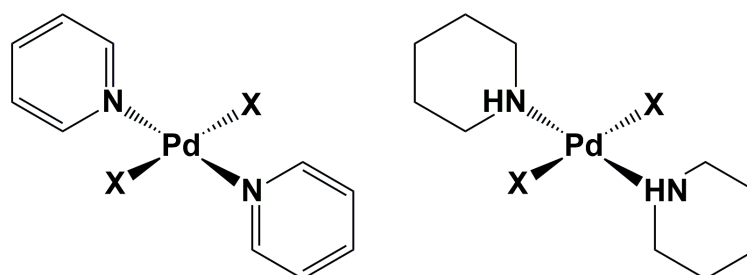


Figure 1

- [1] Marotta, C.; Gabbiani, C.; Pratesi, A. *Inorg. Chim. Acta*, **2023**, 548, 121388.
- [2] Coskun, M. D.; Yilmaz, V. T.; Ulukaya, E. *Bioorg. Med. Chem.*, **2013**, 21, 4698-4705.
- [3] Abu-Surrah, A. S.; Qaroush, A. K.; Abu-Mahtheieh, A. M. *Eur. J. Med. Chem.*, **2010**, 45, 471-475.
- [4] Scattolin, T.; Visentin, F.; Nolan, S. P. *Cell. Rep. Phys. Sci.*, **2021**, 2, 100446.
- [5] Giorgi, E.; Pratesi, A.; Gabbiani, C. *Inorg. Chim. Acta*, **2025**, 581, 122645.

Poster 23

Pendant-base complexes for CO₂ hydrogenation to CH₃OH

Giorgia Gherardini,^{a*} Bas de Bruin^a, Joost N.H. Reek^a

^a University of Amsterdam, Van't Hoff Institute for Molecular Sciences, Homogeneous, Supramolecular and Bio-Inspired Catalysis. * g.gherardini@uva.nl

The hydrogenation of CO₂ and CO₂-derivatives using a homogeneous, molecularly defined catalyst has been widely explored in recent years, but most examples are limited to low TONs, which limit their applicability compared to heterogeneous catalysts for the same reaction. This is mostly due to slow steps in the catalysis, one of the most relevant being the H₂ splitting. In this project, this slow step is tackled using metal-ligand cooperation. [Cp*Ir(bipy)] complexes have been widely studied for CO₂ or formic acid hydrogenation and they present advantageous easy synthesis and air-stability. In this project, these catalysts are further optimized by synthesizing Ir- and Co-based homogeneous catalysts bearing a pendant base in the ligand backbone were synthesized, using the commercially available and air-stable terpyridine ligand, but affording a dynamic bidentate coordination. The dynamicity of the coordination allows for a proton shuttle behavior that can aid H-H splitting by metal-ligand cooperation, which allows for facile hydride formation and therefore a faster catalytic cycle. These catalysts also show pH-responsive activity and present unprecedented selectivity towards methanol and formic acid formation.

- [1] Himeda, Y. (2021). *J. Am. Chem. Soc.*, 143(3), 1570-1576.
- [2] Himeda, Y. & Fujita, E. (2013). *Inorganic Chemistry*, 52(21), 12576-12586.
- [3] He, P. (2023), *Inorg. Chem.*, 62(28), 11225-11232.

Poster 24

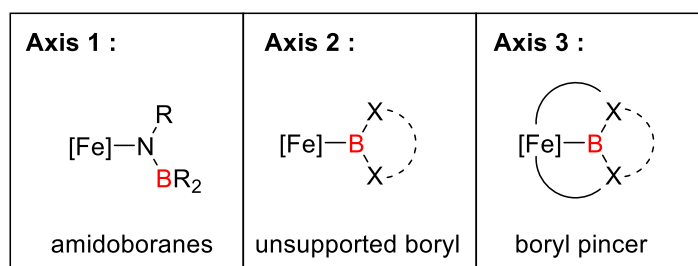
Synthesis and reactivity of low valent open-shell Iron complexes with Boron-containing ligands

Caroline Goncalves,^{a*} Sébastien Bontemps,^a

^a LCC-CNRS, Université de Toulouse, 205 route de Narbonne, 31077 Toulouse cedex 4, France.
caroline.goncalves@lcc-toulouse.fr

Transition metal complexes are of interest due to the wide range of properties and multiple possibilities for structural modifications. However, low-valence and/or low-coordination open-shell complexes are rare and not well studied. This is largely due to the difficulty of characterizing these species which are poorly stabilized by the ligand sphere and which exhibit paramagnetic properties. Nonetheless, these particular properties are of great interest. Firstly, low-valence complexes are often transient during catalytic reactions and therefore play a key role in activation processes. Moreover, open-shell structures are fundamental for 1e-transformations, such as those observed in enzymatic reactions.

Recent discoveries related to the use of complexes featuring boron-containing ligands have demonstrated the specific properties of the boron element, compared to functionalities more conventionally employed in coordination chemistry. This coordination chemistry has so far focused on shell-closed transition metal complexes.^[1–3] We believe that the field of borated ligands is now ready to take on new challenges. As such, the combination of a low valence iron complex with a high electron density with a Lewis acid boron fragment to be able to finely modulate the electronic structure and the reactivity of the targeted complexes is particularly attractive. We present here our approach and our advances on iron complexes featuring three types of boron containing ligands.



- [1] G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, 98, 2685–2722.
 [2] D. L. Kays, S. Aldridge, in *Contemporary Metal Boron Chemistry I: Borylenes, Boryls, Borane σ-Complexes, and Borohydrides* (Eds.: T.B. Marder, Z. Lin), Springer, Berlin, Heidelberg, **2008**, pp. 29–122.
 [3] H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, 110, 3924–3957.

Poster 25

Ligand improvement for the preparation of [Zinc(II)(Pyridine-Containing Ligand)] complexes as efficient catalyst for the cycloaddition of CO₂ to epoxides

Simone Grosso,^a Paolo Razzetti,^a Matteo Alberti,^a Djihed Boucherabine,^a Alessandro Caselli*^a

^a Department of Chemistry Università degli Studi di Milano, Via Golgi 19, 20133 Milano (MI), Italy.
alessandro.caselli@unimi.it

Carbon dioxide is the principal greenhouse gas, largely recognized as responsible for global warming and related climate changes. Driven by the inherent synthetic potential of CO₂ as an abundant, inexpensive and renewable C1 source, the recent years have witnessed renewed interest in devising catalytic CO₂ fixations into organic matter.¹ For decades chemists have been challenged to design novel technologies for converting CO₂ into fine chemicals.² Based on our ongoing research interests devoted to the development of innovative catalysts that align with green chemistry principles,³ we became interested to investigate a too little explored area of homogeneous catalysis: the use of zinc(II) polyazamacrocyclic complexes for the cycloaddition of CO₂ to epoxides.

Herein, we describe the development of a novel approach for the synthesis of cyclic carbonates using carbon dioxide and epoxides employing as catalyst zinc(II) complexes of pyridine containing macrocyclic ligands (Figure 1). Remarkably, the catalytic activity of the catalyst has been improved through a structural modification of its ligand which has allowed full conversions of terminal epoxides to cyclic carbonates under solvent-free and mild reaction conditions. The development of this process and its scope and limitations will be discussed.

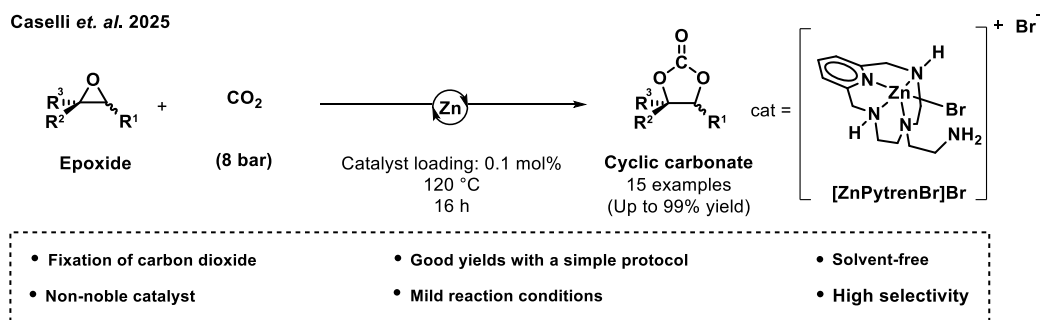


Figure 1

We thank the CARIPLO Foundation: project 2022-0781 “CO₂ Valorization by A Low Economic impact biorefinery, CO₂VALE”, for financial support.

- [1] Tortajada, A.; Juliá-Hernández, F.; Börjesson, M.; Moragas, T.; Martin, R. *Angew. Chem. Int. Ed.* **2018**, *57*, 15948.
 [2] Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 5933.
 [3] a) Tseberlidis, G.; Intrieri, D.; Caselli, A. *Eur. J. Inorg. Chem.* **2017**, *30*, 3589. b) Cavalleri, M.; Panza, N.; Di Biase, A.; Tseberlidis, G.; Rizzato, S.; Abbiati, G.; Caselli, A. *Eur. J. Org. Chem.* **2021**, *19*, 2764. c) Panza, N.; Tseberlidis, G.; Caselli, A.; Vicente, R. *Dalton Trans.* **2022**, *51*, 10635.

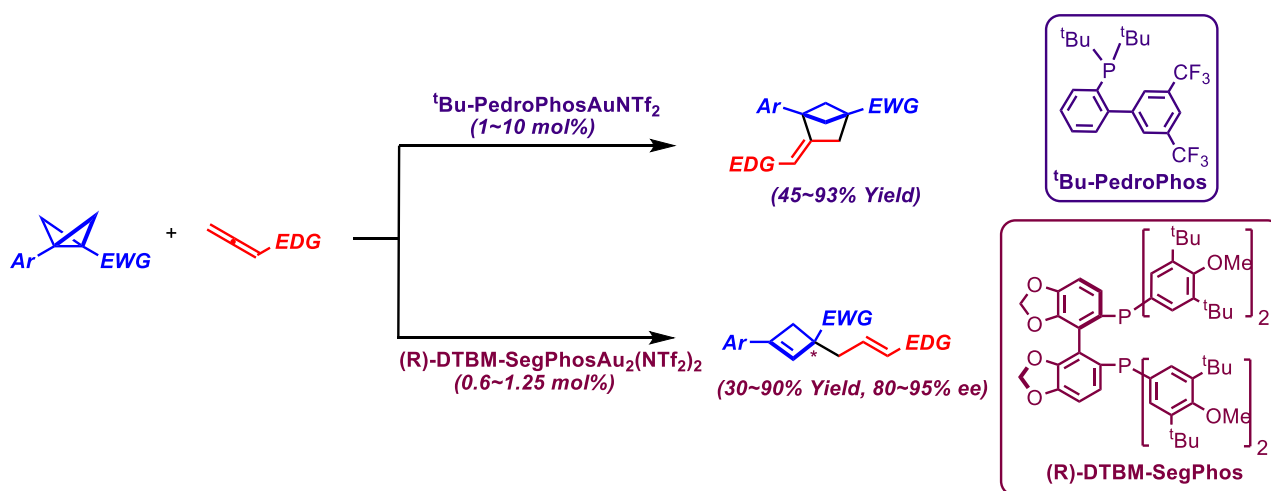
Poster 26

[Au(I)]-Catalyzed Functionalization of Bicyclo[1.1.0]butanes with Allenes

Yuhao Huang,^{a,b,*} Giulio Bertuzzi,^{a,b} Marco Bandini,^{a,b}

^a Dipartimento di Chimica “Giacomo Ciamician”, Alma Mater Studiorum – Università di Bologna, Via P. Gobetti 85, 40129 Bologna, Italy. ^b Center for Chemical Catalysis – C³ Alma Mater Studiorum – Università di Bologna, via P. Gobetti 85, 40129 Bologna, Italy.
*yuhao.huang3@unibo.it.

Bicyclo[1.1.0]butanes (BCBs) have recently attracted particular attention, due to their unique reactivity of the strained bridgehead C α -C γ bond from the 'butterfly' like double cyclopropane ring structures.¹ In continuation to our interest in homogenous Au(I) catalysis,² we developed a novel dual catalytic strategy for the electrophilic activation BCB species. In particular, the use of [Au(PedroPhos)NTf₂] enable to unlock an unprecedented [2 σ +2 π]-cycloaddition with electron-rich allenes. Here, a large series of bicyclo[2.1.1]hexanes was generated in high yield with excellent regio- and stereoselectivity.³ Furthermore, when the chiral gold complex [((R)-DTBM-SegPhos)Au₂(NTf₂)₂] was utilized, the cycloaddition process was interrupted in favor of a second proto-elimination step, to lead chiral 1,3-disubstituted cyclobutanes. Here high enantiomeric excesses were also gained in the final compounds.⁴



Scheme 1

[1] M. Golfmann, J. C. L. Walker, *Commun Chem*, **2023**, 6, doi.org/10.1038/s42004-022-00811-3

[2] R. Pedrazzani, S. Kiriakidi, M. Monari, I. Lazzarini, G. Bertuzzi, C. Silva López, M. Bandini, *ACS Catal.* **2024**, 14, 6128.

[3] R. Giovanelli, G. Gallorini, H. Huang, A. Brunetti, K.D. Nikopoulos, M. Monari, C. Silva López, S. Kiriakidi, G. Bertuzzi, M. Bandini, *submitted*.

[4] H. Huang, C. Silva López, S. Kiriakidi, G. Bertuzzi, M. Bandini, *unpublished*.

Poster 27

Iron-mesoionic carbene complexes for catalytic intramolecular C-H amination: novel ligand synthesis

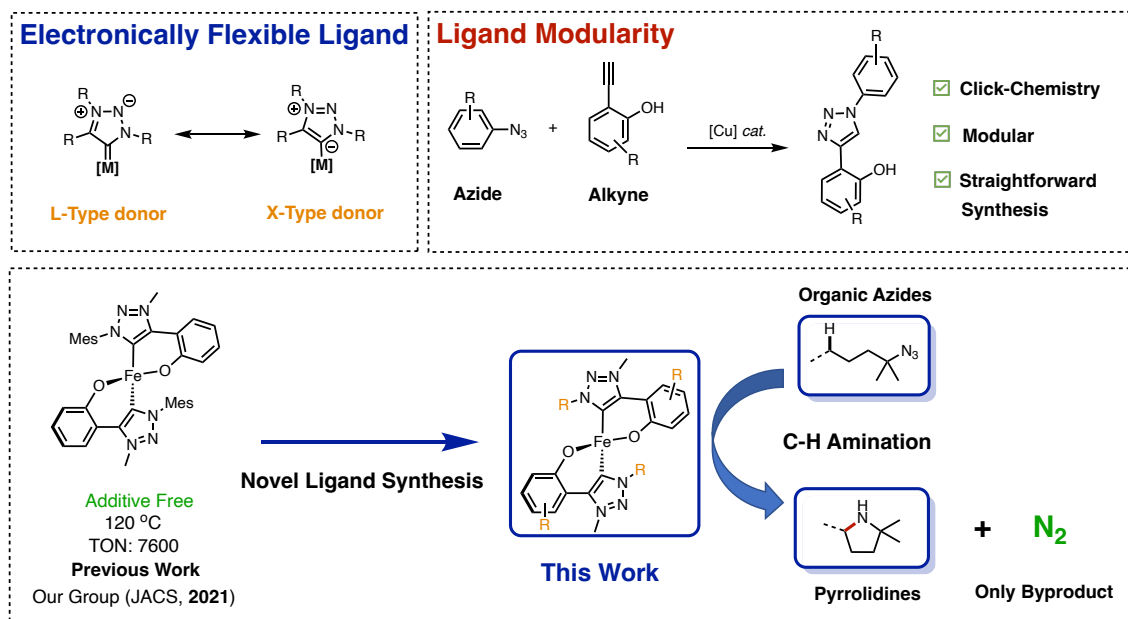
Luke Alexander Hudson,^a Wowa Stroek,^a Martin Albrecht^{*a}

^aDepartment of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, CH-3012 Bern (Switzerland)

*luke.hudson@unibe.ch

Nitrogen containing heterocycles are ubiquitous across nature and industry with C-N bonds being found in numerous natural products and pharmaceutically relevant molecules.^{1,2} Therefore carbon-nitrogen bond formation is of utmost importance with catalytic and atom economical syntheses being particularly attractive. In this context, Betley in 2013 reported iron-catalysed direct C-H bond amination using an iron-dipyrrinato catalyst to yield a range of pyrrolidines.³ However, the activity was limited to only single digit TONs requiring 20 mol% catalyst loading and an equivalent of Boc₂O to prevent product inhibition. More recently, Betley also reported the additive-free C-H amination of nickel-dipyrrin complexes.⁴ In 2021, our group disclosed a highly efficient iron(II) mesoionic carbene complex, which afforded a range of C-H aminated pyrrolidine products in excellent yield with no need of additives, generating only N₂ as the sole side product with TONs exceeding the state of the art by an order of magnitude.⁵

Herein, we aim to better understand the influence of the ligand and to improve the catalytic performance of the iron complex by designing and synthesising novel ligands. Our data shows that appropriate ligand substitution enhances both the activity and selectivity of C-H amination.



[1] R. Hili and A. K. Yudin, *Nat Chem Biol*, 2006, **2**, 284–287.

[2] E. Vitaku, D. T. Smith and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 10257–10274.

[3] Betley, Hennessy, *Science*, 2013, **340**, 591–595.

[4] Y. Dong, R. M. Clarke, G. J. Porter and T. A. Betley, *J. Am. Chem. Soc.*, 2020, **142**, 10996–11005.

[5] W. Stroek, M. Keilwerth, D. M. Pividori, K. Meyer and M. Albrecht, *J. Am. Chem. Soc.*, 2021, **143**, 20157–20165.

Poster 28

Valorization of Ambient Pressure CO₂ via Sustainable Catalytic Strategies

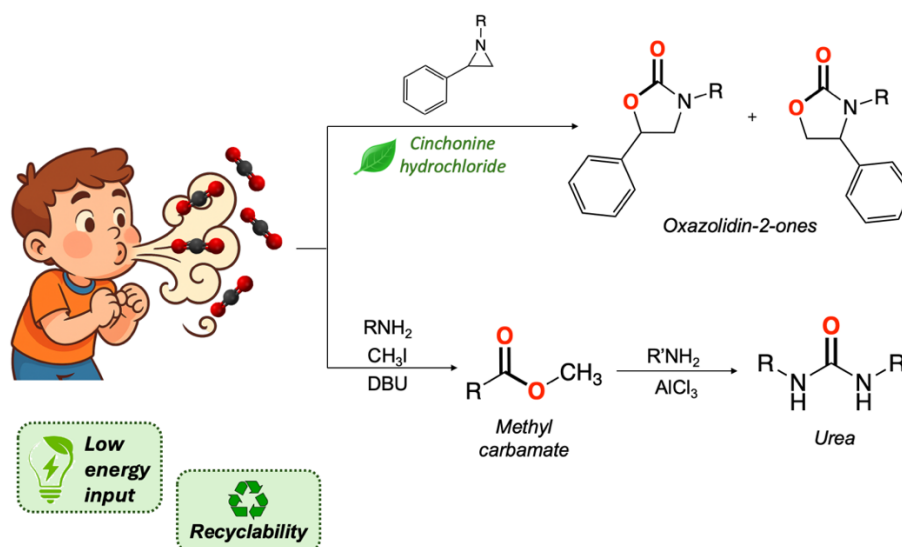
Lucia Invernizzi,* Shabana Thaseen Yusuff Sheriff, Caterina Damiano, Emma Gallo

Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milano (MI), Italy.

*lucia.invernizzi@unimi.it

As one of the most abundant greenhouse gases, carbon dioxide (CO₂) poses a major environmental challenge but also offers a unique opportunity. Its direct conversion into valuable products offers a sustainable route to emission reduction and a circular carbon economy. CO₂ valorization can proceed through both non-reductive and reductive pathways. In both cases, truly sustainable processes require careful control of reaction conditions, since the need for high CO₂ pressures impacts energy consumption and overall costs.

In this work, we present two catalytic systems for the non-reductive valorization of CO₂ at ambient pressure. First, the biocompatible cinchonine hydrochloride was found to be able to catalyze the cycloaddition of CO₂ to aziridines, enabling the 100% atom-economical synthesis of oxazolidin-2-ones, key pharmaceutical intermediates and organic synthons.¹ The excellent regioselectivity and catalyst stability enhanced the high synthetic value of this approach.² On the other side, we developed a mild, two step protocol for the synthesis of organic ureas using ambient pressure CO₂. Initially, the reaction of this gas with amines and CH₃I in the presence of DBU (1,8-diazabicyclo(5.4.0)undec-7-ene) allowed the formation of methyl carbamates.³ Subsequently, these carbamates reacted with a second amine molecule in the presence of AlCl₃ to yield the desired ureas. Optimization of both steps led to a process characterized by direct CO₂ fixation, low energy input and amine recoverability, offering a green and practical route to valuable ureas from waste CO₂. Together, these methodologies demonstrate the potential of ambient pressure CO₂ valorization as a viable and sustainable strategy for the synthesis of fine chemicals.



[1] Damiano, C.; Cavalleri, M.; Invernizzi, L.; Gallo, E. *Eur. J. Org. Chem.* **2024**, 27, e202400616.

[2] Invernizzi, L.; Damiano, C.; Gallo, E. *Chem. Eur. J.* **2025**, 31, e202500473.

[3] Mora Vargas, J.A.; Burtoloso, A.C.B. *ChemSusChem*. **2023**, 16, e202300936.

Poster 29

Towards Novel Radiopharmaceuticals: Synthesis and Characterization of Rhenium(I) Complexes with Bis(N-heterocyclic carbene) Ligands

Davide Lucchini,^{a*} Nicola Salvarese,^b Cristina Bolzati^b, Alessandro Dolmella,^c Marco Baron^a

^a Dipartimento di scienze chimiche, Università degli Studi di Padova, Via F. Marzolo 1, 35131 Padova (PD), Italy.

^b Istituto di chimica della materia condensata e di tecnologie per l'energia ICMATE-CNR, Corso Stati Uniti 4, 35127 Padova (PD), Italy. ^c Dipartimento di scienze del farmaco, Università degli Studi di Padova, Via F. Marzolo 5, 35131 Padova (PD), Italy.

*davide.lucchini@phd.unipd.it

Technetium-99m, with its ideal physicochemical properties and availability, is the most used radionuclide in SPECT imaging, while rhenium-188 has emerged as an attractive candidate for endoradiotherapy.¹ The biodistributive equivalence of stable technetium and rhenium complexes with identical coordination spheres underscores the importance of studying their coordination chemistry to develop matching theranostic pairs for diagnosis and therapy.

N-heterocyclic carbenes (NHCs), known for their strong σ -donor properties, form robust bonds with various metal ions and have been extensively studied in catalysis, luminescence, and pharmaceutical chemistry. However, the chemistry of Tc and Re with NHCs has been primarily explored in oxidation state I, with limited studies in states III and V.²⁻⁴

This work presents the synthesis and the crystal structures of novel Re(I) complexes with chelating bis(NHCs) ligands. By varying the bis(NHC) ligand the formation of different *exo* and *endo* isomers was observed (fig. 1). We are currently investigating the factors influencing the formation of these isomers also via DFT calculations. These studies not only elucidate the structural diversity of these complexes, but also offer valuable information for the rational design of new radiopharmaceuticals.

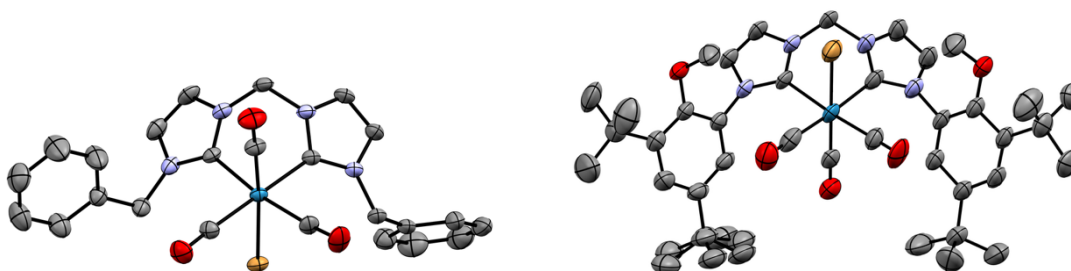


Figure 1

[1] Lewis S. L., Windhorst A. D., Zeglis B. M. (Ed.s) *Radiopharmaceutical Chemistry*; Springer Nature Switzerland: Cham (Switzerland), 2019, pp. 311-333, 439.

[2] Hock, S. J.; Schaper, L.-A.; Herrmann, W. A.; Kühn, F. E. *Chem. Soc. Rev.* **2013**, 42 (12), 5073.

[3] Hille, C.; Kühn, F. E. *Dalton Trans.* **2016**, 45 (1), 15.

[4] Friães, S.; Realista, S.; Mourão, H.; Royo, B. *Eur. J. Inorg. Chem.* **2022**, 2022 (10), e202100884.

Poster 30

Coordination compounds with substituted azoles displaying unexpected photophysical properties

Lorenzo Luciani,^a Gabriele Manca,^b Andrea Ienco,^c Rossana Galassi^a

^a School of Science and Technology, Chemistry Division, University of Camerino, Via Madonna delle Carceri, 62032, Camerino, Italy. ^b CNR-ICCOM, Sede di Bari, via Orabona 4, 70126 Bari, Italy. ^c CNR-ICCOM, Sede di Firenze, via Madonna del Piano 10, 50019 Sesto Fiorentino (Firenze) Italy

Azoles are a class of ligands that can stabilize a wide variety of transition metals, including those of group 11th. Among them, imidazolyl NHC carbenes or pyrazoles are particularly prominent because their stereo-electronic properties can be easily modulated by modifying the azoles' ring with diversely functionalized organic groups.¹ For example, carbazole scaffolds are widely known for their optoelectronic features, mostly consisting of high triplet energies and hole-transporting capabilities.² These properties make them suitable chromophores in the design of host materials for organic light-emitting diodes (OLEDs).² For this reason, the functionalization of azoles with carbazole moieties represents a reasonable strategy to obtain efficient blue-emitting materials based on coordination compounds. Noteworthy, even if the emission behavior seems to be dominated by IL transitions attributed to the carbazole scaffold, their incorporation in NHC ligands, furtherly coordinated to gold(I), affects their intrinsic emissive properties, by blue-shifting the emission band positions³ and/or by enhancing the emission quantum yields compared to the bare carbazole scaffold.⁴ In this communication, we present the photophysical characterization of a series of coordination compounds obtained with azoles functionalized with photoactive substituents. For example, mono and bis(NHC carbazole)gold(I)halide-based complexes have been investigated; the mono NHC gold(I) carbene complex, *1-(1,4-phenylene-1yl)-4-carbazolyl-9yl)-3-benzyl-2-imidazolyl-2yl-gold(I)chloride* shifts the blue emission of the ligand toward the violet canceling the green components upon irradiation at 360 nm, while there is no evidence of the typical ³MC phosphorescence.⁵

[1] Visbal, R.; Gimeno, M. C., *Chem. Soc. Rev.*, **2014**, 43, 3551.

[2] Kim, S. M.; Byeon, S. Y.; Hwang, S.H.; Lee, J. Y., *Chem. Commun.*, **2015**, 51, 10672-10675

[3] Dinda, J.; Adhikary, S. D.; Seth, S. K.; Mahapatra, A., *New J. Chem.*, **2013**, 37, 431-438.

[4] Yam, V. W. W.; Lee, J. K. W.; Ko, C. C.; Zhu, N., *J. Am. Chem. Soc.* **2009**, 131, 3, 912-913.

[5] Zhou Lu, Z.; Luciani, L.; Li, S.; Nesterov, V. N.; Zuccaccia, C.; Macchioni, A.; Fripp, J. L.; Zhang, W.; Omary, M.A.; Galassi, R., *Chem. Eur. J.*, **2024**, 30, 51, 1-11.

Poster 31

Cytotoxic gold(I)-NHC complexes with potential targeted anticancer activity

Ester Giorgi,^{a*} Tania Gamberi,^b Chiara Gabbiani,^a Alessandro Pratesi^a

^a Department of Chemistry and Industrial Chemistry, Via G. Moruzzi 13, 56124 Pisa (PI), Italy

^b Department of Experimental and Clinical Sciences "Mario Serio", Via Morgagni 50, 50134 Florence (FI), Italy

ester.giorgi@phd.unipi.it

Although the mechanism of action for which gold-based compounds cause cellular apoptosis in cancer cells has not been completely clarified yet, is commonly accepted that the inhibition of thioredoxin reductase (TrxR) plays a pivotal role.[1] The mitochondria-mediated apoptosis induction presents several advantages, including the potential overcoming of resistance that often occurs after treatment with conventional Pt-based drugs. In this project, we report the synthesis, characterization, and cytotoxicity studies of eight new gold(I) complexes. Two new NHC-based gold(I) complexes bearing a fluorescent probe were initially synthesized, characterized and furthermore conjugated to three selected molecules able to target ovarian cancer cells according to different targeting strategies. Two gold(I) complexes were firstly conjugated with 2,3,4,6-tetra-O-acetyl-1-thio- β -D-glucopyranose, a biomimetic glucose substrate, potentially able to increase the metal-complex uptake in tumour cells by exploiting the overexpressed GLUT-mediated transport (Warburg effect).[2] Biological tests on A2780 ovarian cancer cell lines showed a significant enhancement in the cytotoxicity of the complexes when conjugation with 1-thio- β -D-glucose tetraacetate is present. Cellular localization experiments by confocal microscopy confirmed the latter results. Subsequently, the same gold(I) complexes were conjugated with two targeting peptides: C- β Ala-RGD, which targets the overexpressed integrin receptors on the A2780 cell line, and CrFrFrF, a mitochondria-targeting peptide which allows the drug to accumulate in this organelle, where TrxR is mainly present. In this contribution, the cytotoxic activity promoted by the conjugates will be discussed, comparing the results obtained through the three different targeting strategies.

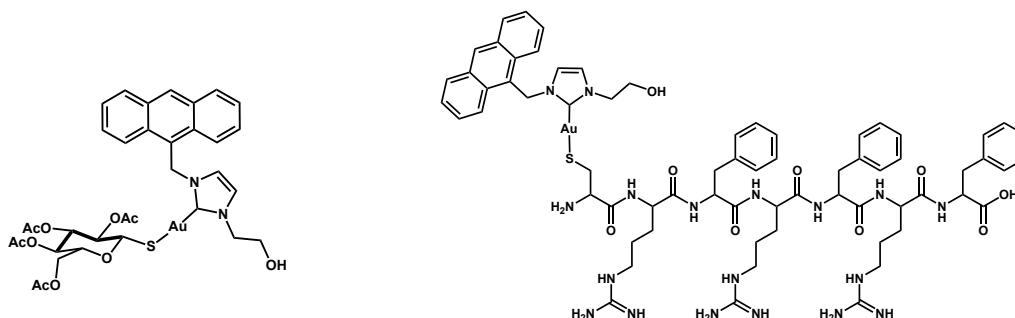


Figure 1: Two examples of the synthesized conjugates. The 2,3,4,6-tetra-O-acetyl-1-thio- β -D-glucopyranose conjugate (left) and the CrFrFrF peptide conjugate (right).

[1] Rigobello M. et al. *Free Radic.Biol.Med.* **2018**, 127, 62-79.

[2] Dada O. et al. *Tetrahedron Lett.* **2018**, 59, 2904-2908.

Poster 32

Nickel Catalyzed Carbonylation/Carboxylation Sequence with CO₂: Direct Access to 1,4-Keto Acids

Riccardo Giovanelli,^{a*} Lorenzo Lombardi,^a Riccardo Pedrazzani,^a Magda Monari,^a Giulio Bertuzzi,^a
Marco Bandini^a

^aDipartimento di Chimica “Giacomo Ciamician”, Alma Mater Studiorum - Università di Bologna, Via P. Gobetti 85,
40129 Bologna (BO), Italy.

riccardo.giovanelli3@unibo.it

Carbon dioxide has long been explored as a C1 chemical feedstock by the chemical community, although carboxylic moiety generation remains an important topic nowadays it is facing application in organic synthesis as well as for material preparation or as energetic vector.¹ Nevertheless, CO₂ has recently emerged as a cheap and safe carbonylating reagent. Methodologies for carbonylation with CO₂ have been developed (*i.e.* *alkene hydroformylations*; *amino-* or *alkoxycarbonylation*) but not all routes have already been fully explored.²

In this regard, a new nickel catalyzed cross-electrophile coupling (XEC) protocol is documented to simultaneously generate a carbonyl and a carboxyl moiety under low-pressure carbon dioxide (CO₂) atmosphere. A pivotal role is played by AlCl₃ which already resulted compatible with nickel catalyzed carboxylation protocol.³

The combined use of bipyridyl-NiCl₂ complexes and AlCl₃ enabled a range of 1,4-keto acids (19 examples) to be collected in good to high yields (up to 74%), with the formation of three new C-C bonds (Figure 1). Additionally, we have formulated a mechanistic hypothesis, supported by DFT investigation, control and ¹³C labeling experiments. The dual role exerted by AlCl₃ accounting as oxygen atom scavenger and activator of CO₂ in the carboxylation step represents a main novel feature in XEC area⁴.

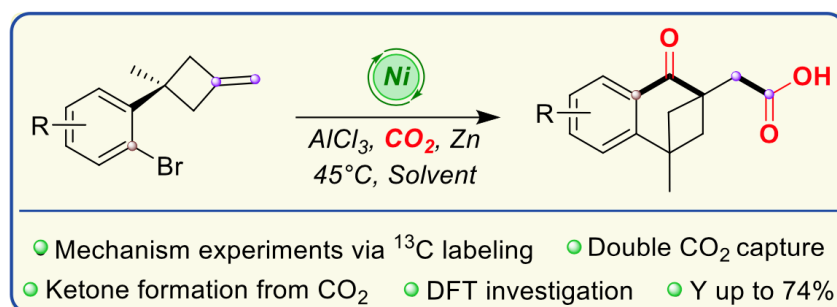


Figure 1 Nickel catalyzed XEC for sequential carbonylation/carboxylation

[1] Modak, A.; Bhanja, P.; Dutta, S.; Chowdury, B.; Bhaumik, B., *Green Chem.*, **2020**, 22, 4002.

[2] Sang, R.; Hu, Y.; Razzaq, R.; Mollaert, G.; Atia, H.; Bentrup, U.; Sharif, M.; Neumann, H.; Jurge, H.; Jackstell, R.; Maes, B.U.W.; Beller, M., *Nat. Commun.* 2022, 13, 4432.

[3] a) Lombardi, L.; Cerveri, A.; Ceccon, L.; Pedrazzani, R.; Monari, M.; Bertuzzi, G.; Bandini, M., *Chem. Commun.* 2022, 58, 4071. b) Giovanelli R.; Lombardi L.; Pedrazzani R.; Monari M.; Castiñeira Reis, M.; Silva López, C.; Bertuzzi, G.; Bandini, M., Nickel Catalyzed Carbonylation/Carboxylation Sequence with CO₂: Direct Access to 1,4-Keto Acids. (*submitted*).

[4] a) Sheng W.; Xi C. *Chem. Soc. Rev.*, **2019**, 48, 382. b) Meng-Meng W.; Sheng-Mei L.; Can L. *ACS Catal.*, **2022**, 12, 10801.

Poster 33

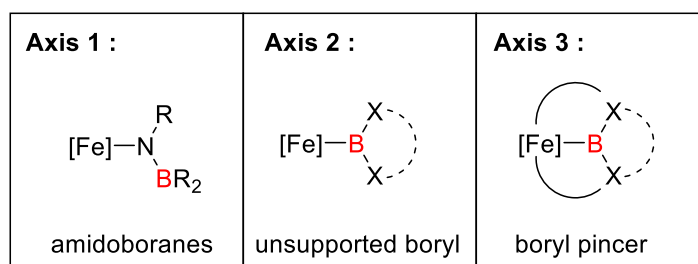
Synthesis and reactivity of low valent open-shell Iron complexes with Boron-containing ligands

Caroline Goncalves,^{a*} Sébastien Bontemps,^a

^a LCC-CNRS, Université de Toulouse, 205 route de Narbonne, 31077 Toulouse cedex 4, France.
caroline.goncalves@lcc-toulouse.fr

Transition metal complexes are of interest due to the wide range of properties and multiple possibilities for structural modifications. However, low-valence and/or low-coordination open-shell complexes are rare and not well studied. This is largely due to the difficulty of characterizing these species which are poorly stabilized by the ligand sphere and which exhibit paramagnetic properties. Nonetheless, these particular properties are of great interest. Firstly, low-valence complexes are often transient during catalytic reactions and therefore play a key role in activation processes. Moreover, open-shell structures are fundamental for 1e-transformations, such as those observed in enzymatic reactions.

Recent discoveries related to the use of complexes featuring boron-containing ligands have demonstrated the specific properties of the boron element, compared to functionalities more conventionally employed in coordination chemistry. This coordination chemistry has so far focused on shell-closed transition metal complexes.^[1–3] We believe that the field of borated ligands is now ready to take on new challenges. As such, the combination of a low valence iron complex with a high electron density with a Lewis acid boron fragment to be able to finely modulate the electronic structure and the reactivity of the targeted complexes is particularly attractive. We present here our approach and our advances on iron complexes featuring three types of boron containing ligands.



- [1] G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, 98, 2685–2722.
 [2] D. L. Kays, S. Aldridge, in *Contemporary Metal Boron Chemistry I: Borylenes, Boryls, Borane σ-Complexes, and Borohydrides* (Eds.: T.B. Marder, Z. Lin), Springer, Berlin, Heidelberg, **2008**, pp. 29–122.
 [3] H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, 110, 3924–3957.

Poster 34

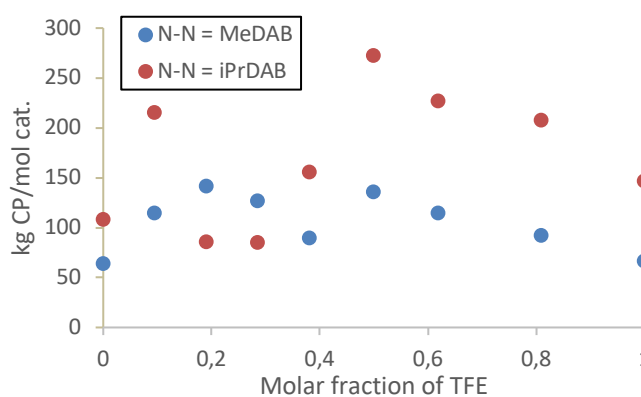
The unprecedented role of solvent in Pd-catalysis for the synthesis of functionalized polyolefins

Karim Abdel Hady,^{a*} Daniele Quattrin,^a Linda De Marchi,^a Chiara Alberoni,^a Barbara Milani^a

^a Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, 34127, Trieste, Italy.

*karim.abdelhady@phd.units.it

During the last two decades Pd(II)-based Brookhart-type complexes, of general formula $[\text{Pd}(\text{Me})(\text{MeCN})(\text{N-N})][\text{PF}_6]$ (N-N = α -diimines), have been extensively studied as homogeneous catalysts for the copolymerization of ethylene with polar vinyl comonomers, such as acrylic esters, to produce functionalized polyolefins (FPO).^{1,2} FPO are very interesting macromolecules because they could represent an environmentally friendly alternatives to simple polyolefins, which nowadays are the most worldwide produced thermoplastic materials.³ Some of us recently discovered that when the ethylene/methyl acrylate (MA) copolymerization, catalysed by $[\text{Pd}(\text{Me})(\text{MeCN})(\text{MeDAB})][\text{PF}_6]$ (MeDAB = 1,4-bis(2,6-dimethylphenyl)-1,4-diaza-2,3-butadiene), is carried out either in dichloromethane (DCM) or in 2,2,2-trifluoroethanol (TFE), the nature of solvent remarkably affects the way of MA enchainment into the macromolecules, from almost exclusively at the end of the branches (T(MA)) to almost a 1:1 ratio T(MA):M(MA) (M(MA) = MA into the main chain), respectively.⁴ We are now investigating the effect of using different mixtures of the two solvents, DCM and TFE, as reaction medium. The study was performed with the two precatalysts $[\text{Pd}(\text{Me})(\text{MeCN})(\text{N-N})][\text{PF}_6]$ (N-N = MeDAB, iPrDAB (iPrDAB = 1,4-bis(2,6-isopropylphenyl)-1,4-diaza-2,3-butadiene)). In both cases we found that: *i.* the trend of catalyst productivity with DCM/TFE ratio is not linear and reaches a maximum at a specific DCM/TFE ratio (Figure); *ii.* the way of MA enchainment is affected by the DCM/TFE ratio and the percentage of M(MA) increases from a specific DCM/TFE value on; *iii.* the copolymer molecular weight also varies upon DCM/TFE variation.



[1] Johnson, L.K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

[2] Wang, F.; Chen, C., *Polym. Chem.* **2019**, *10*, 2354.

[3] Luckham, S.L.J.; Nozaki, K. *Acc. Chem. Res.* **2021**, *54*, 344.

[4] Alberoni, C., D'Alterio, M. C., Balducci, G., Immirzi, B., Polentarutti, M., Pellecchia, C., Milani, B. *ACS Catal.* **2022**, *12*, 3430.

Poster 35

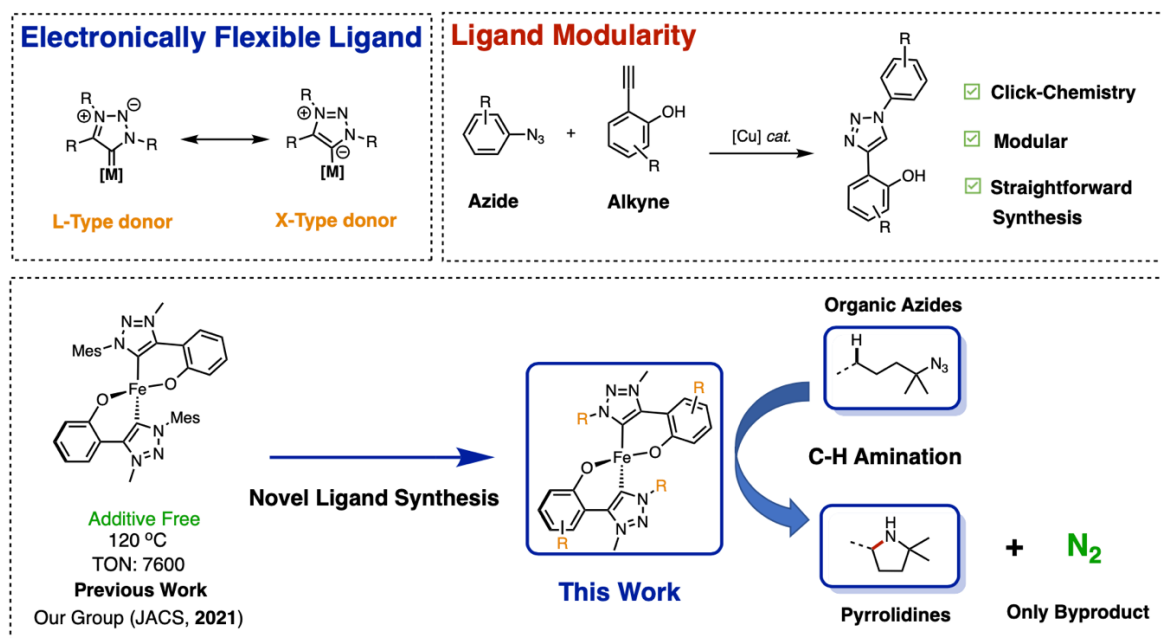
Iron-mesoionic carbene complexes for catalytic intramolecular C-H amination: novel ligand synthesis

Luke Alexander Hudson,^a Wowa Stroek,^a Martin Albrecht^{a*}

^aDepartment of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, CH- 3012 Bern (Switzerland)

luke.hudson@unibe.ch

Nitrogen containing heterocycles are ubiquitous across nature and industry with C-N bonds being found in numerous natural products and pharmaceutically relevant molecules.^{1,2} Therefore carbon-nitrogen bond formation is of utmost importance with catalytic and atom economical syntheses being particularly attractive. In this context, Betley in 2013 reported iron-catalysed direct C-H bond amination using an iron-dipyrrinato catalyst to yield a range of pyrrolidines.³ However, the activity was limited to only single digit TONs requiring 20 mol% catalyst loading and an equivalent of Boc₂O to prevent product inhibition. More recently, Betley also reported the additive-free C-H amination of nickel-dipyrrin complexes.⁴ In 2021, our group disclosed a highly efficient iron(II) mesoionic carbene complex, which afforded a range of C-H aminated pyrrolidine products in excellent yield with no need of additives, generating only N₂ as the sole side product with TONs exceeding the state of the art by an order of magnitude.⁵ Herein, we aim to better understand the influence of the ligand and to improve the catalytic performance of the iron complex by designing and synthesising novel ligands. Our data shows that appropriate ligand substitution enhances both the activity and selectivity of C-H amination.



- [1] R. Hili and A. K. Yudin, *Nat Chem Biol*, 2006, **2**, 284–287.
- [2] E. Vitaku, D. T. Smith and J. T. Njardarson, *J. Med. Chem.*, 2014, **57**, 10257–10274.
- [3] Betley, Hennessy, *Science*, 2013, **340**, 591–595.
- [4] Y. Dong, R. M. Clarke, G. J. Porter and T. A. Betley, *J. Am. Chem. Soc.*, 2020, **142**, 10996–11005.
- [5] W. Stroek, M. Keilwerth, D. M. Pividori, K. Meyer and M. Albrecht, *J. Am. Chem. Soc.*, 2021, **143**, 20157–20165.

Poster 36

Impact of Hydrophobic Chains in Five-Coordinate Glucoconjugate Pt(II) Anticancer Agents

Vincenzo Langelotti,^{a*} Alfonso Annunziata,^{a,b} Maria Elena Cucciolito,^{a,c} Roberto Esposito,^{a,c}
Giarita Ferraro,^a Paola Imbimbo,^a Alessandra Marano,^a Massimo Melchiorre,^{a,c} Antonello Merlino,^a
Daria Maria Monti,^a Francesco Ruffo,^{a,c} Gabriella Tito,^a Marco Trifuoggi,^a

^a *Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II (Complesso Universitario di Monte S. Angelo), Via Cintia 21, 80126 Napoli, Italy.*

^b *Institute of Chemical Research of Catalonia (ICIQ), Avda. Paisos Catalans 16, 43007 Tarragona, Spain.*

^c *Consorzio Interuniversitario di Reattività Chimica e Catalisi (CIRCC), Via Celso Ulpiani 27, 70126 Bari, Italy.*

vincenzo.langellotti@unina.it

Cisplatin and its derivatives have been successfully employed in the clinical treatment of cancer. However, their usage often leads to side effects that significantly impact the patients' quality of life.^[1] An important strategy to enhance the performance of platinum-based drugs involves the accurate tuning of the coordination environment of the metal centre.^[2] In this respect, *N*-heterocyclic carbene ligands (NHC) emerge as a promising solution, thanks to their highly versatile synthetic platforms and stability.^[3] Additionally, the utilization of glucoconjugate complexes can improve the selectivity towards cancer cells through the "Warburg effect".^[4]

On these basis, this work described the synthesis and characterization of new platinum(II) cationic five-coordinate complexes (**1-R,R'**) with the formula [PtR(NHC-R')(dmphen)(ethene)]CF₃SO₃ (dmphen = 2,9-dimethyl-1,10-phenanthroline). These compounds presented a trigonal bipyramidal (*tbp*) geometry, containing in their axial positions an alkyl group R (methyl or *n*-octyl), and an imidazole-based NHC-carbene ligand, with a substituent R' of variable length (methyl or *n*-octyl) on one nitrogen atom and a sugar moiety (Figure 1).

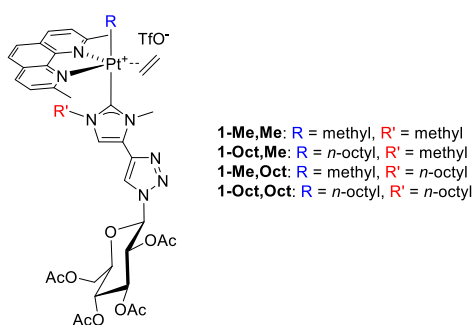


Figure 1

The impact of hydrophobic groups R and R' in the coordination sphere of the metal (methyl or *n*-octyl) was evaluated considering the stability in solution of related complexes, their lipophilicity, interaction with biological molecules (DNA and proteins), cytotoxicity, and cellular uptake.

[1] Oun, R. et al. *Dalton Trans.* **2018**, 47, 6645.

[2] Kenny, R.G. et al. *Chem. Rev.* **2019**, 119, 1058.

[3] Hopkinson, M., et al. *C. Nature* **2014**, 510, 485.

[4] Cucciolito, M.E. et al. *Inorg. Chem. Front.* **2018**, 5, 2921.

Poster 37

Controlled self-assembling of mixed metals cyclic trinuclear metallacycles (CTCs)

Lorenzo Luciani,^{a*} Nicola Sargentoni,^a Zhou Lu,^b Vladimir N. Nesterov,^c Cristiano Zuccaccia,^d Alceo Macchioni,^d Mohammad A. Omary,^c Rossana Galassi^a

^aSchool of Science and Technology, Chemistry Division, University of Camerino, ChIP Via Madonna delle Carceri, 10, I-62032 Camerino, Italy; ^bDepartment of Chemistry, Rochester University, 252 Elmwood Ave, Rochester, NY 14611, USA; ^cDepartment of Chemistry, University of North Texas, Denton, Texas 76203, USA; ^dDepartment of Chemistry, Biology and Biotechnology, University of Perugia and CIRCC, Via Elce di Sotto 8, I-06123, Perugia, Italy

lorenzo.luciani@unicam.it

11th group cyclic trinuclear metallacycles (CTCs) can be visualized as building blocks to make supramolecular entities, with well-defined solid-state patterns such as {ADAD}_n, {ADDA}_n (where D or A are donor or acceptor units and n goes from 1 to infinite), or extended stacks. The self-assembling of CTCs is guided by intermolecular dispersive forces, π -basic/ π -acidic interactions, and homometallic (M-M) or heterobimetallic (M-M') d¹⁰-d¹⁰ closed-shell interactions, which strength depends on the metals/ligands combinations.^{[1][2]} Recently, our research group has synthesized new Au/Ag and Au/Cu stacked adducts by mixing homometallic π -basic Au(I)-imidazolate CTCs with π -acidic Ag(I)- or Cu(I)-pyrazolate CTCs; single crystal XRD analyses revealed short unassisted Au/Ag and Au/Cu intertrimer distances, with a lower limit of 2.868(2) Å for Au-Ag^[3] and of 2.8750(8) Å for Au-Cu,^[2] which substantiate the coordinate-covalent character of the M-M' bonding.^{[2][3]} Moreover, solution studies have demonstrated that these interactions survive even in solution, with binding constants up to 4.67×10⁵ L/mol. Stacked heterobimetallic CTCs with AuAg₂ and Au₂Ag cores were recently obtained by mixing homonuclear Au and Ag CTCs, both bearing the same fluorinated pyrazolate ligand, thus achieving almost neat metallophilic-driven metal exchanges and stackings. For these latters, binding constants inferior by two orders of magnitude (10³ L/mol) were obtained in DCM solutions. Solid-state photoluminescence studies revealed intense metal-centered phosphorescent (³MC) emission bands, promoting them as likely candidates in OLED technology applications.

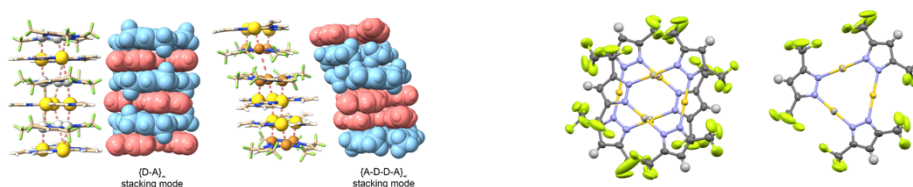


Figure 1

Crystalline packings of stacking products with ADAD and ADDA stacking modes (left). Crystalline packing unit and crystallographic unit of [Ag₂Au(μ-N,N-3,5(CF₃)₂pyrazolyl)₃] (right).

[1] Tekarli, S. M.; Cundari, T. R.; Omary, M. A.; *J. Am. Chem. Soc.* **2008**, *130*, 1669–1675.

[2] Galassi, R.; Ghimire, M.M.; Otten, B. M.; Ricci, S.; McDougald R. N.; Almotawa R. M.; Alhmoud, D.; Ivy, J.F.; Rawashdeh A. M. M.; Nesterov, V. N.; Reinheimer, E. W.; Daniels, L. M.; Burini, A.; Omary, M.A.; *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, E5042–E5051.

[3] Zhou, L.; Luciani, L.; Li, S.; Nesterov, V.; Zuccaccia, C.; Macchioni, A.; Fripp, J.; Zhang, W.; Chi, Y.; Omary, M.A.; *Chem* **2023**, submitted.

Poster 38

A domino organometallic addition/Cope-House rearrangement to nitrones affords novel 3-methylindolizidines related to Castanospermine.

Thomas Lulli,^{a*} Camilla Matassini,^a Filippo Dei,^a Francesca Cardona,^a and Andrea Goti^a

^a Department of Chemistry ‘Ugo Schiff’, University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy.

thomas.lulli@unifi.it

Iminosugars are one of the most significant classes of glycomimetics known nowadays, exhibiting their activity as antiviral, antidiabetic, anticancer, and – more recently – therapeutic agents for lysosomal storage disorders¹. The biological activity of polyhydroxylated indolizidines has already been reported, as well as that of pyrrolizidines bearing a methyl substituent adjacent to the bridge-head nitrogen atom¹. Nevertheless, the synthesis of polyhydroxylated 3-methylindolizidines has not been accomplished yet, and their bioactivity is unknown. Herein, we report the synthesis of 3-methylindolizidines analogous to Castanospermine **1**, with potential biological activity, starting with nitrones derived from inexpensive sugars and using butenyl-type organometallic reagents addition and Cope-House reaction² as key steps (Figure 1).

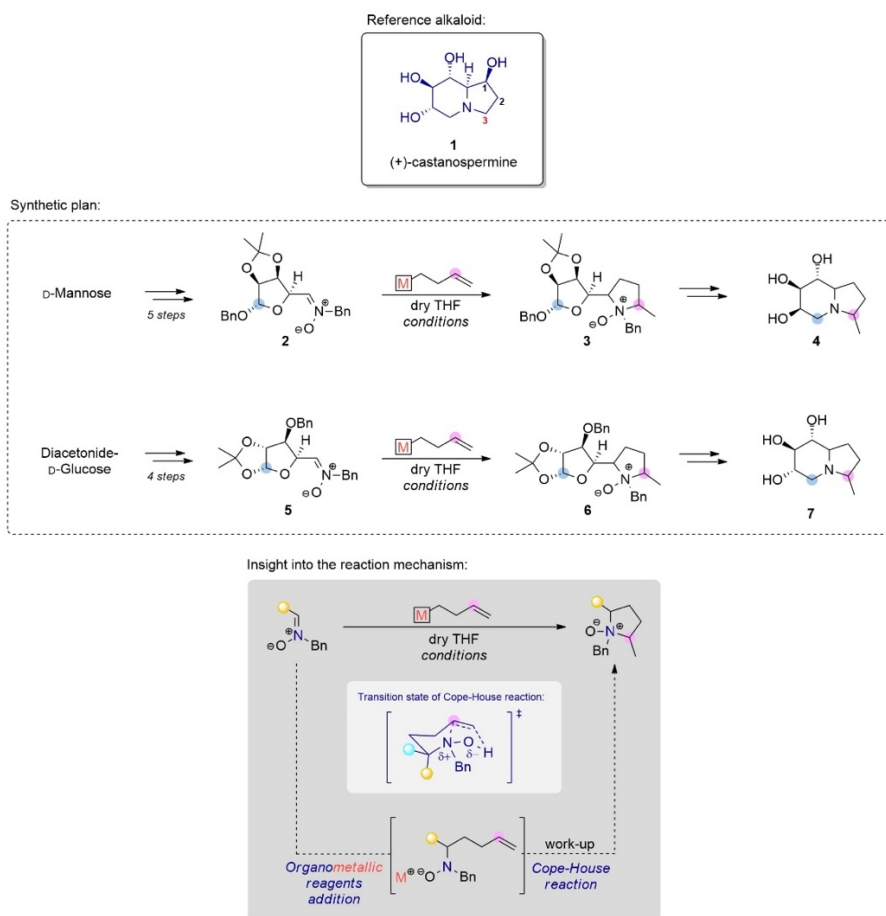


Figure 1

[1] Iminosugars: from synthesis to therapeutic applications (Editors: Compain, P.; Martin, O.R.), Wiley-VCH, Weinheim, **2007**.

[2] Cooper, N.J., Knight, D.W., *Tetrahedron*, **2004**, *60*, 243-269.

Shortened Salen-Type Ligands and Their Complexation Ability Toward Transition Metals

Lorenzo Marchi,^{a*} Serena Maria Fantasia,^b Carlo Castellano,^c Francesco Demartin,^c Lara Gigli,^d Anna M. Ferretti,^e Alessandro Ponti,^e Luca Rigamonti^a

^a Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Modena e Reggio Emilia, via G. Campi 103, 41125 Modena, Italy; ^b Department of Synthetic Molecules Technical Development, Process Chemistry & Catalysis, F. Hoffmann-La Roche Ltd, Basel, Switzerland; ^c Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133 Milano, Italy; ^d Elettra Synchrotron Trieste, Strada Statale 14 - km 163,5 in AREA Science Park, 34149 Basovizza, Trieste, Italy; ^e Istituto di Scienze e Tecnologie Chimiche “Giulio Natta”, Consiglio Nazionale delle Ricerche (SCITEC-CNR), Via G. Fantoli 16/15, 20138 Milano, Italy.

lorenzo.marchi@unimore.it

H₃salmp, H₂salben and H₂salmen (**Figure 1**) are oligodentate Schiff bases derived from the condensation of two salicylaldehydes (salH) with arylmethanediimine or methanediimine. These ligands possess only one carbon atom between the two donor iminic groups with respect to the two carbon atoms of the well-known H₂salen, and this drives toward the selective formation of oligonuclear metal complexes against mononuclear ones. The pentadentate N₂O₃ H₃salmp is mostly suitable to complex trivalent ions like iron(III) and manganese(III) giving rise to dinuclear species whose nature is strongly dependent on the deprotonating base and the presence of water [4]. On the other hand, the N₂O₂ tetradentate H₂salben and H₂salmen can also coordinate divalent metal ions like copper(II) [1] and cobalt(II) [2,3] to form dinuclear or pentanuclear clusters. In the case of iron(III), salen ligands with substituents on the central aryl ring can form either dinuclear [4] or tetranuclear complexes [5], depending on the position of the substituent on the aryl ring and the solvent employed. The investigation of the complexation ability of these ligands is then worthy thanks to the tuneability and variability of the obtained molecular species, which can show interesting magnetic behavior [1-5], but can be further investigated for their biological, optical and catalytic properties and potential applications as new materials.

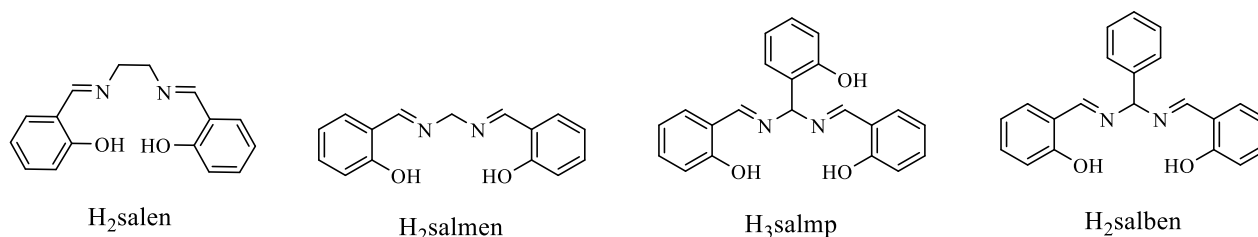


Figure 1 Molecular schemes of H₂salen, H₂salmen, H₃salmp and H₂salben.

- [1] Pasini, A. et al., *J. Chem. Soc., Dalton Trans.* **2000**, 3467–3472.
- [2] Chiari, B. et al., *J. Chem. Soc., Dalton Trans.* **2001**, 3611–3616.
- [3] Chiari, B. et al., *J. Chem. Soc., Dalton Trans.* **2002**, 4672–4677.
- [4] Rigamonti, L. et al., *Int. J. Mol. Sci.* **2020**, *21*, 7882.
- [5] Marchi, L. et al, *Int. J. Mol. Sci.* **2023**, *24*, 5808.

Poster 40

Ir-NHC Catalysts for Selective Glycerol Oxidation through Acceptorless Dehydrogenation

Joaquín Martínez Sal,^{a*} Jesús J. Pérez Torrente,^a M. Victoria Jiménez Rupérez,^a

^a Instituto de Síntesis Química y Catálisis Homogénea, Universidad de Zaragoza – CSIC, Pedro Cerbuna 12, 50009 Zaragoza, Spain.
jmsal@unizar.es

Nowadays, the mainstream of commodities is generated from non-renewable fuel resources. Within the context of biomass exploitation, the main byproduct in biodiesel processing is crude glycerol, precursor of a wide range of compounds. In particular, Lactic Acid (LA) is one of the most appealing ones, widely handled in food, cosmetic, pharmaceutical, polymer and fine chemical industries. In this sense, catalytic acceptorless dehydrogenation (ADH) of glycerol (Figure 1) is regarded as an outstanding process as it generates both LA and molecular hydrogen, a key energy vector in the front row when it comes to the development of sustainable energy systems.^[1]

Homogeneous catalysis provides excellent results in glycerol dehydrogenation, achieving high selectivity towards LA. Currently, Ir-NHC complexes play a prominent role in the area,^[2-3] as they have been revealed as robust catalysts for numerous dehydrogenation reactions. In particular, the presence of hydrophylic moieties in the NHC structure enhances the solubility of these complexes in polar media and, in turn, their performance in these dehydrogenative processes. Herein, we depict the synthesis of several Ir-NHC catalysts with one or more N-heterocyclic carbenic units bearing different N- and O-donor functions in the ligand structure, which have shown to be efficient in these acceptorless dehydrogenation processes.

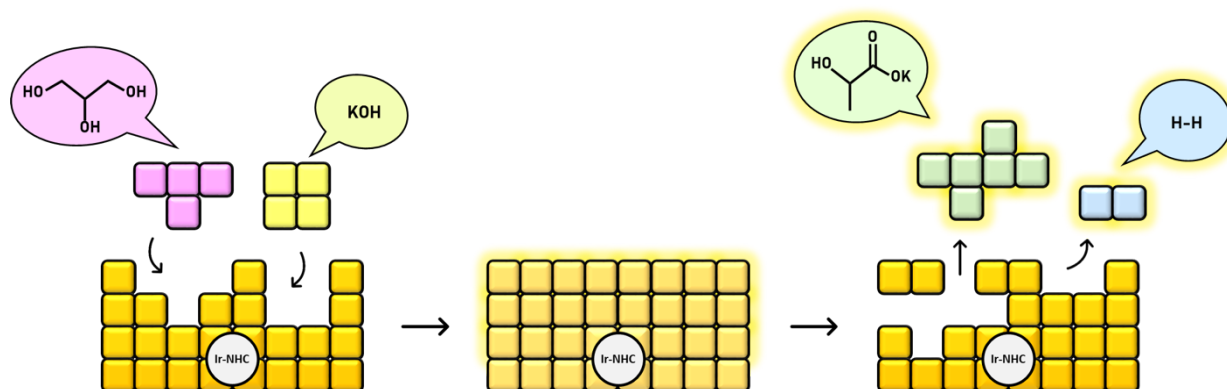


Figure 1. Glycerol transformation into LA and H₂ through Ir-NHC-catalyzed ADH.

- [1] Wang, K.; Yang, Z.; Ma, Y.; Zhao, W.; Sun, J.; Lu, T.; He, H. *Biofuels Bioprod. Bioref.* **2022**, *16*, 1428.
 [2] Jiménez, M.V.; Ojeda-Amador, A.I.; Puerta-Oteo, R.; Martínez-Sal, J.; Passarelli, V.; Pérez-Torrente, J.J. *Molecules* **2022**, *27*, 7666.
 [3] Kirchhecker, S.; Spiegelberg, B.; de Vries, J.G. Homogenous Iridium Catalysts for Biomass Conversion. Iridium Catalysts for Organic Reactions, Germany, **2020**.

Poster 41

Tetravalent β -Diketonate Molybdenum Complexes as Highly Active Catalysts for Allylic Substitution Reactions

Fabio Masero,^a Victor Mougel,^{a*}

^a ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zurich (ZH), Switzerland.
mougel@inorg.chem.ethz.ch

We present here the isolation, characterization and catalytic activities for C-C and C-N bond coupling of a new family of octahedral Mo(IV) compounds.¹ In opposition to the well-developed π -allyl metal complex-based coupling reactions catalyzed by precious metals such as iridium and palladium,^{2,3} molybdenum has found much fewer applications.^{4,5} This stands in contrast to its earth abundancy, rich redox-chemistry, and capability to easily undergo metal-carbon bond formation and cleavage, rendering molybdenum an attractive choice for the development of new metal-based catalysts for a variety of different organic transformations. We have optimized the preparation and fully analyzed a series of Mo(IV) bis- β -diketonate complexes.^{6,7} Detailed solid- and solution state studies gave unprecedented insights into the geometry and coordination chemistry of these compounds, *e.g.* displaying solvent dependent dynamic equilibria involving *cis*- and *trans*-isomers in solution.

Reactivity and catalytic activity of the complexes were further explored, providing one of the most active and stable earth-abundant metal-based molecular catalyst for the substitution of allylic alcohols by electron-rich carbon-based nucleophiles (*e.g.* phenols). Reactivity studies involving the isolation of a Mo(V)-oxo resting state species combined with *in-situ* spectroscopic investigations provided insights into the present mechanistic pathway.

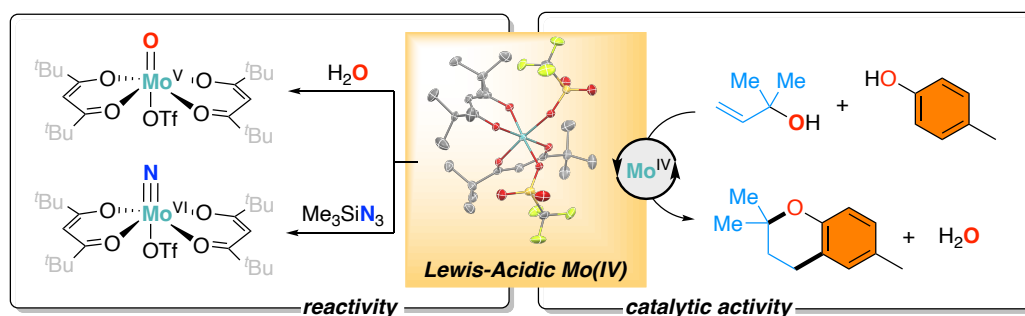


Figure 1

- [1] F. Masero, V. Mougel, *Chem. Commun.* **2023**, 59, 4636.
- [2] Q. Cheng, H. Tu, C. Zheng, J. Qu, G. Helmchen, S.-L. You, *Chem. Rev.* **2019**, 119, 1855.
- [3] B. Sundararaju, M. Achard, C. Bruneau, *Chem. Soc. Rev.* **2012**, 41, 4467.
- [4] A. V. Malkov, P. Spoor, V. Vinader, P. Kočovský, *J. Org. Chem.* **1999**, 64, 5308.
- [5] M. Salman, Y. Xu, S. Khan, J. Zhang, A. Khan, *Chem. Sci.* **2020**, 11, 5481.
- [6] G. Doyle, *Inorg. Chem.* **1971**, 10, 2348.
- [7] den B. A. Van, K. Murray, B. West, *Aust. J. Chem.* **1972**, 25, 705.

Poster 42

Design, Synthesis and Characterization of New Metal Chelates for Novel Applications as Fertilizers

Andrea Masetti,^{a*} Rita Mazzoni,^a Elisa Degli Esposti^b

^a Department of Industrial Chemistry “Toso Montanari”, University of Bologna, Viale Risorgimento 4, 40136 Bologna (BO), Italy.

^b Biolchim S.p.A., Via San Carlo 2130, 40059 Medicina (BO), Italy.

andrea.masetti9@unibo.it

Iron chlorosis is a major nutrient deficiency condition highly widespread in plants grown in calcareous soils, which leads to the development of a yellow leaf with a network of dark green veins. In severe cases, or if iron chlorosis persists over several years, individual limbs or the entire plant may die. The most common Fe chlorosis remediation technique consists in the application of iron fertilizers; however, since the synthetic processes of these complexes are dated back to the '70s, the research of innovative and optimized processes is necessary to guarantee a cheaper and more sustainable production. In collaboration with Biolchim S.p.A. we are currently focusing on improving pre-existing processes via process optimization and homogenous catalysis, while concurrently developing innovative and sustainable chelating systems able to stabilize Fe in soil solution in any condition.

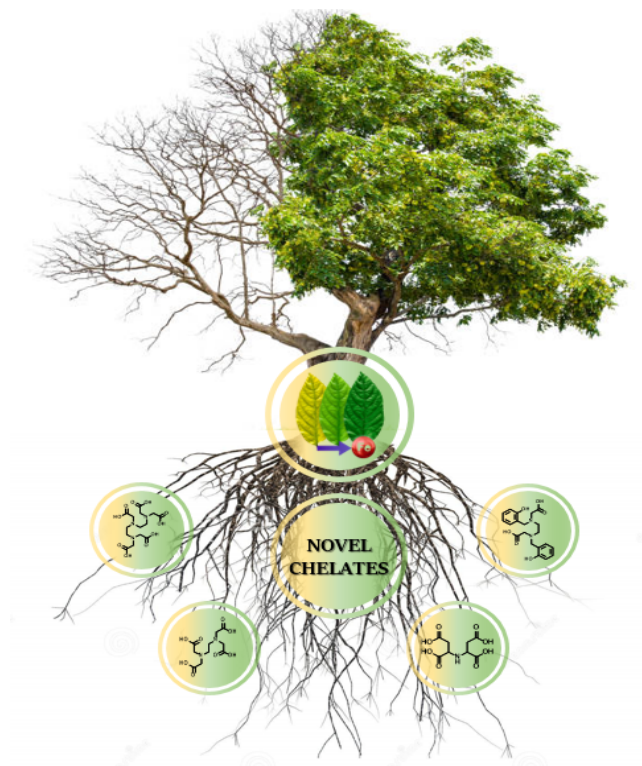


Figure 1: Fe chelates for iron chlorosis treatment.

Poster 44

Exploring the reductive CO₂ fixation to amines using stable NHC–phenolate copper(II) complexes

Giammarco Meloni,^{a,b*} Marco Baron,^{a,b} Cristina Tubaro^{a,b}

^a Department of Chemical Sciences, Via Marzolo 1, 35131 Padova, Italy.

^b Interuniversity Consortium Chemical Reactivity and Catalysis, Via Celso Ulpiani 27, 70126 Bari, Italy.

giammarco.meloni@phd.unipd.it

One of the most important issues that today concerns our society is sustainable development, a goal that humankind must achieve to ensure a future for the next generations. In this context, one of the main challenges is to reduce the concentration of CO₂ in the atmosphere, and one of the most promising approaches involves its capture from energy power plants waste. The high cost related to the capture processes are thereby a limit to the applicability of the method, and several problems are also related to CO₂ storage. The utilization of captured CO₂ as C1 building block for the synthesis of added-value compounds would potentially cover the capture costs and overcome the storage problem.¹ In this frame, the development of new efficient catalysts is important to avoid drastic reaction conditions and to get access to a plenty of different chemical transformations. For this purpose, organometallic metal complexes are great candidates.² However, organometallic chemistry was historically focused on rare and expensive late transition metal centers, resulting in active but expensive metal catalysts. In the last years, a renaissance of the organometallic chemistry of Earth-abundant metals is taking place, helped by different features like the metal precursor's cheap price, their biocompatibility, and the capability of undergoing single electron transfer (SET) processes.^{3,4} In this contribution, we report our study on the synthesis and characterization of NHC-phenolate copper(II) complexes. The performance of these complexes as catalysts for the reductive fixation of CO₂ with amines, for the synthesis of formamides and methylamines, was also explored (Figure 1).

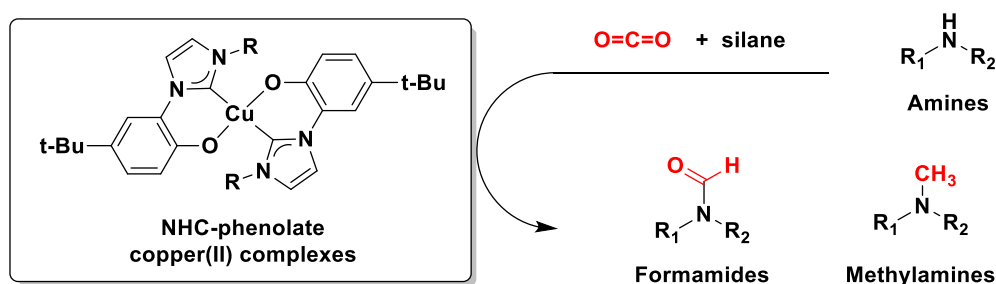


Figure 1

[1] Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, 5933.

[2] Dibenedetto, A.; Angelini, A.; Stufano, P. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 334.

[3] Albrecht, M.; Bedford, R.; Plietker, B. *Organometallics* **2014**, *33*, 5619.

[4] Loup, J.; Dhawa, U.; Pescioli, F.; Wencel-Delord, J.; Ackermann, L. *Angew. Chem. Int. Ed.* **2019**, *58*, 12803.

Poster 45

A robust, versatile, and reusable heterogeneous hydrogenation catalyst based on a simple Ni(II) diimine complex and its application to the syntheses of amines

Jessica Michalke,^{a,b} Dominik Böhm,^a Fabian Schmiedbauer,^a Julia Felicitas Schwarz,^c

Lukas Stefan Vogl,^d Stephan Bartling,^e Nils Rockstroh,^e Christoph Topf,^{a,*}

^a Institute of Catalysis (INCA), Johannes Kepler University (JKU), Altenbergerstraße 69, 4040 Linz, Austria; ^b Institute of Inorganic Chemistry, Johannes Kepler University (JKU), Altenbergerstraße 69, 4040 Linz, Austria; ^c Institute for Chemical Technology of Organic Materials (CTO), Johannes Kepler University (JKU), Altenbergerstraße 69, 4040 Linz, Austria; ^d Institute of Organic Chemistry, Johannes Kepler University (JKU), Altenbergerstraße 69, 4040 Linz, Austria; ^e Leibniz Institute for Catalysis, University of Rostock (LIKAT Rostock), Albert-Einstein-Straße 29a, 18059 Rostock, Germany

christoph.topf@jku.at

A Ni(II) diimine complex was prepared, immobilized onto silica through wet impregnation and pyrolyzed.¹⁻
³ The resulting composite material shows high catalytic activity in the reductive amination reaction of ketones in methanolic ammonia solution. Exploration of the applicability included, but was not limited to methoxy- and phenol-tagged compounds, halogen-containing substrates, and aliphatic ketones. The catalyst was further utilized for the liquid phase hydrogenation of nitroarenes under flow conditions, where the substrates were chemoselectively converted into the corresponding primary amines. In both cases the heterogeneous catalyst allowed for facile recyclability and straightforward product isolation by treatment of the crude product with dry HCl solution, leading to the organic ammonium salts without any further purification steps.

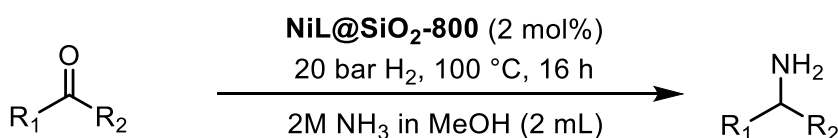


Figure 1: Reductive amination of ketones with the NiL@SiO₂-800 catalyst in 2 M NH₃ in methanol solution, yielding the corresponding primary amine.

[1] J. Michalke, K. Faust, T. Bögl, S. Bartling, N. Rockstroh, C. Topf, *Int. J. Mol. Sci.* **2022**, *23*, 8742.

[2] J. Michalke, M. Haas, D. Krisch, T. Bögl, S. Bartling, N. Rockstroh, W. Schöfberger, C. Topf, *Catalysts* **2021**, *12*, 11.

[3] R. Ferraccioli, D. Borovika, A.-E. Surkus, C. Kreyenschulte, C. Topf, M. Beller, *Catal. Sci. Technol.* **2018**, *8*, 499–507.

Poster 46

Water-Soluble two-photon excitable Eu, Sm and Yb Complexes with Circularly polarized Luminescence activity in the Vis and NIR spectral region

Silvia Mizzoni,^{a,b,*} Annika Sickinger,^b Silvia Ruggieri,^a François Riobé,^b Laure Guy,^b Olivier Maury,^b Bruno Baguenard,^c Amina Bensalah-Ledoux,^c Stephan Guy,^c Martina Sanadar,^d Andrea Melchior^d Xuan-Nhi Nguyene,^c Andrea Cimarelli,^c and Fabio Piccinelli^a

^a Luminescent Materials Laboratory, DB, Università di Verona, Verona, Italy. ^b Univ Lyon, ENS de Lyon, Lyon, France. ^c Univ. Lyon, Institut Lumiere Matière, Lyon 1, Villeurbanne Cedex, France. ^d Dipartimento Politecnico di Ingegneria e Architettura, Università di Udine, Udine, Italy. ^e Centre International de Recherche en Infectiologie, Univ Lyon 1, Lyon, France. silvia.mizzoni@univr.it

In this contribution, two couples of cationic enantiomeric complexes [(*R,R*)-[LnL]Cl and (*S,S*)-[LnL]Cl, with Ln = Eu, Sm and Yb and L = N,N'-bis(2-pyridylmethyl)-1,2-(*R,R* or *S,S*)-cyclohexanediamine functionalized at sp³ N with the picolinate *antennae*¹] have been synthesized and spectroscopically characterized in polar protic solvents, such as water and methanol. The good sensitization of Ln(III) luminescence by the picolinate *antenna* is documented², upon both a one photon absorption process (at about 330 nm) and a two photon absorption process (at 720 nm). The complexes exhibit good CPL activity (**Figure 1**) and are highly stable in aqueous solution (logK = 20.13 for the EuL species chosen as the representative); only one main species is present at physiological pH (7.4). Preliminary biphotonic imaging experiments on the (*S,S*)-[EuL]Cl complex reveal that it can be easily internalized in two different cell lines with perinuclear diffuse localisation in the cytosol. These complexes can be considered promising candidates as NIR-to-RED (Eu and Sm) and NIR-to-NIR (Yb) *in cellulo* chiroptical bioprobes and a possible extension to the *in vivo* experiments will be further investigated.

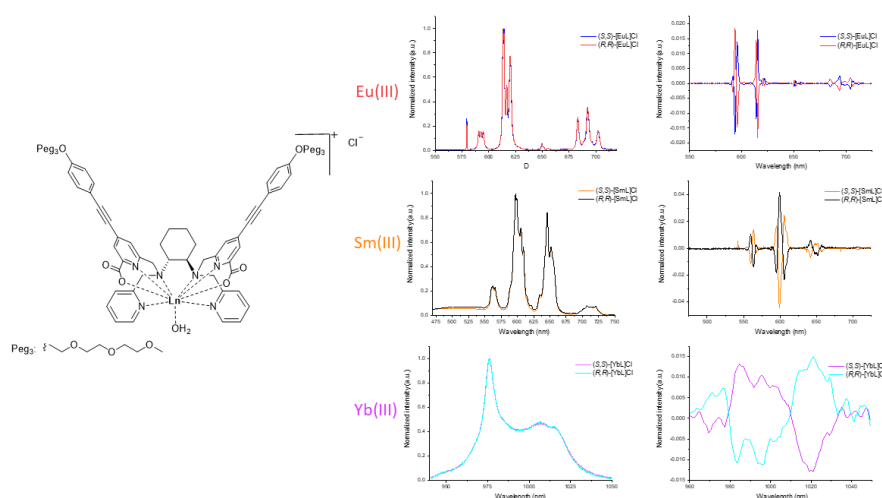


Figure 1 (Left) Structure of (*S,S*)-[LnL]Cl complex presented. (Middle) Normalized PL and (Right) CPL spectra of both enantiomers of [LnL]Cl in aqueous solution at room temperature. λ_{exc} at 336 nm.

[1] S. Mizzoni; et al. *J. Mater. Chem. C*; **2023**; *11*, 4188.

[2] N. Hamon, et al. *J. Am. Chem. Soc.*; **2020**, *142*, 22, 10184.

Poster 47

A Homogeneous Ni-catalyst for the Synthesis of Pyrrolidones from Bio-based Keto Acid using Molecular Hydrogen

Jan-Ole Moritz, Soumyadeep Chakraborty, Fabian Kallmeier, Helfried Neumann,

Johannes G. de Vries,* Matthias Beller*

^a Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany

*Matthias.Beller@catalysis.de, Johannes.deVries@catalysis.de

Levulinic acid (LA) is a promising biomass-derived platform chemical allowing a broad variety of valorizations. Among these, the conversion of LA to heterocycles has attracted considerable interest. Especially reductive transformations involving primary amines and molecular hydrogen offer interesting possibilities to access *N*-substituted pyrrolidones. Nevertheless, the research effort in this field is mostly focused on heterogeneous systems.^{[1][2][3][4][5]} Approaches utilizing homogeneous systems remain scarce so far.^{[6][7]} In order to close this gap, we developed a homogeneous Ni/triphos-based system allowing simple and facile access to a variety of *N*-functionalized pyrrolidones (as described in Figure 1). The reaction shows remarkable selectivity towards the desired products and high to excellent isolated yields after simple work-up procedure. Mechanistic studies to elucidate the role of TFE in the reaction are currently underway in our lab.

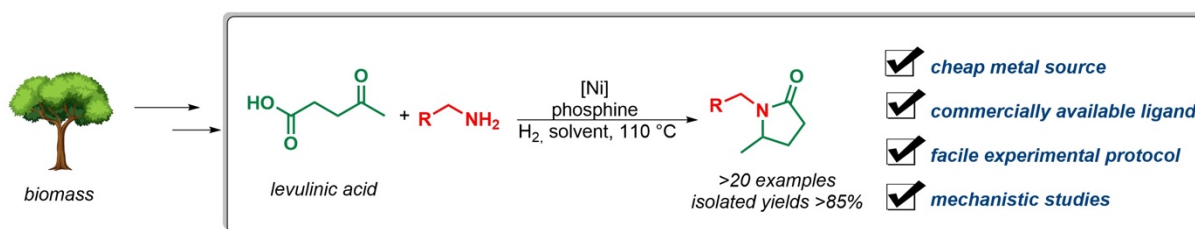


Figure 1 Synthesis of *N*-functionalized pyrrolidones from levulinic acid.

- [1] Touchy, A. S.; Hakim, S. M. A. H.; Kon, K.; Shimizu, K.-i. *ACS Catal.* **2014**, *4*, 3045.
- [2] Vidal, J. D.; Climent, M. J.; Concepcion, P.; Corma, A.; Iborra, S.; Sabater, M. J. *ACS Catal.* **2015**, *5*, 5812.
- [3] Gao, G.; Sun, P.; Li, Y.; Wang, F.; Zhao, Z.; Qin, Y.; Li, F. *ACS Catal.* **2017**, *7*, 4927.
- [4] Xie, C.; Song, J.; Wu, H.; Hu, Y.; Liu, H.; Zhang, Z.; Zhang, P.; Chen, B.; Han, B. *J. Am. Chem. Soc.* **2019**, *141*, 4002.
- [5] Gao, J.; Feng, L.; Ma, R.; Su, B.-J.; Alenad, A. M.; Liu, Y.; Beller, M.; Jagadeesh, R. V. *Chem Catal.* **2022**, *2*, 178.
- [6] Pan, Y.; Luo, Z.; Yang, J.; Han, J.; Yang, J.; Zhen, Y.; Xu, J.; Wang, P.; Shi, Q. *Adv. Synth. Catal.* **2022**, *364*, 2830.
- [7] Chakraborty, S.; Zheng, S.; Kallmeier, F.; Baráth, E.; Tin, S.; de Vries, J. G. *ChemSusChem* **2023**, *16*, e2022023

Poster 48

Synergistic experimental and computational investigation of CO₂ capture mechanism by using water-free amine sorbents

Jakub Nagy,^{a*} Gabriele Manca,^{b**} Francesco Barzagli^{b***} and Andrea Ienco^b

^a Faculty of Science, Department of Chemistry, Masaryk University, Czech Republic. *461147@mail.muni.cz

^b Istituto di Chimica dei Composti OrganoMetallici, CNR-ICCOM, Via Madonna del Piano 10, I-50019, Sesto Fiorentino, Italy. **gabriele.manca@iccom.cnr.it, ***francesco.barzagli@iccom.cnr.it,

The search for effective methods to capture CO₂ from flue gasses using liquid sorbents to mitigate global warming has been highly prioritized over the recent years.^{1,2} The high-energy demanding regeneration of the sorbents represents the major challenge.^{3,4,5} To overcome this difficulty, the application of solvent-free liquid sorbent such as pure dipropylamine (DPA), through synergic experimental and computational study, was investigated. By conducting precise ¹H and ¹³C NMR speciation study over time in the solution during the CO₂ capture process, different molecular entities and their variations were determined. The quantities of these species were estimated by measuring the weight change of the solution as well as from ¹³C NMR analysis. Additional evidence for the presence of carbamic acid, that is dependent on CO₂ loading, was given by the FT-IR analysis. The detailed density functional theory (DFT) investigation validated the experimental findings, identifying all potential species and explaining their formation and interconversion through reasonable energetic pathways. Based on the complementary results the series of equilibria describing the CO₂ process with solvent-free DPA was proposed.

- [1] Barzagli F, Lai S, Mani F. A new class of single-component absorbents for reversible carbon dioxide capture under mild conditions. *ChemSusChem* **2015**;8:184–91. <https://doi.org/10.1002/cssc.201402421>.
- [2] Bhatti UH, Ienco A, Peruzzini M, Barzagli F. Unraveling the Role of Metal Oxide Catalysts in the CO₂ Desorption Process from Nonaqueous Sorbents: An Experimental Study Carried out with ¹³C NMR. *ACS Sustain Chem Eng* **2021**;9:15419–26. <https://doi.org/10.1021/acssuschemeng.1c04026>.
- [3] Barzagli F, Giorgi C, Mani F, Peruzzini M. Reversible carbon dioxide capture by aqueous and non-aqueous amine-based absorbents: A comparative analysis carried out by ¹³C NMR spectroscopy. *Appl Energy* **2018**;220:208–19. <https://doi.org/10.1016/j.apenergy.2018.03.076>.
- [4] Didas SA, Sakwa-Novak MA, Foo GS, Sievers C, Jones CW. Effect of Amine Surface Coverage on the Co-Adsorption of CO₂ and Water: Spectral Deconvolution of Adsorbed Species. *J Phys Chem Lett* **2014**;5:4194–200. <https://doi.org/10.1021/jz502032c>.
- [5] Yu J, Chuang SSC. The Structure of Adsorbed Species on Immobilized Amines in CO₂ Capture: An in Situ IR Study. *Energy & Fuels* **2016**;30:7579–87. <https://doi.org/10.1021/acs.energyfuels.6b01423>.

Poster 49

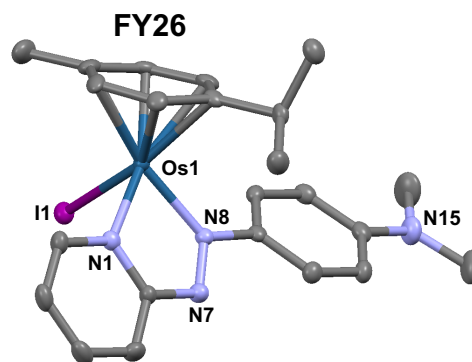
New Insights into the Chemistry of Organo-osmium Anticancer Complexes

Russell J. Needham,* Peter J. Sadler.

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK.

R.Needham.1@Warwick.ac.uk

Exploration of the medicinal chemistry of metal complexes offers potential for the discovery of new drugs with novel mechanisms of action.^[1] For example, half-sandwich osmium(II) phenylazopyridine complexes such as $[\text{Os}(\eta^6\text{-}p\text{-cym})(\text{AZPY-NMe}_2)\text{I}]\text{X}$, exhibit potent anticancer activity. The complex with $\text{X}=\text{PF}_6$ (FY26) is capable of delaying the growth of HCT-116 human colon cancer xenographs in mice,^[2] and is 49× more potent than conventional anticancer drug cisplatin in the 809-cell line screen of the Sanger Institute.^[3] Complex FY26 is relatively inert towards hydrolysis and reactions with DNA. Its intracellular activation mechanism was discovered through labelling the monodentate iodido ligand with radio-isotope ^{131}I . ^{131}I -FY26 was traced *in vitro* and undergoes conversion to the hydroxido-species, $[\text{Os}(\eta^6\text{-}p\text{-cym})(\text{AZPY-NMe}_2)\text{OH}]^+$, in the presence of MCF-7 breast cancer cells.^[4] Dissociation of the iodido ligand occurs in the presence of cellular antioxidants *L*-glutathione and ascorbic acid, which play a key role in its activation. Complex FY26 has a chiral osmium centre and is synthesised as a racemic mixture of two enantiomers. The enantiomers were separated by chiral HPLC, and analyses of their individual toxicities show they have similar activities against cancer cell lines.^[5] Furthermore, its solubility can be drastically improved $>10^4$ -fold by changing X from PF_6 to Cl, enabling better formulation for clinical use. The ^{187}Os isotopically enriched bromido analogue, $[\text{Os}(\eta^6\text{-}p\text{-cym})(\text{AZPY-NMe}_2)\text{Br}]\text{PF}_6$, was synthesised. The ^{187}Os spin $\frac{1}{2}$ -nucleus was readily detected via high res. MS, and ^1H & ^{13}C couplings, and allowed the chemical shift of ^{187}Os to be determined as -4671.3 ppm (relative to OsO_4) by ^1H - ^{187}Os HMBC NMR.^[6]



Acknowledgements: We thank Anglo American Platinum and EPSRC for their support and all our collaborators.

[1] a) R. J. Needham, P. J. Sadler, *A Periodic Table for Life and Medicines. The Periodic Table II: Catalytic, Materials, Biological and Medical Applications*, **2019**, pp 175-201; b) E. J. Anthony, E. M. Bolitho, H. E. Bridgewater, O. W. L. Carter, J. M. Donnelly, C. Imberti, E. C. Lant, F. Lermite, R. J. Needham, M. Palau, P. J. Sadler, H. Shi, F.-X. Wang, W.-Y. Zhang and Z. Zhang, *Chem. Sci.* **2020**, *11*, 12888-12917.

[2] S. D. Shnyder, Y. Fu, A. Habtemariam, S. H. van Rijt, P. A. Cooper, P. M. Loadman and P. J. Sadler, *MedChemComm* **2011**, *2*, 666-668.

[3] J. M. Hearn, I. Romero-Canelón, A. F. Munro, Y. Fu, A. M. Pizarro, M. J. Garnett, U. McDermott, N. O. Carragher and P. J. Sadler, *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, E3800-3805.

[4] R. J. Needham, C. Sanchez-Cano, X. Zhang, I. Romero-Canelón, A. Habtemariam, M. S. Cooper, L. Meszaros, G. J. Clarkson, P. J. Blower and P. J. Sadler, *Angew. Chem. Int. Ed.* **2017**, *56*, 1017-1020.

[5] S. A. Kumar, R. J. Needham, K. Abraham, H. E. Bridgewater, L. A. Garbutt, H. Xandri-Monje, R. Dallmann, S. Perrier, P. J. Sadler and F. Lévi, *Metallomics* **2020**, *13*.

[6] R. J. Needham, I. Prokes, A. Habtemariam, I. Romero-Canelón, G. J. Clarkson and P. J. Sadler, *Dalton Trans.* **2021**, *50*, 12970-12981.

Poster 50

Alumina-based fillers functionalized with polyhedral silsesquioxane units for enhancing the thermal conductivity of polymeric nanocomposites

Roberto Nisticò,^{a*} Massimiliano D'Arienzo,^a Andreia Amighini Alerhush,^a Lorenzo Mirizzi,^a

Sandra Diré,^b Giulia Fredi,^b Andrea Dorigato,^b Emanuela Callone,^b Silvia Mostoni,^a

Barbara Di Credico,^a Roberto Scotti,^a

^a University of Milano-Bicocca, Via R. Cozzi 55, 20125 Milano (MI), Italy.

^b University of Trento, Via Sommarive 9, 38123 Trento (TN), Italy.

roberto.nistico@unimib.it

Overheating represents one of the major causes of the in-service degradation of polymeric formulations, as this class of materials possess an intrinsic low thermal conductivity that limits their employment in several modern applications, ranging from (opto)electronics, photonics, to the tire industry.¹ In order to face this critical issue, several efforts have been dedicated to the design of thermally conductive polymeric nanocomposites, mainly by introducing highly thermally conductive fillers into polymeric matrices.² However, this apparently simple approach hides a huge complexity, which is the necessity of forming a continuous network of thermally conductive fillers crossing the entire composite to achieve an efficient heat transfer. In this context, interfacial phenomena play a major role as they favor the homogeneous distribution of the conductive fillers within the polymer matrix. In a previous study, it has been already verified that the surface functionalization of inorganic fillers (i.e., silica) with Polyhedral Oligosilsesquioxane (POSS) units, a family of hybrid inorganic-organic systems composed of an inorganic core of cage-like silicon oxide and several organic functional groups, significantly improved the dispersion and compatibilization of the inorganic fillers in the polymer matrix.³ Recently, we successfully demonstrated the potentiality in terms of heat transport and mechanical reinforcement of introducing a hybrid filler made by spherical γ -alumina nanoparticles decorated with POSS units at low filler loadings in a polybutadiene polymer.⁴ Here, we extend the investigation by considering the development of a hybrid filler made by anisotropic α -alumina nanorods decorated with POSS units.

[1] Mirizzi, L.; Carnevale, M.; D'Arienzo, M.; Milanese, C.; Di Credico, B.; Mostoni, S.; Scotti, R. *Molecules*, **2021**, *26*, 3555.

[2] Hu, Z.; Zhao, T.; Dong, L.; Zhang, Y. *J. Electron. Mater.* **2022**, *51*, 2308.

[3] D'Arienzo, M.; Redaelli, M.; Callone, E.; Conzatti, L.; Di Credico, B.; Diré, S.; Giannini, L.; Polizzi, S.; Schizzi, I.; Scotti, R.; Tadiello, L.; Morazzoni, F. *Mater. Chem. Front.* **2017**, *1*, 1441.

[4] Mirizzi, L.; D'Arienzo, M.; Nisticò, R.; Fredi, G.; Diré, S.; Callone, E.; Dorigato, A.; Giannini, L.; Guerra, S.; Mostoni, S.; Di Credico, B.; Scotti, R. *Compos. Sci. Technol.* **2023**, *236*, 109977.

Poster 51

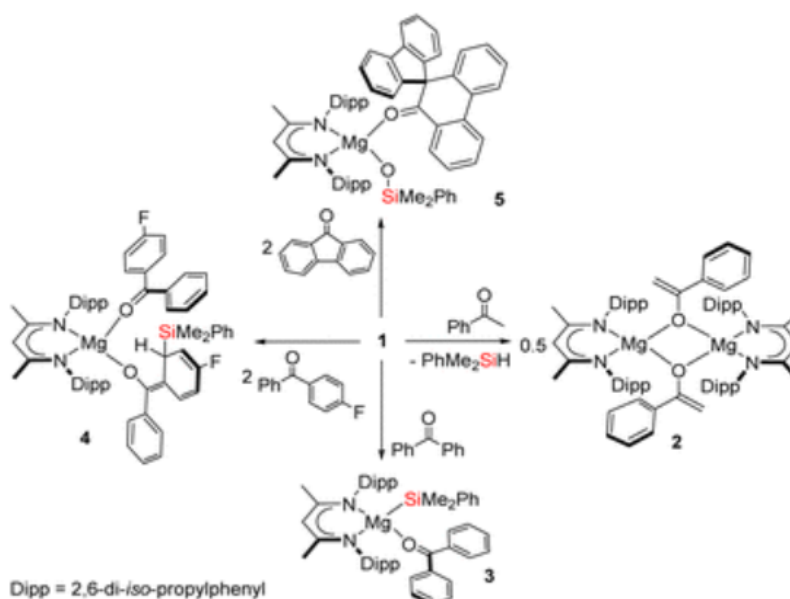
Diverse reactivity of β -diketiminato magnesium silyl towards ketones

Bibian Okokhere-Edeghoghon, Michael S. Hill, * Mary F. Mahon and Claire L. McMullin*

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom

booe20@bath.ac.uk; bibidion2002@yahoo.com

The stoichiometric reactivity of a β -diketiminato (BDI) magnesium silanide (1) towards a variety of commercially available ketones; benzophenone, 9-fluorenone, 4-fluorobenzophenone and acetophenone has been assessed. Benzophenone was found to form an adduct with β -diketiminato (BDI) magnesium silanide, whereas 9-fluorenone produced the corresponding siloxide in a manner reminiscent of the isocyanate reactivity¹, but in which Mg was further coordinated by an apparent product of carbene C-C insertion. The enhanced electrophilicity of 4-fluorobenzophenone led to its deraromatisation by the silyl anion while, in the case of the acetophenone, the silyl group was observed to behave as a base to provide CH deprotonation of the acetophenone and enolate formation.



Scheme 1. Synthesis of compounds 2–5.

[1]. B. Okokhere-Edeghoghon, S.E Neale, M.S Hill, M.F Mahon, CL McMullin Dalton Transactions 51 (1), 136-144.

Poster 52

Oxidative Alkoxy carbonylation of Olefins Catalyzed by Aryl α -diimine/Palladium(II) Complexes

Diego Olivieri,^{a*} Riccardo Tarroni,^b Carla Carfagna^b

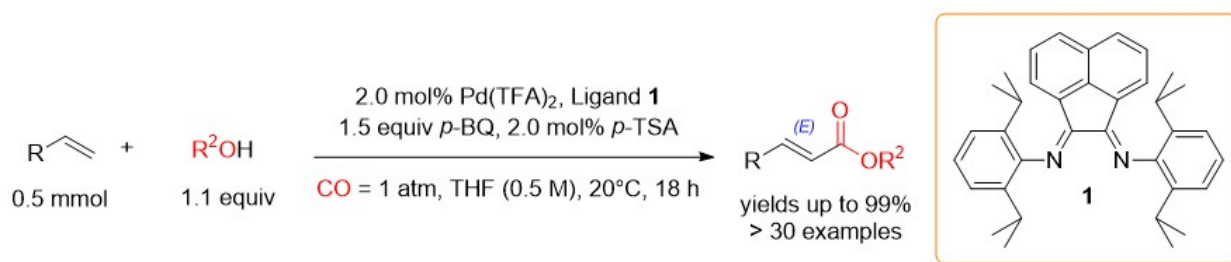
^a Department of Biomolecular Sciences, University of Urbino “Carlo Bo”, Piazza Rinascimento 6, Urbino (PU), Italy. ^b

Department of Industrial Chemistry “T. Montanari”, University of Bologna, Viale Risorgimento 4, Bologna (BO), Italy

diego.olivieri@uniurb.it

Cinnamic acid esters are utilized in cosmetic and pharmaceutical industries,^[1] as they possess a variety of biological activities.^[2] One of the most efficient methods to produce these compounds is through oxidative alkoxy carbonylation of olefins, which allows the coupling of an alkene with carbon monoxide and an alcohol to form the respective α,β -unsaturated ester.^[3] However, only a few examples of this reaction are reported in the literature, often requiring relatively high temperatures or large amounts of alcohol,^[4] and, to the best of our knowledge, detailed mechanistic studies have not been performed so far.

Here we report an efficient and selective oxidative alkoxy carbonylation of olefins, catalyzed by an aryl α -diimine/palladium(II) complex, for the synthesis of cinnamates, utilizing *p*-benzoquinone as an oxidant (Scheme 1). Various *ortho*, *meta* and *para* substituted styrene derivatives, bearing both electron-donating and electron-withdrawing groups, have been successfully employed and different alcohols (primary, secondary, tertiary and polyols) can be utilized. The reaction is completely stereoselective, since only the *trans* isomer is formed, and good to high yields of various cinnamic esters were obtained at room temperature and 1 atm of CO. The catalytic cycle has been investigated by means of experimental mechanistic studies and DFT calculations, highlighting a further role played by the oxidant *p*-benzoquinone, in the final step of the process, which probably allows the reaction to proceed under such mild conditions. Finally, some synthetic applications of the developed reaction are proposed.



Scheme 1 - Aryl α -diimine/palladium(II) catalyzed oxidative alkoxy carbonylation of olefins

[1] Gunia-Krzyżak, A.; Słoczyńska, K.; Popiół, J.; Koczurkiewicz, P.; Marona, H.; Pękala, E. *Int. J. Cosmet. Sci.* **2018**, 40, 356.

[2] N. Kumar, A. Parle. *Pharma Innovation* **2019**, 8, 580.

[3] Zhang, S.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2020**, 49, 3187.

Poster 53

Synthesis of organic sensitizers for water splitting in DS-PEC

Alessandra Pace,^{a,b,c*} Daniele Franchi,^a Massimo Calamante,^{a,b} Alessio Dessì,^a Lorenzo Zani^{*,a},
Gianna Reginato,^a and Alessandro Mordini,^{a,b}

^a Institute of Chemistry of Organometallic Compounds (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy; ^b Department of Chemistry “U. Schiff”, University of Florence, Via della Lastruccia 13, 50019 Sesto Fiorentino, Italy; ^c Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via A. Moro 2, 53100 Siena, Italy. pace3@student.unisi.it, lorenzo.zani@iccom.cnr.it

In a growing global energy demand combined with the excessive use of fossil fuels, renewable sources of energy are considered a good alternative to avoid the use of hydrocarbon deposit.^[1] In this scenario Visible-light-driven splitting of water into oxygen and hydrogen is an attractive way to convert solar energy into fuels: artificial photosynthesis and dye-sensitized photoelectrochemical cells (DS-PECs), have been deeply investigated as a promising route to convert solar energy into renewable hydrogen fuel. A crucial strategy to increase the efficiency of DS-PEC is the optimization of the dye used in the sensitization of nanostructured TiO₂ photoanode that must match with the ruthenium complex used as water oxidation catalyst (WOC).^[2] Our goal is the design, synthesis, and optimization of a metal-free sensitizer having D(donor)- π -A(acceptor) structure and photoelectrochemical properties for applicability in DS-PEC.

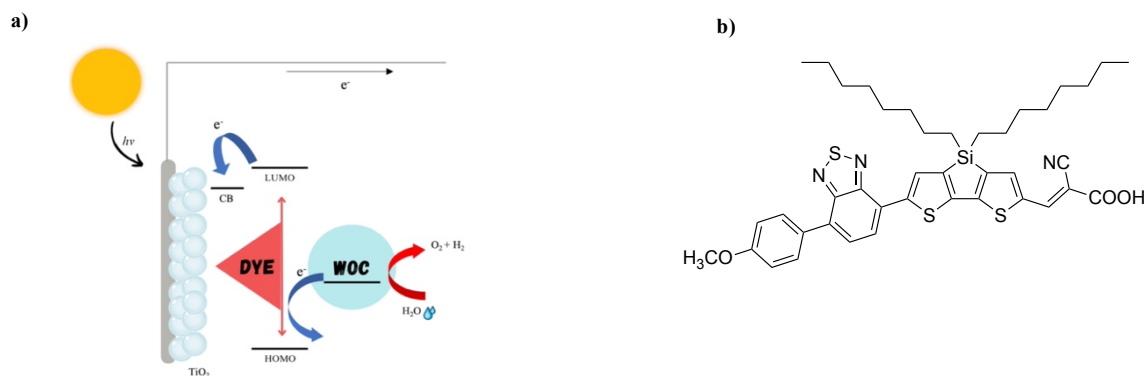


Figure 1. a) DS-PEC; b) Structure of Sensitizers.

In this study, we report the synthesis of the dye **1** (figure), based on a dioctyl-4*H*-silolo[3,2-*b*:4,5-*b'*] dithiophene central cores and having a 2-cyanoacrylic acid as acceptor group and a 4-(4-methoxyphenyl) benzo[*c*] [1,2,5] thiadiazol as donor group. The challenging synthesis was optimized through recent approaches as direct arylation reactions instead of common C-C bond formation by Pd-catalyzed cross coupling reactions.

Acknowledgments: This research was funded by the European Union – NextGeneration EU through the Italian Ministry of Environment and Energy Security, POR H2 AdP MMES/ENEA with CNR and RSE, PNRR - Mission 2, Component 2, Investment 3.5 “Ricerca e sviluppo sull’idrogeno”, CUP: B93C22000630006.

POSTERS

- [1] Zhang, S.; Ye, H.; Hua, J.; Tian, H. *EnergyChem*, **2019**, *1*, 100015.
 [2] Li, H.; Li, F.; Wang, Y.; Bai, L.; Yu, F.; Sun, L. *Chempluschem*, **2016**, *81*, 1056.

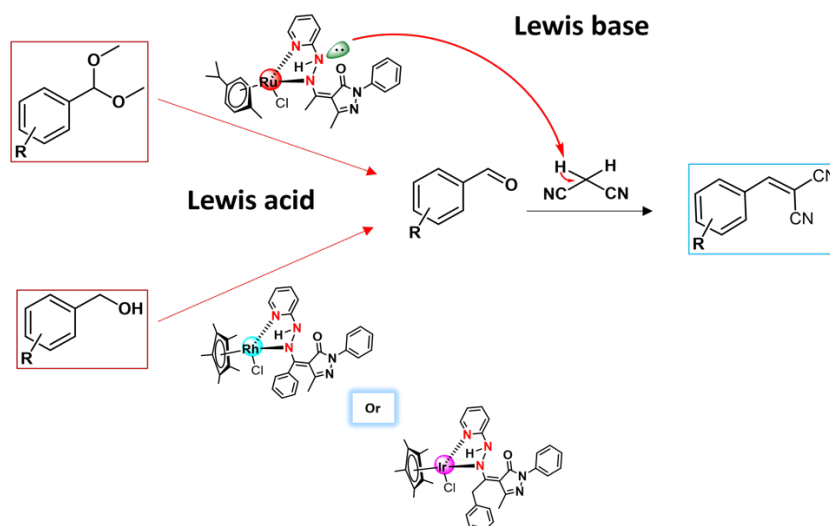
Poster 54

Ru(II), Rh(III) and Ir(III)- Arene Complexes containing Pyrazolone-Based Hydrazones Ligands as suitable catalysts for tandem Knoevenagel condensation reactions

Noemi Pagliaricci,^{a*} Riccardo Pettinari,^a Fabio Marchetti,^b Claudio Pettinari,^b Anirban Karmakar,^c
 Armando J.L. Pombeiro.^c

^a School of Pharmacy, Via Madonna delle carceri 1, 62032 Camerino (MC), Italy; ^b School of Science and Technology, Via Madonna delle carceri 1, 62032 Camerino (MC), Italy; ^c Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais, Lisbon, Portugal. noemipagliaricci@unicam.it

The formation of carbon–carbon bonds is a quest that has required a lot of research throughout the last 125 years of history of chemistry. These new bonds are the key to produce a wide variety of advanced products, with great impact in every aspect of the human life, and the Knoevenagel condensation reaction is one of the most important methodologies for this purpose. All the Knoevenagel reactions are performed with nitrogen-based catalysts which are able to deprotonate the alpha-carbon of one of the two starting material.[1] Indeed, some studies show that the presence of Schiff base as ligands for metal complexes, has effectiveness in many catalytic processes since has been observed that the -NH moiety play an important role in involving atom-transfer intermediate species. According to what reported, in this work we exploited the presence of pyrazolone-based hydrazones as ligands for complexes having, in addition, the synergistic effect of a metal atom, which can behave as a Lewis-acid centre, able to promote tandem reactions where the Knoevenagel condensation is one of the step. In this research project we report the synthesis of several Ru(II), Rh(III) and Ir(III) complexes containing hydrazone-ligands for which we explored the catalytic activity toward Knoevenagel condensation reaction starting from different substrates in one-pot tandem reaction. The starting materials change according to the different metal centre consistently with their ability to catalyse either deacetalization or oxidation reactions (Figure 1).



POSTERS

[1] Trost, B. M.; Frederiksen, M. U.; Rudd, M. T. *Angew. Chem. Int. Ed.* **2005**, *44*, 6630.

Poster 55

Palladium-Catalyzed Arylation of Hydantoins with Aryl Chlorides Enabled by Ylide-Functionalized Phosphines (YPhos)

Florian Papp,^a Daniel Sowa Prendes,^a Sourav Manna,^a Ann-Katrin Seitz,^a Sofiya Kostiukovska,^a
Julian Löffler,^b Viktoria H. Gessner,^{b*} Lukas J. Gooßen^{a*}

^aFakultät Chemie und Biochemie, Organische Chemie I, Ruhr Universität Bochum, Universitätsstr. 150, 44801 Bochum, Germany; ^bFakultät Chemie und Biochemie, Anorganische Chemie II, Ruhr Universität Bochum, Universitätsstr. 150, 44801 Bochum, Germany

The hydantoin moiety is an important structural motif present in various pharmaceuticals like the anticonvulsant phenytoin. The arylation of protected hydantoins was achieved by the group of Clayden with aryl iodides applying Xantphos as ligand.¹ However, an arylation with cheap and broadly abundant aryl chlorides was not achieved. In previous work, palladium catalysts bearing highly electron-rich, bulky Ylide-functionalized phosphine (YPhos) ligands were found to efficiently promote arylations with aryl chlorides at low temperatures.^{2–5} In this work⁶, YPhos ligands enabled the arylation of *N*-protected hydantoins in good to excellent yields (Figure 1). By adjustment of the YPhos ligand, a selective monoarylation of a 5-unsubstituted hydantoin was achieved. This has opened up an expedient access to a wide variety of hydantoins, including derivatives of the anticonvulsant drugs phenytoin and mephenytoin, sequential diarylations and arylation-alkylation sequences in combination with stepwise deprotection strategies.

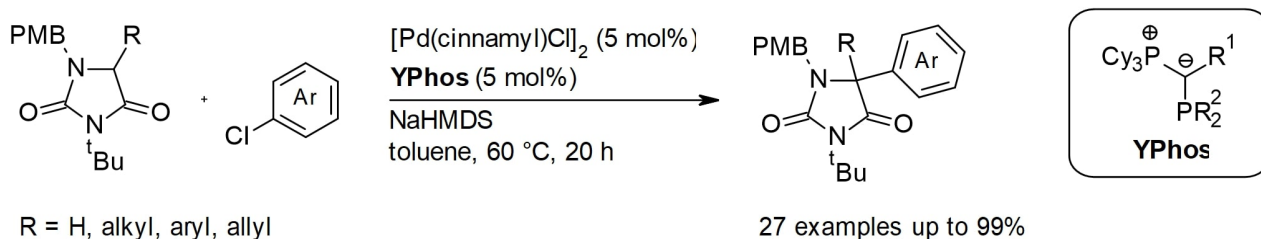


Figure 1. Pd-catalyzed arylation of hydantoins with aryl chlorides.

[1] Fernández-Nieto, F.; Mas Roselló, J.; Lenoir, S.; Hardy, S.; Clayden, J. *Org. Lett.*, **2015**, *17*, 3838.

[2] Scherpf, T.; Schwarz, C.; Scharf, L. T.; Zur, J.-A.; Helbig, A.; Gessner, V. H. *Angew. Chem. Int. Ed.*, **2018**, *57*, 12859.

[3] Weber, P.; Scherpf, T.; Rodstein, I.; Lichte, D.; Scharf, L. T.; Gooßen, L. J.; Gessner, V. H. *Angew. Chem. Int. Ed.*, **2019**, *58*, 3203.

[4] Hu, Z.; Wei, X.; Handelsmann, J.; Seitz, A.; Rodstein, I.; Gessner, V. H.; Gooßen, L. J. *Angew. Chem. Int. Ed.*, **2021**, *60*, 6778.

[5] Goebel, J. F.; Löffler, J.; Zeng, Z.; Handelsmann, J.; Hermann, A.; Rodstein, I.; Gensch, T.; Gessner, V. H.; Gooßen, L. J. *Angew. Chem. Int. Ed.*, **2023**, e202216160.

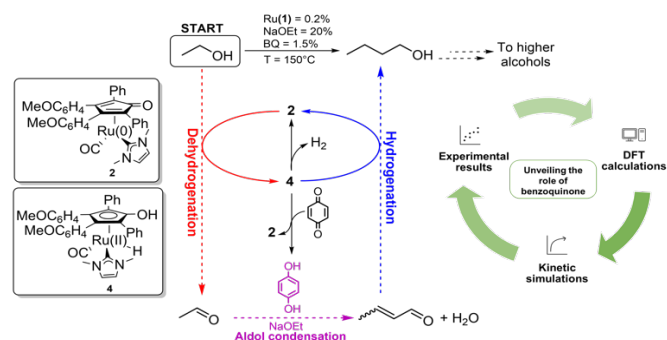
Poster 56

Experimental and theoretical study on the homogeneous catalyzed Guerbet reaction with ruthenium-NHC complexes

Andrea Piazzì,^{a,b*} Francesco Calcagno,^{a,b} Ivan Rivalta,^{a,b} Alessandro Messori,^{a,b} Anna Gagliardi,^{a,b} Cristiana Cesari,^{a,b} Tommaso Tabanelli,^{a,b} Rita Mazzoni,^{a,b} Fabrizio Cavani,^{a,b}

^aDepartment of Industrial Chemistry "Toso Montanari", University of Bologna, Viale Risorgimento 4 40136 Bologna, Italy. ^bCenter for Chemical Catalysis – C3, University of Bologna, Viale Risorgimento 4 40136 Bologna, Italy.

The benzoquinone was found as an effective co-catalyst in the ruthenium/NaOEt-catalyzed Guerbet reaction,[1-2] which is widely investigated as a promising process for the conversion of bioethanol into more valuable chemicals such as n-butanol.[3-4] The co-catalyst behavior is here investigated through experimental and computational methods. The experimental results show an increase in both ethanol conversion (+25%) and higher alcohols yields (+18%), while the side-production of molecular hydrogen is reduced by 13%. DFT calculations were performed to investigate two hypotheses related to this kinetic effect: i) a hydrogen storage mechanism and ii) a basic co-catalysis of 4-hydroxiphenolate. The most promising outcomes were obtained following the latter hypothesis, where a new mixed mechanism for the aldol condensation step involves hydroquinone (*i.e.* the reduced form of benzoquinone) as an alternative proton source to ethanol. This mechanism was found to be more favorable compared to the aldol condensation in the absence of additive, therefore it could positively affect the overall process' kinetics.



Scheme 1. Mechanistic insights on the role of benzoquinone in the Ru/NaOEt catalytic

A select group of phenol derivatives were tested as co-catalysts in the Guerbet reaction. A boost in process performance was recorded for each of them, suggesting that an aromatic acid (stronger than ethanol) could effectively improve the reaction kinetics. This hypothesis was further verified by conducting theoretical kinetic simulations based on the DFT computations: the experimental outcomes were well replicated only when the mixed mechanism was considered in the simulated kinetic network.

[1] Mazzoni, R.; Cesari, C.; Zanotti, V.; Lucarelli, C.; Tabanelli, T.; Puzzo, F.; Passarini, F.; Neri, E.; Marani, G.; Prati, R.; Viganò, F.; Conversano, A.; Cavani, F. *ACS Sustain. Chem. Eng.* **2019**, 7, 224.

[2] Cesari, C.; Gagliardi, A.; Messori, A.; Monti, N.; Zanotti, V.; Zacchini, S.; Rivalta, I.; Calcagno, F.; Lucarelli, C.; Tabanelli, T.; Cavani, F.; Mazzoni, R. *J. Catal.* **2022**, 405, 47.

POSTERS

[4] Messori, A.; Gagliardi, A.; Cesari C.; Calcagno F.; Tabanelli T.; Cavani F.; Mazzoni R. *Catalysis Today* **2023**. <https://doi.org/10.1016/j.cattod.2023.01.010>

Poster 57

Steric and Electronic Effects Responsible for N,O- or N,N-Chelating Coordination of Pyrazolones Containing a Pyridine Ring in Ruthenium Arene Systems

Lorenzo Pietracci,^a Riccardo Pettinari,^{b*} Alessia Tombesi,^b Fabio Marchetti,^a Claudio Pettinari,^b Agustín Galindo, Farzaneh Fadaei-Tirani, Mouna Hadiji, and Paul J. Dyson

^a School of Science and Technology, Via S. Agostino 1, 62032 Camerino (MC), Italy.

^b School of Pharmacy, Via S. Agostino 1, 62032 Camerino (MC), Italy.

lorenzo.pietracci@unicam.it

Half-sandwich arene-Ru(II) complexes have been found as very interesting antiviral, antibiotic, and anticancer agents.¹ They represent potential alternatives to platinum-based drugs due to several attractive properties such as biocompatible ligand exchange rates, covalent binding with DNA and/or proteins, redox-accessible oxidation states, combined with a low toxicity.² In this study we have shown that in pyrazolone ligands containing a pyridine ring, the presence of a phenyl in position 3 of the pyrazole ring in HL^{py,ph} in place of a methyl as in HL^{py,me} induces electronic and structural changes that determine the preference for a bidentate *N,O*-coordination, instead of the *N,N*-coordination observed in ruthenium complexes with HL^{py,me}. The presence of an acyl moiety in the ligand HQ^{py,CF₃} also leads to a preference for an *N,N*-chelated coordination. Different *N,N* and *N,O* coordination of similar pyrazolones and acylpyrazolones ligands were investigated with DFT calculations. Anticancer activities were tested also, on several cell lines: A2780, A2780cis and HEK293T.³



Figure 1

[1] Yan, Y. K.; Melchart, M.; Habtemariam, A.; Sadler, P. J. *Chem. Commun.* **2005**, 4764.

[2] Simović, A. R.; Masnikosa, R.; Bratsos, I.; Alessio, E. *Coord. Chem. Rev.* **2019**, 398, 113011.

POSTERS

Agustín Galindo, Farzaneh Fadaei-Tirani, Mouna Hadiji, and Paul J. Dyson, *Organometallics* **2023**, 42 (13), 1495-1504.

Poster 58

Continuous organometallic reactions in flow assisted by Deep Eutectic Solvents

Andrew Platten,^{a*} Eva Hevia,^a

^a Department für Chemie und Biochemie, Universität Bern, CH3012, Bern, Switzerland,

andrew.platten@unibe.ch

Grignard and organolithium reagents are found widely in modern chemistry, with most syntheses of medicinal and agrochemical products involving one or more steps, utilizing Grignards or organolithiums. Yet, despite their immense popularity, their use has often been hampered by their requirement for an inert atmosphere along with dried solvents and cryogenic temperatures (-78°C). We, along with others, have reported the use of Deep Eutectic Solvents (DES) to overcome these issues¹. Formed by the combination of a hydrogen bond acceptor (e.g. choline chloride) and hydrogen bond donor (e.g. glycerol), DES are recognized as inexpensive, environmentally friendly, and tunable solvents with growing applications². In this work we apply the use of DES to flow chemistry showing how organolithium and Grignard reagents can be used in segmented flow for the addition to ketones and imines, whilst showing improved moisture tolerance and clogging resistance (figure 1).³

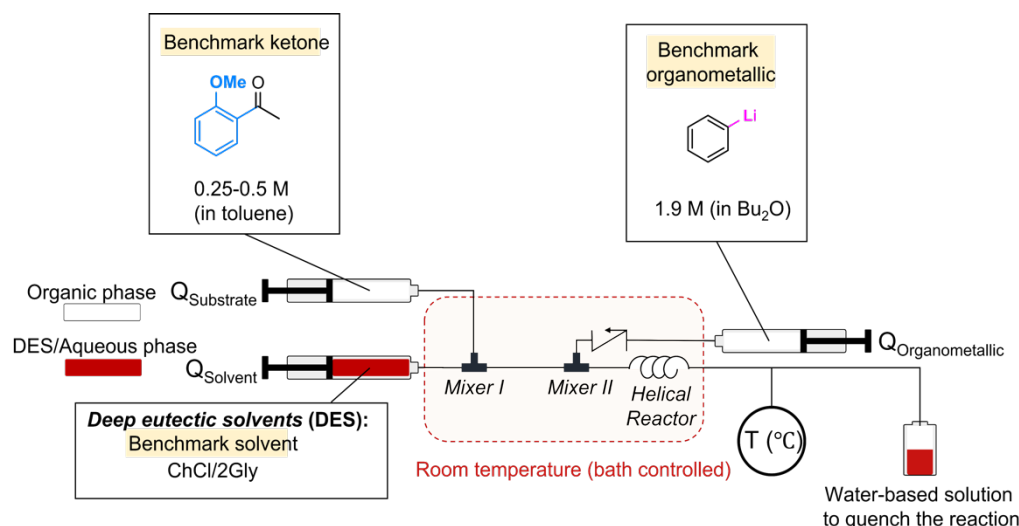


Figure 1

- [1] J. García-Álvarez, E. Hevia. *Angew. Chem. Int. Ed.*, **2014**, 53, 5969–5973; E. Hevia. *Angew. Chem. Int. Ed.*, **2016**, 55, 16145; S. E. García-Garrido, A. Presa Soto, E. Hevia, J. García-Álvarez. *Eur. J. Inorg. Chem.*, **2021**, 3116–3130.
 [2] A. P. Abbott, G. Capper, D. L. Davies, H L. Munro, R K. Rasheed, V Tambyrajah. *Chem Commun.*, **2001**, 2010-201; J. R. Sangor. *Chem Rev*, **2021**, 121 (3), 1232-1285.

Poster 59

Hydrogenation of esters promoted by phosphine-NHC manganese catalyst

Romane Pointis,* Karim Azouzi, Lucie Pedussaut, Ruqaya Buhaibeh, Yves Canac, Dmitry A. Valyaev, Stéphanie Bastin, Jean-Baptiste Sortais

LCC-CNRS, Université de Toulouse, 205 route de Narbonne, 31077 Toulouse cedex 4, France.

Alcohols are highly valuable synthetic intermediates for the production of pharmaceutical, agrochemical and fine chemical products. Therefore, carboxylic esters, considered as an important class of natural products, are interesting candidates to produce alcohols through their reduction. Hydrogenation catalyzed by transition metal complexes is a well-known method for the reduction of carboxylic esters. Although noble metals are known to be highly efficient in this category of transformation, their scarcity and potential toxicity have prompted chemists to seek a more sustainable alternative: the use of more environmentally friendly and inexpensive Earth-abundant transition metal of the first row such as iron and manganese.¹ In the literature, the catalysts developed so far are mainly based on tridentate ligands involved in a metal- ligand cooperativity.² In this context, we have focused our research on the development of a catalytic system based on a manganese complex carrying a bidentate NHC-phosphine ligand, which is not a priori capable of inducing metal-ligand cooperativity. The results obtained in the hydrogenation reactions of carboxylic esters are presented here. A series of 28 examples of ester were hydrogenated at a catalyst loading of 0.5 mol% in the presence of 50 bar of H₂ pressure and 10 mol% of KHBet₃ at 100 °C.³ All the results will be detailed in the present communication.

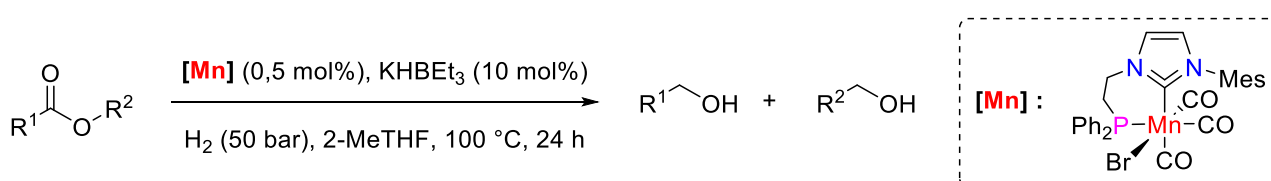


Figure 1

[1] “Homogeneous Hydrogenation with Non-Precious Catalysts”: J. F. Teichert, Wiley, 2019.

[2] J.-B. Sortais, R. Buhaibeh, Y. Canac, Manganese-Catalyzed Hydrogenation and Hydrogen Transfer Reactions in Manganese Catalysis in Organic Synthesis (Ed.: J.-B. Sortais), Wiley-VCH GmbH, Weinheim, Germany, 2021, pp.39-66.

POSTERS

Poster 60

Enantioselective Synthesis of Arylglycines via Pd-Catalyzed Coupling of Schöllkopf Bis-Lactim Ethers with Aryl Chlorides

Daniel Sowa Prendes, Florian Papp, Nagesh Sankaran, Nardana Sivendran, Lukas J. Gooßen*

Ruhr-Universität Bochum, Universitätsstraße 150, 44801 Bochum (Deutschland).

lukas.goossen@ruhr-uni-bochum.de

Chiral α -aryl amino acids are important structural motifs present in various pharmaceuticals like the penicillin derivative amoxicillin. Usually, these important compounds are synthesized by asymmetric variants of the Strecker synthesis¹ or the Petasis-Borono Mannich reaction², which are however limited to the use of toxic cyanide sources or prefunctionalized expensive boronic acids. For this reason, in the last decades the direct arylation of glycine derivatives was explored, while only few examples for the asymmetric synthesis of arylglycines are reported.^{3–6} In previous works, the group of Barrett explored a diastereoselective aryne-mediated arylation of the Schöllkopf bis-lactim ether using aryl halides and *n*/sec-BuLi at low temperatures.⁷ This compound class has now been made accessible from abundant aryl chlorides by a Pd-catalyzed Schöllkopf-type amino acid synthesis. In the presence of the catalyst methylnaphthyl(XPhos)-palladium bromide, the base lithium 2,2,6,6-tetramethylpyrrolidide and the additive ZnCl₂, bis-lactim ethers were efficiently arylated at room temperature, reaching yields of 95% and diastereoselectivities of 98:2. Subsequent hydrolysis gave the corresponding arylglycines in high enantiomeric excess and arylation-alkylation pathways enabled the synthesis of quaternary amino acid derivatives.

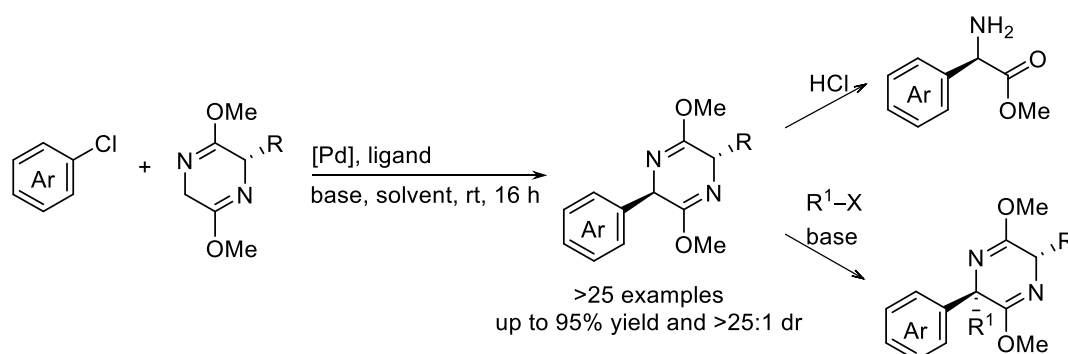


Figure 1: Pd-catalyzed asymmetric arylation of the bis-lactim ether with aryl chlorides.

- [1] Wang, J.; Liu, X.; Feng, X. *Chem. Rev.* **2011**, *111* (11), 6947–6983.
- [2] Candeias, N. R.; Montalbano, F.; Cal, P. M. S. D.; Gois, P. M. P. *Chem. Rev.* **2010**, *110* (10), 6169–6193.
- [3] Beenen, M. A.; Weix, D. J.; Ellman, J. A. *J. Am. Chem. Soc.* **2006**, *128* (19), 6304–6305.
- [4] Chen, J.; Lu, X.; Lou, W.; Ye, Y.; Jiang, H.; Zeng, W. *J. Org. Chem.* **2012**, *77* (19), 8541–8548.
- [5] Zhang, F.; Sun, H.; Song, Z.; Zhou, S.; Wen, X.; Xu, Q.-L.; Sun, H. *J. Org. Chem.* **2015**, *80* (9), 4459–4464.
- [6] Demory, E.; Farran, D.; Baptiste, B.; Chavant, P. Y.; Blandin, V. *J. Org. Chem.* **2012**, *77* (18), 7901–7912.

POSTERS

Poster 61

Designing polymerizable ligands for luminescent metallapolymers

Eleonora Previati,^{a,b*} Giulia Vigarani,^b Joshua J. Armstrong,^c Anna De Carlonis,^b Stefano Stagni,^b

^a Department of Applied Science and Technology, C.so Duca degli Abruzzi 24, 10129 Turin (TO), Italy.

^b Department of Industrial Chemistry “Toso Montanari”, Viale Risorgimento 4, 40136 Bologna (BO), Italy.

^c Department of Chemistry, Curtin University Bentley, Kent Street, 6102 Perth, Australia.

eleonora.previati@polito.it

Luminescent metallapolymers have recently gained great interest due to the possibility of endowing polymer materials with the bright and often color tunable phosphorescent emission typical of some specific families of transition metal complexes chemically bounded to the solid matrix.¹ In this context, we designed a series of “polymerizable ligands” capable of coordinating a metal center and, at the same time, being able to copolymerize with methacrylic monomers. To this end, we equipped three well-known diimine ligands,^{2,3} with a polymerizable styryl unit. The final Ir-based metallapolymers displayed intense phosphorescence, with emission colors spanning from green to orange depending on the nature of the ancillary ligand (Figure 1). In all cases, the luminescence performances were superior to those displayed by the corresponding mononuclear “model” complexes. These promising results pave the way for the application of this new class of hybrid materials as Luminescent Solar Concentrators for the photovoltaic technology and/or to solid state lighting.

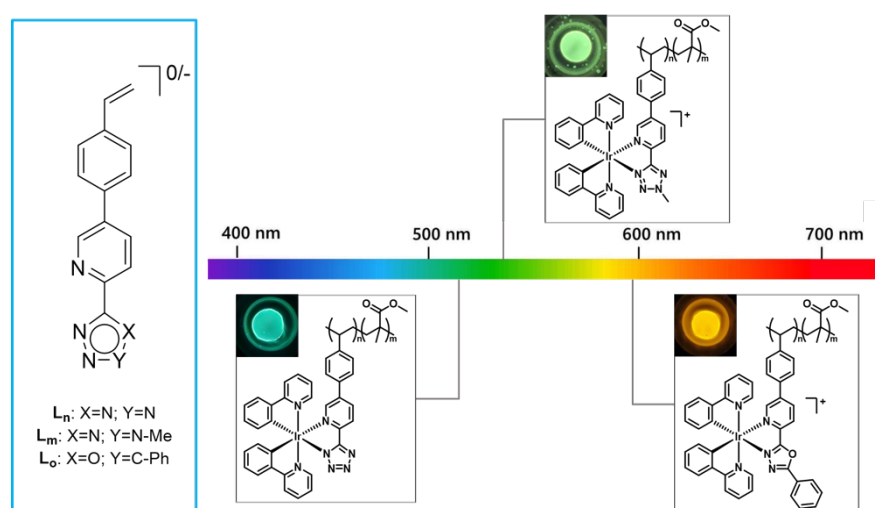


Figure 1

[1] Ho, C. L.; Wong, W. Y. *Coordination Chemistry Reviews* **2011**, 255, 2469.

[2] Stagni, S.; Colella, S.; Palazzi, A.; Valenti, G.; Zacchini, S.; Paolucci, F.; Marcaccio, M.; Albuquerque, R. Q.; Cola, L. D. *Inorganic Chemistry* **2008**, 47, 10509.

POSTERS

Acknowledgments: PhD programme funded by the European Union in the framework of Next Generation EU and PNRR.

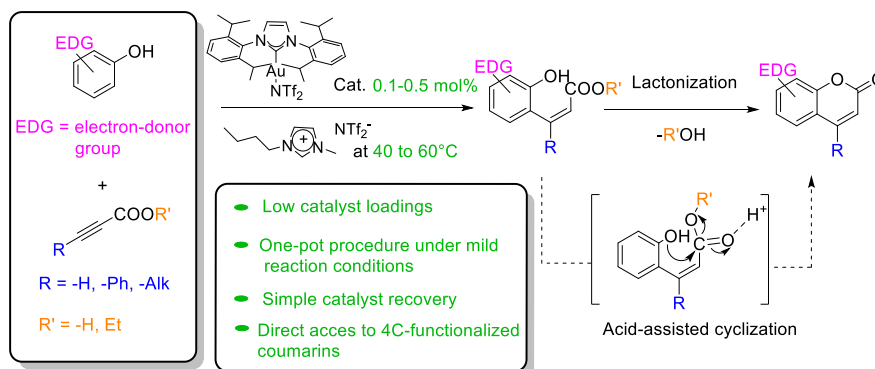
Poster 62

Direct coumarin synthesis by Au(I)/Au(III)-catalyzed hydroarylation of alkynes in ionic liquids

F. Ravera,^a P. Bax,^a S. Bonfante,^a D. Bourissou^b, A. Biffis^{*a,c}

^a Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, 35131 Padova; ^b CNRS/Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR, 5069), 31062 Cedex 09 Toulouse; ^c Consorzio per le Reattività Chimiche e la Catalisi (CIRCC), c/o Università di Padova, via Marzolo 1 35131 Padova
andrea.biffis@unipd.it

Modern organic industry is constantly seeking new methodologies for more sustainable and atom-economic pathways to access relevant organic scaffolds for technologic applications. Under this framework, catalysis has always exploited a substantial role in order to assist both the ecologic transition and the growing demand of fine chemicals, like pharmaceuticals and pesticides, due to the increase of population. In 2019, we have described a highly efficient catalytic system for the direct hydroarylation of alkynes with electron-rich (hetero)arenes.^{1,2} The system is based on a gold(I) cationic complex dissolved in a suitable ionic liquid. We now report on the application of this catalytic system to the direct synthesis of coumarins (Figure 1), a class of compounds with extensive applications in diverse fields such as medicine, fluorescence tagging, paint additive etc. Optimized reaction protocols have been developed, both for terminal and substituted propiolic acids and esters as substrates. Synthetically useful yields under mild reaction conditions have been recorded with down to 0.1 mol% gold catalyst. Intramolecular variants of the reaction have been also investigated, in which the amount of catalyst can be further reduced down to 0.01 mol%. Under this conditions we also evaluated the effect of the oxidation state at gold: P,C-cyclometalated gold(III) complexes³ have been used as a comparison. The effect of the nature of the acidic additive and of the ionic liquid was studied as well. Finally, studies towards the application of this reaction to the selective chemical modification of tyrosine-containing peptides and to the valorization of (poly)phenols derived from biomass are currently underway and will be reported in due course.



POSTERS

- [1] Blons, C.; Baron, M.; Biffis, A. *Eur. J. Org. Chem.* **2019**, 10, 1712–1721.
 [2] Baron, M.; Biffis, A. *Eur. J. Org. Chem.* **2019**, 3687–3693.
 [3] Blons, C.; Mallet-Ladeira, S.; Amgoune, A.; Bourissou D. *Angew. Chem. Int. Ed.* **2018**, 57, 11732–1173.

Poster 63

Synthesis and characterization of luminescent copper(I) complexes

Chiara Reviglio,^{a*} Luca M. Cavinato,^b Claudia Barolo,^a Rubén D. Costa,^b Claudio Garino^a

^a Department of Chemistry, University of Turin, Via Giuria 7, 10125 Turin, Italy.

^b Chair of Biogenic Functional Materials, Technical University of Munich, Schulgasse 22, 94315 Straubing, Germany.

chiara.reviglio@unito.it

Light-Emitting Electrochemical Cells (LECs) are solid-state lighting devices, born as economic and sustainable alternatives to OLEDs. Their operational mode is based on the presence of an ionic electroluminescent material in an ionic environment sandwiched between two electrodes. The luminescent material can be, among the others, an ionic transition metal complex (iTMC-LECs).¹ LECs are seen as good candidates for large-area white-light emitting sources for different applications.² Currently, the main limit is the lack of affordable blue emitters. Indeed, blue-LECs have been realized using Ir-iTMCs, but iridium suffers from poor availability and high cost. Research has identified copper, a more abundant and cheaper metal, as the most promising alternative. Recently, Costa and co-workers succeeded in implementing a multivariate analysis method to identify the first blue-emitting $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ complex which can be used in this kind of application. This heteroleptic copper(I) complex is based on Xantphos as $\text{P}^{\wedge}\text{P}$ ligand and on a pyridine-pyrazole as $\text{N}^{\wedge}\text{N}$ ligand. Its experimental thin-film and device performance are in good agreement with the model.³ Herein we present the synthesis and the characterization of a series of complexes obtained modifying the pyridine moiety of the $\text{N}^{\wedge}\text{N}$ ligand (Figure 1). The structural characterization has been performed by NMR and XRD techniques, while the photophysical properties have been investigated through UV-Vis absorption and emission spectroscopies (Figure 1). Cyclic voltammetry has been used to test the electrochemical behavior.

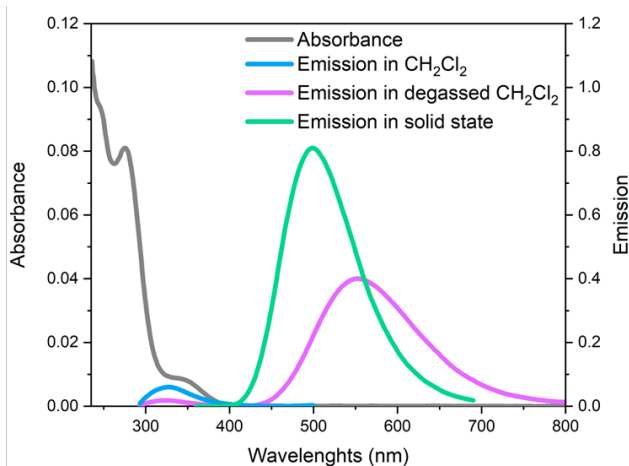
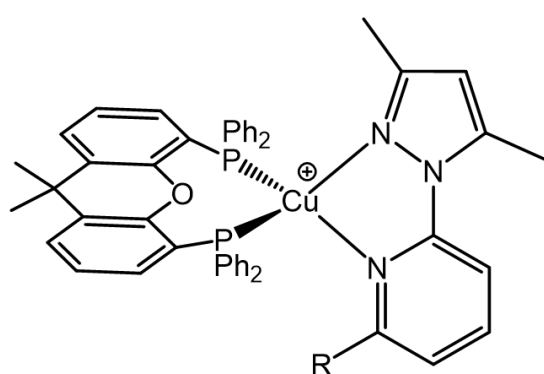


Figure 1. Chemical structure and photophysical properties of synthesized complexes

POSTERS

[3] Cavinato, L. M.; Wölfl, S.; Pöthig, A.; Fresta, E.; Garino, C.; Fernandez-Cestau, J.; Barolo, C.; Costa, R. D. *Adv. Mater.* **2022**, *34*, 2109228.

Poster 64

Synthesis and characterization of novel $\{\text{Ru}(\text{II})(\eta^5\text{-C}_5\text{H}_5)\}$ metallodrugs containing N-donor heterocyclic ligands

Daphne Romani,^a Ricardo G. Teixeira,^b Andreia Valente.^b

^a School of Pharmacy, Via S. Agostino 1, 62032 Camerino (MC), Italy; ^b Centro de Química Estrutural and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.

daphne.romani@unicam.it

$\text{Ru}(\eta^5\text{-cyclopentadienyl})$ complexes are a well established class of metal-organic compounds, particularly renowned for their strong activity towards different cancer cell lines.^{1,2} Our study was focused on the design and development of new metallodrugs with the general formula $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{L})][\text{X}]$, where L is an N-heteroaromatic ligand, specifically a 2,2' bipyridine or 1,10'-phenantroline derivative, and X is the CF_3SO_3 anion (Figure 1). We obtained a series of novel ionic compounds in high yields and purity, with excellent stability in cellular medium. All complexes have been fully characterized via spectroscopic methods and elemental analysis. Biological studies are currently in process for the evaluation of the anticancer activity.

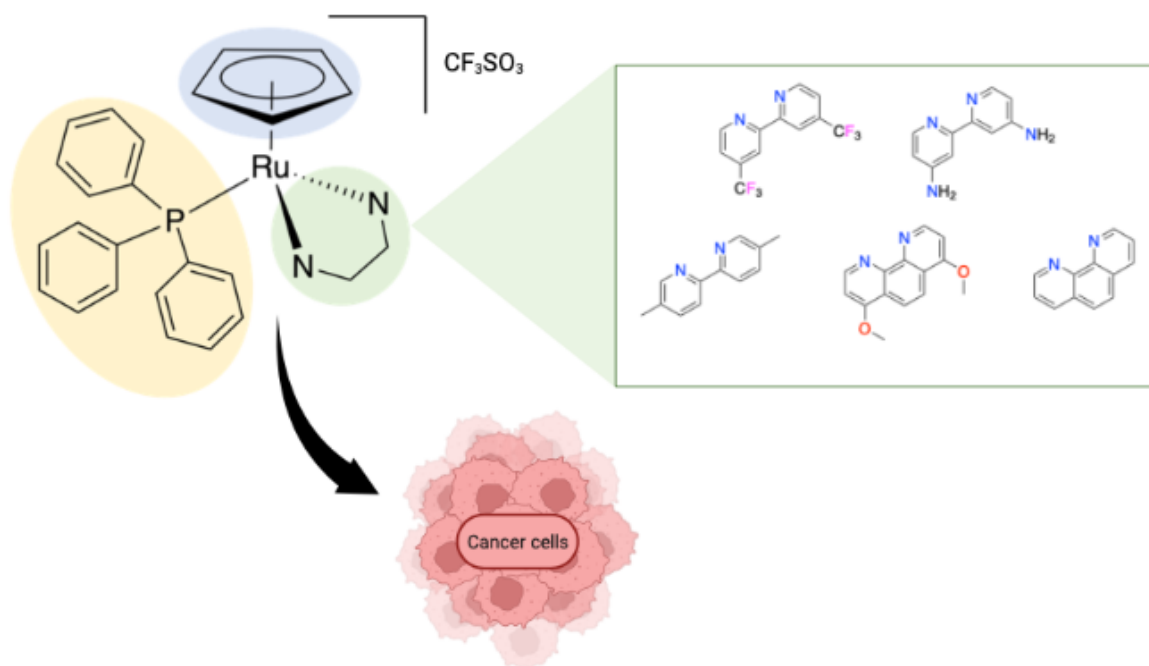


Figure 1

POSTERS

Poster 65

Photocatalytic oxidation of Lignin models using V^V-aminotriphenolate complex

Fátima Sanz Azcona^a, Margarita Escudero-Casao^a, Laura Mucchi^a, Giulia Licini^{a*}

^a Department of Chemical Sciences, CIRCC Padova Unit, University of Padova, via Marzolo 1, 35131 Padova (PD), Italy.

The growing shortage of fossil resources leads to the search of a "greener" alternative for high-value chemicals production. The exploitation of biomass waste materials, in particular lignin, is proposed as a valid solution for the replacement of current non-renewable sources. However, the complex and irregular structure of this biopolymer difficult the obtention of target aromatic organic molecules. Most of the traditional lignin degradation catalytic methods use harsh conditions without reaching high levels of selectivity. However, in recent years photocatalysis in combination with earth-abundant metal catalyst has emerged as a promising methodology for the selective depolymerization of lignin under milder conditions.¹

Our goal for this communication is to present the aerobic C-C bonds oxidative cleavage of Lignin models catalysed by aminotriphenolate complexes of vanadio² under visible light at room temperature. Under these conditions, vicinal diols, β -1 and β -O-4 lignin models have been studied, affording high-value aromatic products as carbonyl compounds (aryl aldehydes, aryl carboxylic acids, aryl formates) or phenols with high selectivity. Future optimization and improvements of our catalytic system will determinate if it could be used on the effective depolymerization of lignin itself.

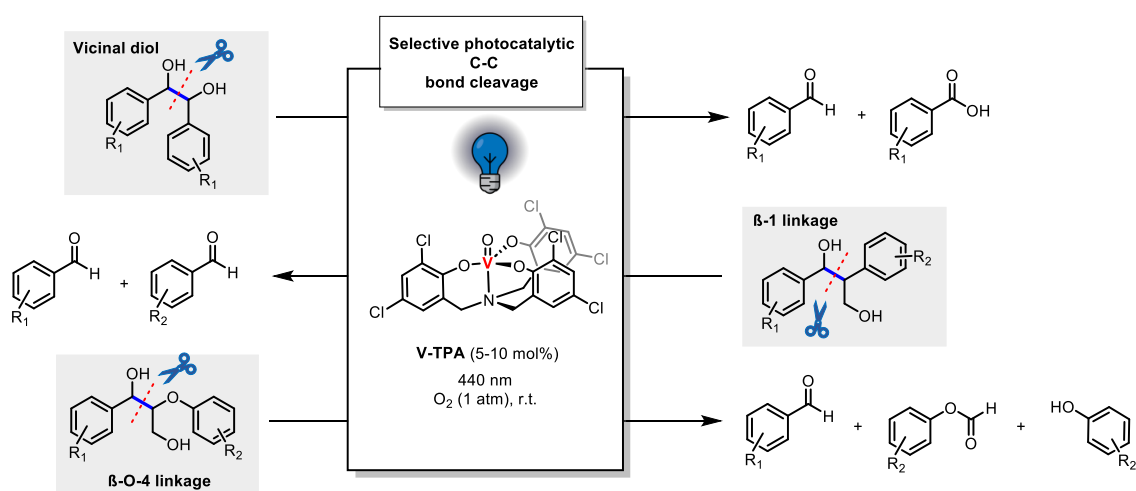


Figure 1. Photocatalytic aerobic C-C bond oxidative cleavage of lignin models.

[1] Wu, X.; Luo, N.; Xie, S.; Zhang, H.; Zhang, Q.; Wang, F.; Wang, Y. Chem. Soc. Rev., 2020, 49, 6198-6223

POSTERS

Poster 66

Synthesis, characterization, and catalytic activity of a new series of NHC-AuX and NHC-AuX₃ complexes

Nicola Sargentoni,^{a*} Rossana Galassi,^a Lorenzo Luciani,^a Andrea Ienco,^b Gabriele Manca,^b Matthias Rudolph,^c A. Stephen K. Hashmi^c

^a University of Camerino, School of Science and Technology, Chemistry Section, Via Madonna delle Carceri, Camerino, I-62032, Italy.

^b Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici, Sesto Fiorentino, Italy

^c Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.

nicola.sargentoni@unicam.it

Besides of phosphane complexes, N-heterocyclic carbene (NHC) complexes of gold(I) and gold(III) have become, among the most important protagonists as catalysts for the synthesis of organic molecules. Most often they are employed as homogeneous catalysts for the activation of π -bonds towards a nucleophilic attack.¹ NHC-gold(I) chloride complexes are stable, convenient and readily available pre-catalysts that normally are activated by silver salts as chloride scavengers to display or enhance their catalytic activity.² In the case of NHC-gold(III) trichloride catalysts, uncertainties still exist regarding the actual structure and even the oxidation state of the catalytic species since the presence of a highly donating chlorido ligand, more than the oxidation state, seems to be responsible for the observed selectivity.³ In this work, starting from [AuCl(IME₂)] (a) and [AuCl(IBnMe)] (b) (Figure 1, left), metathesis with sodium iodide or sodium bromide to get NHC-Au(I)X and their oxidation to get NHC-Au(III)X₃ (X = Cl, Br or I) were performed. These complexes were then tested as catalysts for the cycloisomerization of 4-methoxy-N-(prop-2-yn-1-yl) benzamide^{4a} (Figure 1, right). After 24 hours at a catalysts load of 1 mol% no conversion was observed for the complexes NHC-Au(I)X, NHC-Au(III)Br₃ and NHC-Au(III)I₃. In contrast, the [AuCl₃(IBnMe)] were found to be active and a quantitative 5-*exo*-dig cyclization of the N-propargyl amide^{4b} was surprisingly observed for this reaction in a period of a week.

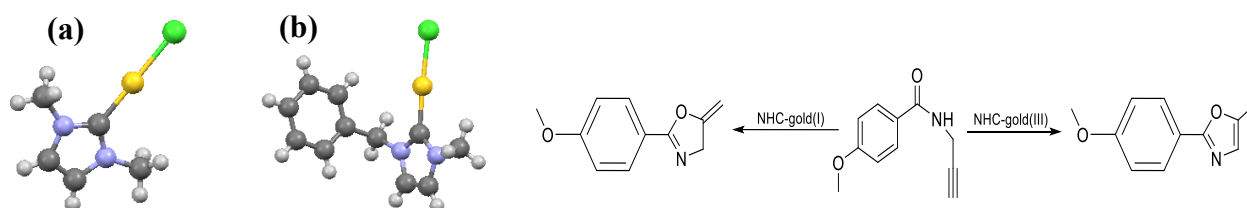


Figure 1: Left: Starting carbene complexes [AuCl(IME₂)] (a) and [AuCl(IBnMe)] (b); Right: Gold-catalyzed cyclization of N-propargyl amide as benchmark reaction to test the gold catalysts.

POSTERS

[4] Weyrauch, J. P.; Hashmi, A. S. K.; Schuster, A.; Hengst, T.; Schetter, S.; Littmann, A.; Rudolph, M.; Hazmic, M.; Visus, J.; Rominger, F.; Frey, W.; Bats, W. J.; *Chem. Eur. J.*, **2009**, *16*, 3, 956.

Poster 67

New N-Ferrocenyl Aminocarbyne Iron Complexes

Chiara Saviozzi,^{a*} Lorenzo Biancalana,^a Tiziana Funaioli,^a Marco Bortoluzzi,^b Michele De Franco,^c
Valentina Gandin,^c Fabio Marchetti^a

^a University of Pisa, Department of Chemistry and Industrial Chemistry, Pisa, Italy.

^b Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Mestre, Venice, Italy.

^c Department of Pharmaceutical and Pharmacological Sciences, University of Padova, Padova, Italy.

chiara.saviozzi@phd.unipi.it

Since the former work of Pombeiro and Fischer, aminocarbyne ligands have been reported combined with a variety of transition elements and complex nuclearity.¹ They display a rich and versatile chemistry, offering many opportunities for the construction of unusual organometallic structures. In this work, the synthesis of the first N-ferrocenyl (N-Fc) aminocarbyne complex (**1**) was achieved on a diiron bis-cyclopentadienyl scaffold via incorporation of isocyanoferrocene (Figure 1). The {CN(Fc)Me} fragment possesses a hybrid aminocarbyne-iminium character, and the ferrocenyl moiety induces unusual steric and electrochemical features with respect to previously investigated analogous diiron complexes.^{1a,2} The structural features, electrochemical properties, and reactivity of **1** to afford a series of triiron derivatives will also be discussed, together with an overview of the new complexes as potential anticancer drugs.

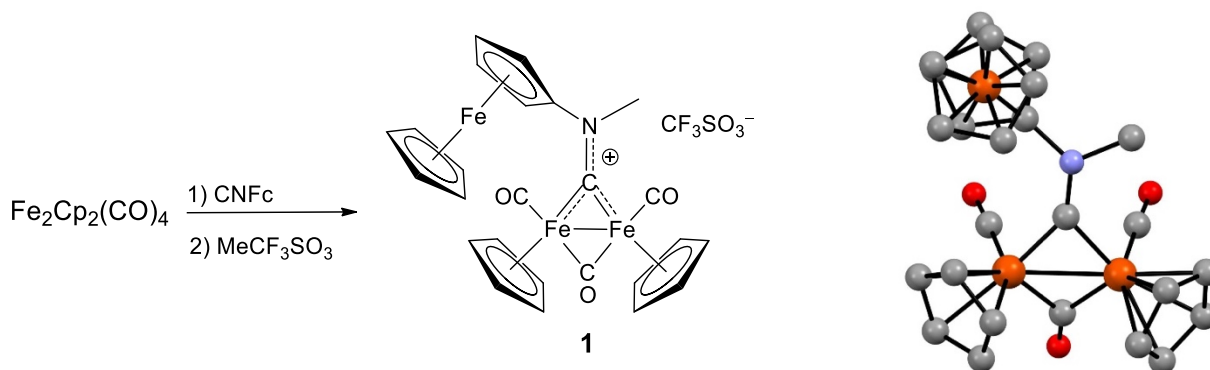


Figure 1. Triiron complex with bridging N-ferrocenyl aminocarbyne ligand: synthesis and DFT-optimized structure of the most stable isomer.

POSTERS

Poster 68

An Ir(III)-Peptide Nucleic Acid (PNA) conjugate as a Singlet Oxygen Photosensitizer for Photodynamic therapy

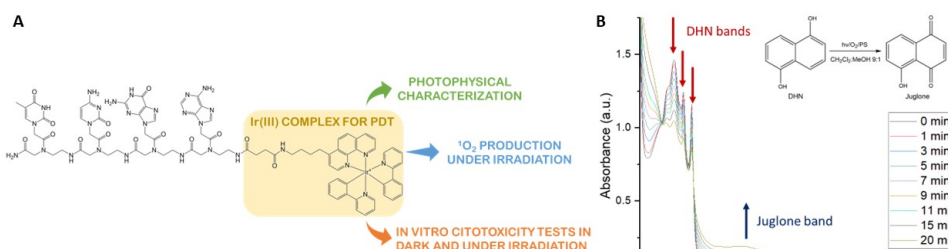
Veronica Schifano,^{a*} Rosa Maria Dell'Acqua,^a Maria Vittoria Dozzi,^a Monica Panigati,^a Paola Rusmini,^b Angelo Poletti,^b Silvia Cauteruccio,^a Daniela Maggioni.^a

^a Dipartimento di Chimica, Università degli Studi di Milano, Via C. Golgi 19, 20133, Milan, Italy.

^b DISFEB "Rodolfo Paoletti", Università degli Studi di Milano, Via G. Balzaretti 9, 20133, Milan, Italy

[*veronica.schifano@unimi.it](mailto:veronica.schifano@unimi.it)

Photodynamic therapy (PDT) is a noninvasive medical treatment used against skin diseases, various types of infections and even cancer. It is based on the excitation of molecular oxygen from its triplet ground-state ($^3\text{O}_2$) to the toxic singlet excited state ($^1\text{O}_2$) using a photosensitizer (PS) which, after exposure to suitable light, is excited to the singlet state (S_1) and then undergoes intersystem crossing (ISC) to the triplet excited state (T_1), where the energy transfer to $^3\text{O}_2$ takes places (Type II PDT).¹ Cyclometallated Ir(III) complexes are suitable as PSs for $^1\text{O}_2$ production in PDT due to the accessibility of triplet excited states having usually metal-to-ligand charge transfer character ($^3\text{MLCT}$).² The positive charge that many of these kind of organometallic compounds possess promotes their solubility in water, allows an interaction with the cellular membrane and enhances their cellular uptake. In our ongoing study, we have synthesized a novel tris cyclometallated Ir(III) complex (**Ir-COOH**), containing a carboxyl group, and the corresponding conjugate with a peptide nucleic acid (PNA) tetramer (**Fig. 1A**). The final aim will be to combine the Ir(III) complex properties with an antisense strategy promoted by specific sequences of PNA. Both the complex and the corresponding **Ir-PNA** conjugate have been characterized with UV-vis absorption and emission spectroscopy, displaying absorptions in the blue and a moderate emission ($\Phi \approx 3\%$) at ca 580 nm. The capability to produce $^1\text{O}_2$ has been also tested for both species in cuvette, employing the indirect reporter DHN (**Fig. 1B**, $\Phi_{\Delta} = 0.54$ for **Ir-PNA** vs. $\Phi_{\Delta} = 0.42$ for **Ir-COOH**). Moreover, preliminary *in vitro* cytotoxicity test were carried out on mouse motor neuronal cell line (NSC34). Since the emission is not completely quenched by O_2 interaction, the cellular uptake will be followed *in vitro* by confocal microscopy even using a low-energy light by exploiting the two-photon excitation. This last feature, together with the possibility to shift toward the NIR region their emission by using different ligands of the Ir(III) complex will be also investigated for *in vivo* treatments.²



POSTERS

- [1] DeRosa, M. C.; Crutchley, R. J. *Coord. Chem. Rev.* **2002**, 233–234, 351.
 [2] Zamora, A.; Viguera, G.; Rodríguez, V.; Santana, M. D.; Ruiz, J.; *Coord. Chem. Rev.* **2018**, 360, 34-76.

Poster 69

Mechanistic DFT studies on the formation of a novel Rh(I)-ethylene complex

Inga L. Schmidtke,^{a*} Christina Erken,^b Timo Repo,^b Ainara Nova,^a

^a Department of Chemistry, Hylleraas Centre for Quantum Molecular Sciences and Centre for Materials Science and Nanotechnology, University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway.

^b Department of Chemistry, University of Helsinki, P.O. Box 55, 00014 Helsinki, Finland.

inga.schmidtke@smn.uio.no

Alkene hydrogenation is considered to be one of the most powerful reactions for applications in pharmaceutical, agrochemical and commodity chemical industries.¹ The discovery of rhodium-phosphine complexes lead to significant advances in catalytic homogeneous hydrogenation of alkenes, allowing for mild reaction conditions like room temperature and atmospheric pressure of H_2 .¹ The most renowned complex of this kind is Wilkinson's catalyst ($RhCl(PPh_3)_3$)² which has been subject to extensive studies for decades, including kinetic reaction mechanism studies.³ In 2015 the Repo group reported the synthesis and isolation of the monohydride analog $RhH(PPh_3)_3$ aided by the use of a superbases and discovered its remarkable reactivity in the hydrogenation of internal alkynes and functionalized alkenes.⁴ This study prompted us to investigate the reactivity of the monohydride rhodium(I) complex further. A combined experimental and computational study was carried out on the reactivity of $RhH(PPh_3)_3$ toward ethylene in the presence of Barton's base (BTMG). The computational investigations focused on unravelling the mechanism that leads to the formation of an isolated novel complex $RhCl(C_2H_4)(PPh_3)_2$ and will provide new insights into the reactivity of Wilkinson's catalyst and related complexes (Figure 1).

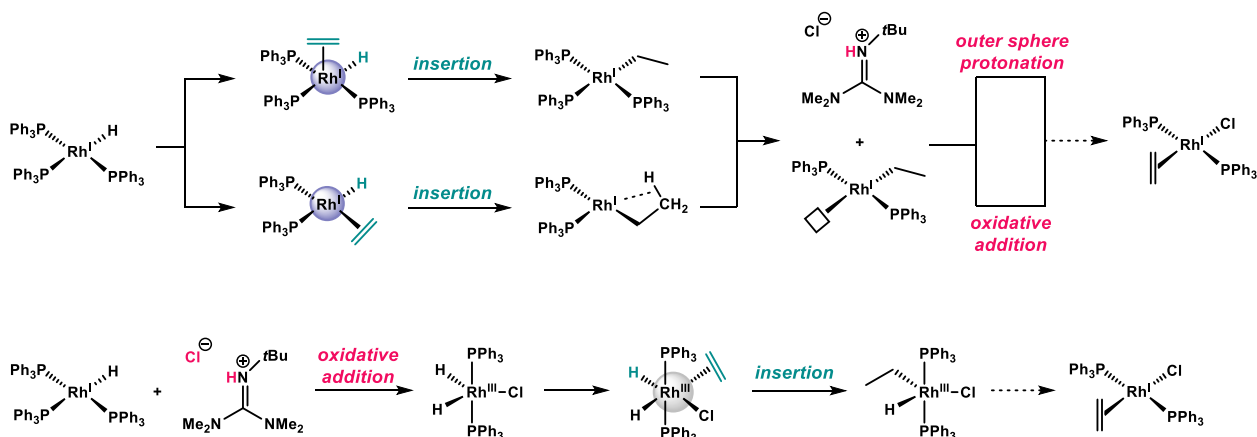


Figure 1

POSTERS

[4] Perea-Buceta, J. E.; Fernández, I.; Heikkinen, S.; Axenov, K.; King, A. W. T.; Niemi, T. Nieger, M.; Leskelä, M.; Repo, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 14321.

Poster 70

Influence of CAAC-Triazene Ligands on Rhodium Complexes

Taj Seaton,^{a*} James Race^a, Martin Albrecht^a

^a Department of Chemistry, Biochemistry and Pharmaceutical Sciences, Freiestrasse 3, 3012 Bern, Switzerland.

[*taj.seaton@unibe.ch](mailto:taj.seaton@unibe.ch)

The versatile structural and electronic properties of cyclic alkyl amino carbenes (CAACs) have led to the synthesis and application of a large variety of transition metal complexes as well as carbene, phosphine or amine adducts.¹ CAACs have gained significant attention to serve as ligands exhibiting advantageous steric and electronic properties.¹ We recently developed a unique donor-flexible triazene ligand stabilized by a CAAC moiety. Here we demonstrated that the CAAC-triazene ligand is strongly coordinated to Rh(I) and induces the activation of C_{alkyl}-Cl bonds.

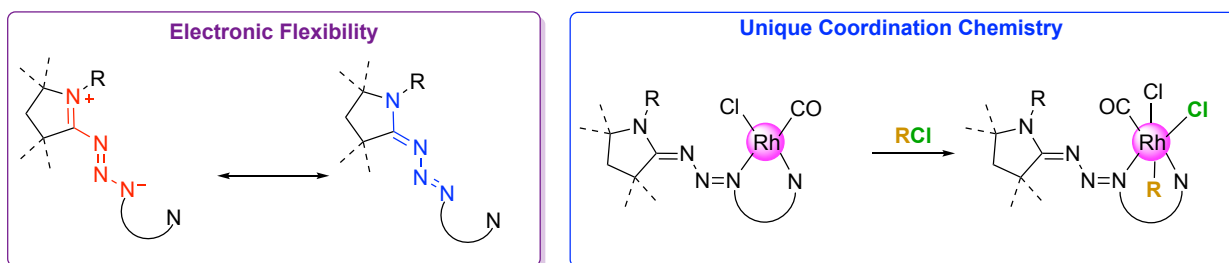


Figure 1: (right) CAAC-triazene ligand electronic flexibility and (left) coordination to rhodium and reactivity towards alkyl chloride.

POSTERS

Poster 71

Different coordinative behaviour of isoelectronic ions Au(III) , Pd(II) and Pt(II) toward (2-pyridyl)imidazo[1,5-*a*]pyridine ligands 3-aryl methoxy substituted

Giacomo Senzacqua,* Sergio Stoccoro, Antonio Zucca

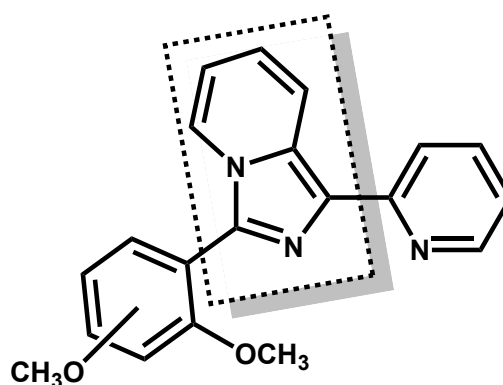
Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali – Uniss

Via Vienna 2, 07100 Sassari (Italy)

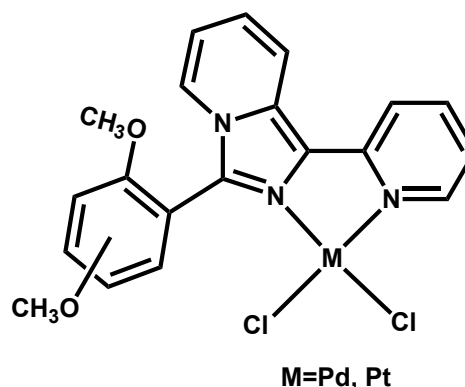
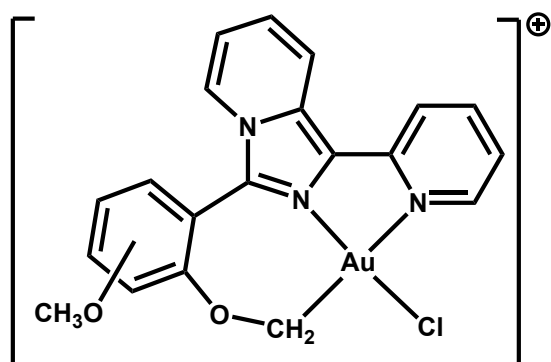
giacomo.senzacqua@gmail.com

Imidazo[1,5-*a*]pyridine (impy)^[1] is a very versatile molecule that is easily functionalizable by introducing substituents at different positions. In this way it can act as a ligand with different metal ions.^[2] Following our interest in the coordination chemistry of (2-pyridyl)imidazo[1,5-*a*]pyridine ligands^[3] here we report the different coordination behaviour between Au(III), on the one hand, and Pd(II) and Pt(II) on the other hand with a series of 3-arylsubstituted 1-(2-pyridyl)imidazo[1,5-*a*]pyridines in which the substituent shows -OCH₃ groups.

What we have been able to observe is that, although trying to operate under the same reaction conditions, in the case of Au(III) we get basically cyclometallated species while with Pd(II) and Pt(II) only adducts. The new complexes, both cyclometallates and adducts, have been extensively characterized spectroscopically and analytically.



Research is still underway to understand why this different behaviour occurs and thus figure out how to obtain cyclometallated species of Pd(II) and Pt(II) as well.



POSTERS

2015, 4921–4934 b) G. Colombo, G. A. Ardizzoia, and S. Brenna, *Inorg. Chim. Acta.*, **2022**, 535, 120849.
 [3] Pischedda S.; Stoccoro S.; Zucca, A.; Sciortino G.; Ortu F.; Clarkson G. J., *Dalton Trans.*, **2021**, 50, 4859-4873.

Poster 72

Catalytic hydroboration of carbonyl compounds mediated by diiron complexes with functionalized allylidene ligands

Francesco Taglieri,^a Marcello Crucianelli,^a Andrea Di Giuseppe,^a Chiara Zappelli,^b Lorenzo Biancalana,^b Fabio Marchetti,^b

^a Università dell'Aquila, Dipartimento di Scienze Fisiche e Chimiche, Via Vetoio, I-67100 L'Aquila, Italy.

^b Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via G. Moruzzi 13, I-56124 Pisa, Italy.

francesco.taglieri@graduate.univaq.it

The renaissance of non-toxic and earth-abundant metal complexes research field is primarily motivated by the demand for sustainable and environmentally friendly catalytic processes. In this context, the role of diiron complexes holds great promise, benefiting from the cooperative effects of two metal centers - an intriguing concept exploited in Nature.^[1] Building upon this concept, novel diiron complexes^[2] with functionalized allylidene ligands^[3] have been synthesized, characterized, and evaluated for their catalytic efficacy in the hydroboration of aromatic aldehydes. The presence of labile sites, combined with the synergy between the two metal centers, allows for their practical application not only in biological field^[4] but also in homogeneous catalysis, with potential in synthetic chemistry for the synthesis of boronate adducts.

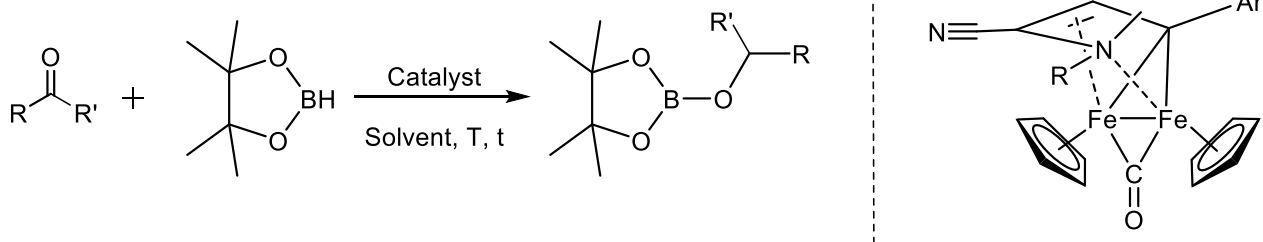


Figure 1

- [1] Orton G. R. F., Ghosh S., Alker L., Sarker J. C., Pugh D., Richmond M. G., Hartl F., Hogarth, *Dalton Trans.* **2022**, 51, 9748.
 [2] Marchetti F., *EurJIC*. **2018**, 36, 3987.
 [3] Schoch S., Batchelor L. K., Funaioli T., Ciancaleoni G., Zacchini S., Braccini S., Chiellini F., Biver T., Pampaloni G., Dyson P. J., Marchetti F., *Organometallics* **2020**, 39, 361.
 [4] Biancalana L., Manja Kubeil M., Silvia Schoch S., Stefano Zacchini S., Marchetti F., *Inorg. Chem.* **2022**, 61, 7887.

POSTERS

Poster 73

Design of Hydrophobic Bimetallic MOFs for Application in Heterogenous Catalysis

Giulia Taini,^{a*} Ester Mazzola,^a Edoardo Bracciotti,^b Segio Rojas Buzo,^b

Silvia Bordiga,^b Elisa Borfecchia,^b Valentina Colombo.^a

^a Department of Chemistry, University of Milan, Via Golgi 19, 20133 Milan, Italy. *giulia.taini1@studenti.unimi.it

^b Department of Chemistry, University of Turin, Via Quarello 15, 10125 Turin, Italy.

The pressing demand to reduce the carbon footprint of all significant polluting industrial sectors has drawn interest in the conversion of CO₂ into valuable compounds. Among the proposed routes, an effective strategy for CO₂ recycling is represented by the catalyst-driven synthesis of dimethyl carbonate (DMC) from CO₂ and methanol.¹ However, the large-scale application of this process has been limited by the high thermodynamic requirements and risk of catalyst deactivation due to the significant amount of water produced by the reaction.² Metal-organic frameworks (MOFs) offer a viable catalytic platform for CO₂ to DMC conversion, by virtue of

their highly tuneable structural features and synthetic control over the functional properties of the final material.

To this aim, we are developing a series of bimetallic (Zr,Ce)UiO-66 MOFs containing dicarboxylate linkers with different degrees of fluorination. As has already been demonstrated,³ the presence of both Zr(IV) and Ce(IV) centers ensures the frameworks' chemical and thermal stability as well as their catalytic activity, making them suitable for application as heterogeneous catalysts. Additionally, the fluorine content, imparted by the functionalized ligands, is responsible for an increase in the hydrophobicity of the MOFs surface, which is crucial to prevent water from obstructing the pores and impeding the desired reaction. These materials were obtained through an environmentally-friendly synthetic approach and their structural characteristics were determined via a combination of X-Ray-based techniques, infrared spectroscopy, and elemental analysis.

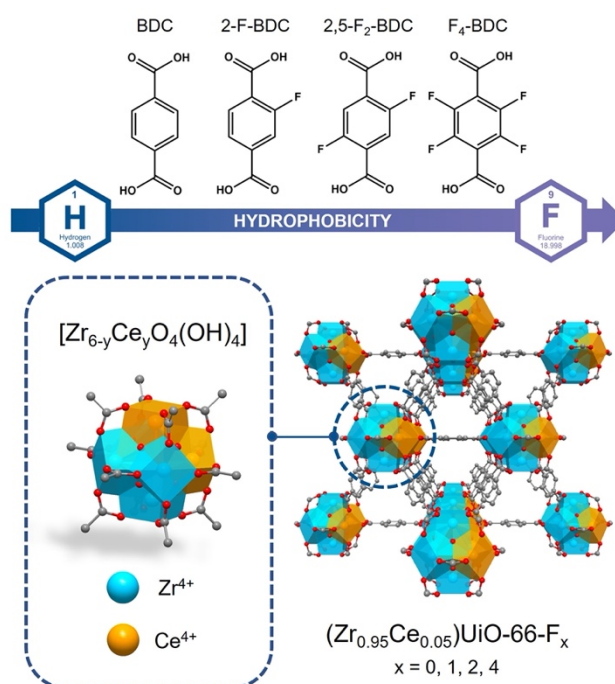


Figure. Representation of linkers, bimetallic clusters, and 3D structure of the synthesized MOFs.

POSTERS

by LAMBERT M., GUICHARD C., BUCK R., *Dalton Trans.*, 2017, 70, 2429.

Poster 74

Zr(IV)-catalyzed Reductive Depolymerization of Polycarbonates

Cyril A. Theulier,^{a*} Jean-Claude Berthet^a and Thibault Cantat^{a*}

^a Université Paris-Saclay, CEA Saclay, CNRS, IRAMIS-NIMBE-LCMCE, 91191 Gif-sur Yvette, France

cyril.theulier@cea.fr

With the emergence of the consumer society in the 1950's, manufacturers turned to plastic for a mass-production at a lower cost. Today plastics are ubiquitous in our ordinary life with about 450 million tons of annual global production in 2019.¹ However, plastics wastes are pollutants and over the 9.2 billion tons (Bt) produced from the 50's, less than 8% have been recycled while 1 Bt have been incinerated and more than 5.3 Bt accumulated in landfills or the natural environment. Although essential to our modern society, plastic boom is causing severe damage to the environment. Moreover, being dependent on fossil fuels, it also releases large quantities of greenhouse gases such as CO₂. Currently, mechanical recycling is by far the most common method to recycle plastic, but is hampered by contamination and mainly limited to plastic bottles. Chemical

recycling which is the depolymerization of materials into valuable monomers or chemicals accounts for less than 1% in Europe but has emerged as a long term sustainable and complementary strategy. Indeed, it enables the regeneration of plastic with virgin quality as well as the access to useful chemicals for industry, thus creating opportunity for up-cycling.² Recently, the reductive catalytic depolymerization strategy, using homogeneous catalyst combined with a reductive source, has proven very promising in the deconstruction of oxygenated and/or nitrogenated plastics.³ We reported that Schwartz's reagent $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$, traditionally used as a stoichiometric reagent for the reduction of unsaturated organic molecules, could act as an efficient catalyst for the hydrosilylation of esters and depolymerization of polyesters.⁴ Herein we extend this methodology to carbonates and polycarbonates materials (e.g. PC-BPA) and report an experimental study with mechanistic details (Figure 1).

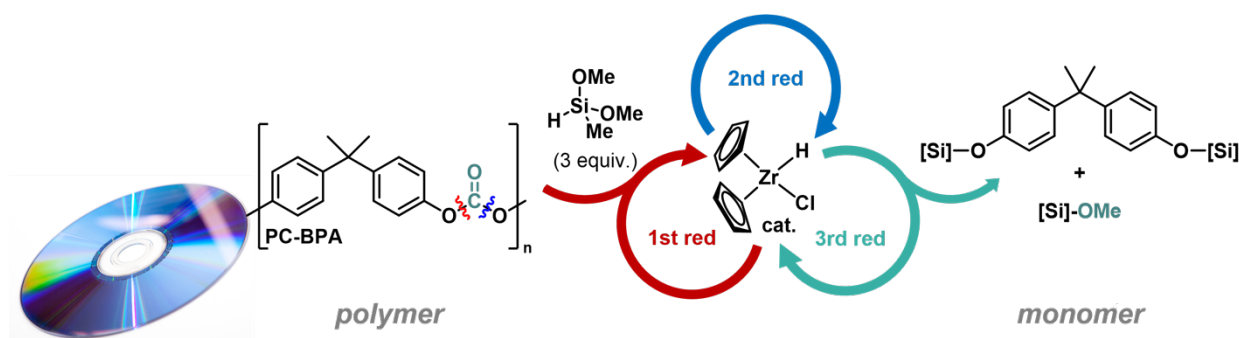


Figure 1

[1] (a) OECD (2022), *Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options*, OECD Publishing, Paris, (b) Ellis, L. D.; Rorrer, N. A.; Sullivan, K. P.; Otto, M.; McGeehan, J. E.; Román-Leshkov, Y.; Wierckx, N.; Beckham, G. T. *Nature Catalysis* **2021**, *4*, 539.

POSTERS

Poster 75

Biindole diketones: a new class of versatile bidentate ligands and their applications

Federico Vavassori,^{a*} Angelo Maspero,^a Luca Nardo,^a Andrea Penoni,^a

^a University of Insubria, Department of Science and High Technology (DiSAT), Via Valleggio 9, 22100 Como (CO), Italy
f.vavassori@uninsubria.it

The 1,3-diketone moiety is notorious for its ability to coordinate metals, both in its neutral and anionic form; its derivatives have been thoroughly studied¹ and have found applications in the field of Medicinal Chemistry.² This fragment can be also found in nature, mainly in the curcuminoid frames. Extensive research has been conducted to use these biocompatible molecules in coordination complexes with biological applications.³ Indole is one of the most important heterocycles and can be found in multiple naturally present compounds, from the simple amino acid tryptophan to the much more complex Vinca alkaloids, employed as anticancer agents.⁴ Cirrincione and coworkers reported the use of 1,3-diindol-3-yl diketones as starting

materials for the synthesis of nortopsentin analogues, a class of marine alkaloids with antitumor and antibacterial properties.⁵ Inspired by Cirrincione's work and given our expertise in the field of indole chemistry^{6,7} we decided to combine the interesting properties of indoles with the chelating ability of β -diketone to create a new class of adducts. We present here some of the research carried out on these structures (Figure 1) and their applications in the field of biomedical and material sciences.⁸

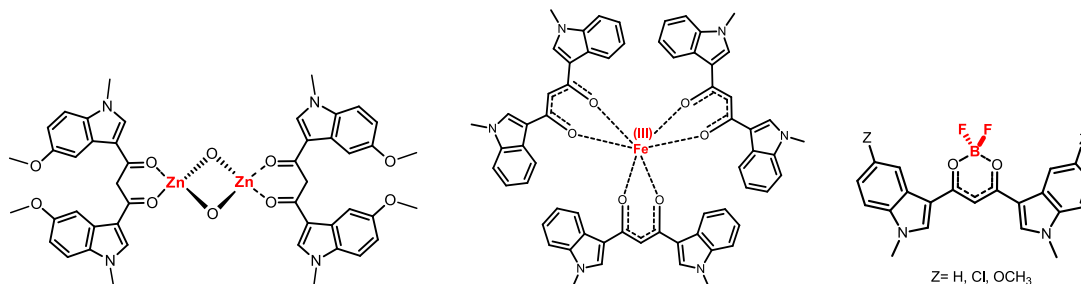


Figure 1

- [1] Vigato, P.A.; Peruzzo, V.; Tamburini, S. *Coord. Chem. Rev.* **2009**, 253, 1099.
 [2] Pettinari, R.; Marchetti, F.; Di Nicola, C.; Pettinari, C. *Eur. J. Inorg. Chem.* **2018**, 2018, 3521.
 [3] Shakeri, A.; Panahi, Y.; Johnston, T.P.; Sahebkar, A. *BioFactors* **2019**, 45, 304.
 [4] G. W. Gribble, *Indole Ring Synthesis: from Natural Products to Drug Discovery*, Wiley & Sons Ltd, 2016.
 [5] Diana, P.; Carbone, A.; Barraja, P.; Kelter, G.; Fiebig, H.-H.; Cirrincione, G. *Bioorg. Med. Chem.* **2010**, 18, 4524.
 [6] Palmisano, G.; Penoni, A.; Sisti, M.; Tibiletti, F.; Tollari, S.; Nicholas, K.M. *Curr. Org. Chem.* **2010**, 14, 2409.
 [7] Ieronimo, G.; Palmisano, G.; Maspero, A.; Marzorati, A.; Scapinello, L.; Masciocchi, N.; Cravotto, G.; Barge, A.; Simonetti, M.; Ameta, K.L.; Nicholas, K. M.; Penoni, A. *Org. Biomol. Chem.* **2018**, 16, 6853.
 [8] Scaninello, I.; Vesco, G.; Nardo, I.; Maspero, A.; Vavassori, F.; Galli, S.; Penoni, A. *Pharmaceuticals* **2021**, 14

POSTERS

Poster 76

Ligand Enabled Oxidation: New Avenues in Gold Chemistry

David Vesseur,^{a*} Didier Bourissou,^a

^a CNRS/Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA, UMR 5069). 118

Route de Narbonne, 31062 Toulouse Cedex 09 (France).

david.vesseur1@univ-tlse3.fr

Gold chemistry has seen a tremendous development in the last two decades, nonetheless Au(I)/Au(III) processes remained challenging due to the high oxidation potential for Au(I) to Au(III) oxidation. In 2017 our group showed that using the Me-Dalphos ligand, oxidative addition to Au(I) of aryl halides proceeded smoothly to give the corresponding Au(III) complexes.¹ Due to its rare ability to stabilize Au(I) and Au(III) complexes as well as cycle between them, the Me-Dalphos ligand has become a staple in gold chemistry.² Taking further advantage of these properties allowed us to prepare a Au(III) π -allyl complex *via* Lewis acid-assisted oxidation from a Au(I) π -alkene.³ These Au(III) π -allyl complexes were employed as key

intermediates in the catalytic allylation of indoles. Additionally the Au(III) π -allyl complex could also be prepared via a ring-opening process from its corresponding Au(III) σ -cyclopropyl complex by halide abstraction.⁴ Furthermore, with mild electrophilic fluorine sources, Me-Dalphos Au(I) complexes could be oxidized to the corresponding Au(III) fluorine complexes.⁵ These Au(III) fluorine complexes could undergo C–F reductive elimination and fluorine assisted trans metalation.

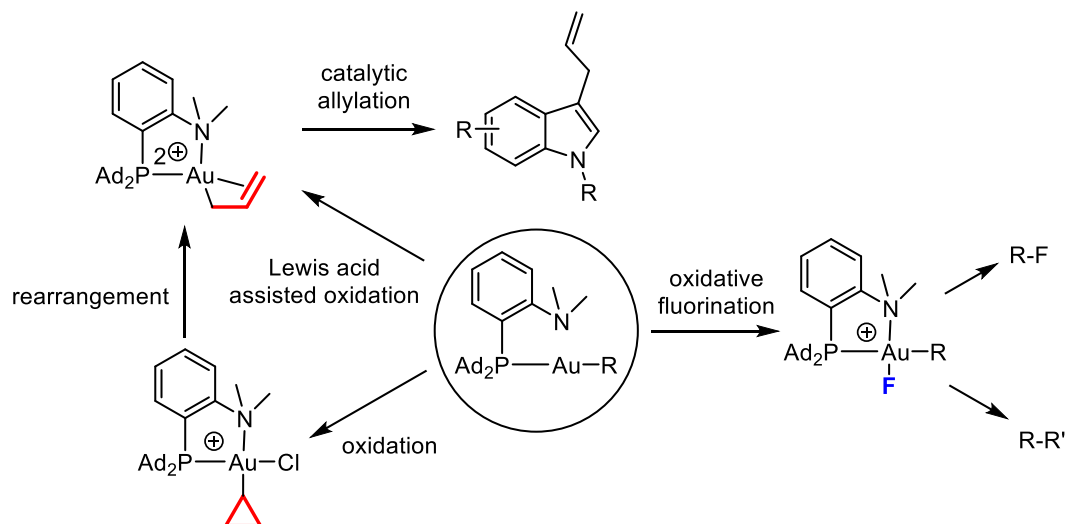


Figure 1

POSTERS

e202305280.

[5] unpublished results

Poster 77

Selective Electrocatalytic Reduction of Low CO₂ Partial Pressure to CO by a Manganese Bis-NHC Complex

Mattia Vettori,^a Federico Franco,^a Sergio Fernandez,^a and Julio Lloret-Fillol^{a,b}

^a Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain; ^b Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Companys, 23, 08010 Barcelona, Spain.

The renewable electricity like solar energy from photovoltaic cells can be used to drive chemical reactions. Resultantly, the electrocatalytic CO₂ reduction (CO₂RR) has emerged as one of the most promising and sustainable ways to produce renewable fuels and chemicals, and therefore can possibly substitute fossil fuels. Nevertheless, condensation processes of CO₂ requires high cost and high energy consumption. CO₂ capture at low concentrations by catalysts is potentially useful to overcome this problem, but often there is the necessity

to introduce additives such as amines or ionic liquids in order to pre-concentrate CO₂ as shown by Ishitani et al. in which a Re(I) molecular complex is employed to electroreduce CO₂ to CO in presence of TEOA as additive. We investigated the ability of a highly active N-heterocyclic carbene Manganese(I) complex to capture and selectively reduce low CO₂ partial pressure with high selectivity. This catalyst has already shown unprecedented activity for the selective electrocatalytic reduction of CO₂ to CO in pure CO₂ atmosphere, exceeding 100 turnovers with excellent faradaic yield ($\eta_{\text{CO}}=95\%$) in anhydrous acetonitrile. In our study, this [Mn(I) (CO)₃(bis-MeNHC)MeCN]⁺ proved his capability to reduce selectively CO₂ at low concentrations. There are rare examples of earth-abundant 1st row transition metals molecular complexes that are able to reduce at low CO₂ partial pressure with no need of additives. Therefore, we have studied the performance of this earth-abundant molecular catalyst extensively at various CO₂ streams.

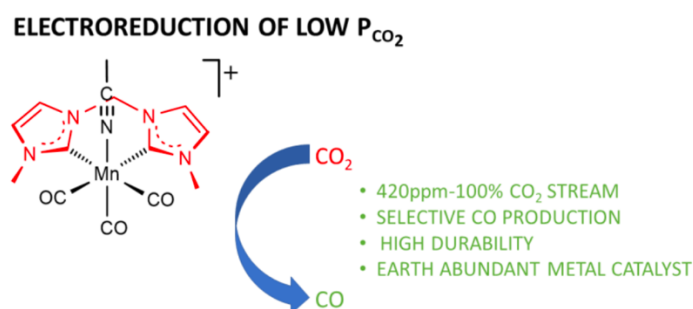


Figure 1

[1] Franco, F.; Pinto, M. F.; Rovo, B.; Lloret-Fillol, J. A Highly Active N-Heterocyclic Carbene Manganese(I) Complex

POSTERS

Electrocatalytic reduction of low concentration CO₂. : Chem. Sci. 2019, 10, 1597.

Poster 78

Novel Zinc(II) Complexes with Pyrazolone-based Ligands displaying Antibacterial Activity

Sonila Xhafa,^{a*} Alessia Tombesi,^b Fabio Marchetti,^a Riccardo Pettinari,^b Corrado Di Nicola,^b
Claudio Pettinari.^b

^a School of Science and Technology, Via S. Agostino 1, 62032 Camerino (MC), Italy.

^b School of Pharmacy, Via S. Agostino 1, 62032 Camerino (MC), Italy.

sonila.xhafa@unicam.it

The widespread use of broad-spectrum antibiotics has led to the development of generations of antibiotic-resistant bacteria, posing a major threat to human health. The development of novel, effective and biocompatible antimicrobial agents, assumes great importance in the replacement of the antibiotics and the limitation of the spread of drug-resistant bacteria.¹ The acylpyrazolone ligands are biologically active, and

thanks to the conjugation and their ability to chelate the transition metal ions, they give rise to metal complexes which show interesting characteristics, such as antitumor, antioxidant, antifungal and antimicrobial activities.^{2,3} Within the development of new metal-based drugs, wide interest is recently turned to the use of Zn(II) coordination complexes, with low toxicity and low side effects, in biological application.^{4,5} Herein, we described the synthesis and characterization of four new Zn(II) complexes containing a novel acylpyrazolone, namely (E)-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)(4-(phenyldiazenyl)phenyl) methanone (HQ^{PhN₂Ph}), incorporating a diazo fragment between two phenyl rings in the acyl moiety, and with additional N/O-donor ligands such as bipyridine, phenanthroline, and hydroxyquinoline in diverse ligand/metal ratios. The antibacterial tests of complexes are in development against both Gram-positive and Gram-negative bacterial strains (Figure 1).

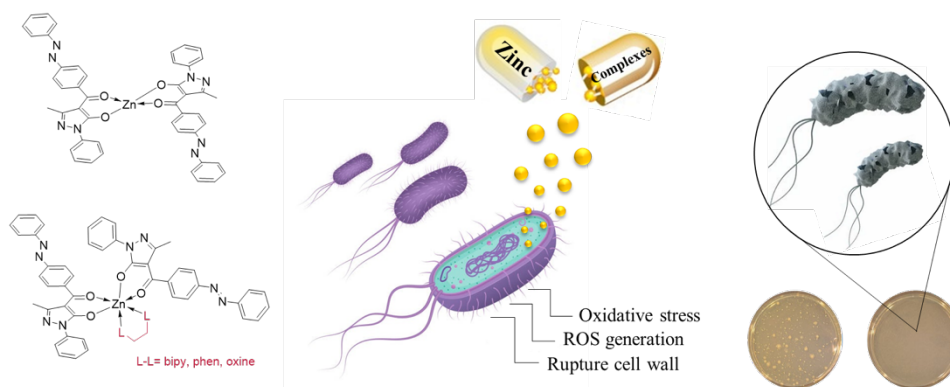


Figure 1. Zn(II) complexes of pyrazolone-based ligands and their biological activities.

[1] Laxminaravan. R.; Matsoso. P.; Pant. S.; Brower. C.; Røttingen. J.-A.; Klugman. K.; Davies. S. *Lancet*. **2016**. 387.

POSTERS

[4] D'Orazi, G., et al. *Journal of Inorganic Biochemistry*. **2022**, 225, 111111.

[5] Gonnella, R., Guttieri, L., Gilardini Montani, M. S., Santarelli, R., Bassetti, E., D'Orazi, G., et al. *Biology*. **2022**, 11, 132.

Poster 79

Synthesis of novel organic sensitizers for artificial photosynthesis through Pd-catalyzed cross-coupling reactions

Xheila Yzeiri,^{a,b,c*} Daniele Franchi,^a Massimo Calamante,^{a,b} Carmen Coppola,^c Adalgisa Sinicropi,^c Alessio Dessì,^a Lorenzo Zani,^a Gianna Reginato,^a and Alessandro Mordini^{a,b}

^a Institute of Chemistry of Organometallic Compounds (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.

^b Department of Chemistry "U. Schiff", University of Florence, Via della Lastruccia 13, 50019 Sesto Fiorentino, Italy.

^c Department of Biotechnology, Chemistry and Pharmacy, University of Siena, Via A. Moro 2, 53100 Siena, Italy.

xheila.yzeiri@gmail.com

In the field of artificial photosynthesis, dye-sensitized photoelectrochemical cells (DS-PECs) for water-splitting have been extremely investigated in the last years in the effort to provide a reliable system to produce solar fuels from water and sunlight¹. Given the crucial role of the dye in the working mechanism of the

device, the design and synthesis of novel sensitizers with a broad optical response, appropriate energy levels, and good stability represents a key-point. Among the different classes of sensitizers employed for such a process, organic metal-free dyes, and especially D (donor)- π -A (acceptor) sensitizers, have been intensely investigated thanks to their low cost, tunable spectroscopic properties, good stability and relatively easy synthesis².

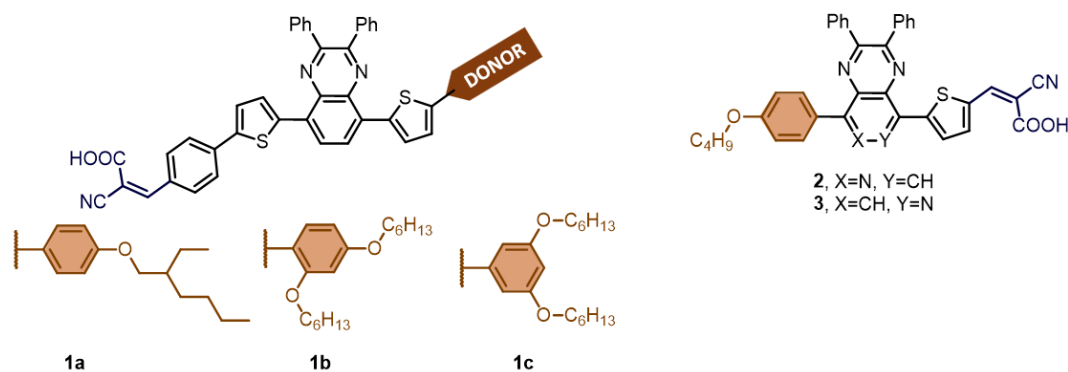


Figure 1 Structure of compounds **1a-c**, **2** and **3**.

In this study, we report the design and synthesis of a family of five new metal-free organic dyes, based on quinoxaline (compound **1a-c**) and pyrido-pirazine (compounds **2,3**) central cores. Moreover, we explored their potential application as sensitizers in DS-PECs in combination with Ru-based water oxidation catalysts³. All the compounds have been successfully synthesized, with good overall yields, through well-known Pd-catalysed C-C cross coupling reactions, such as Suzuki-Miyaura and Stille reactions, or, when possible, through more recent approaches like direct C-H activation reactions. Preliminary studies have been also carried out in order

POSTERS

[2] K. Wee; B.D. Sherman; M.K. Brennaman; M.V. Sheridan; A. Nayak; L. Alibabaei; T.J. Meyer J. Mater. Chem. A, 2016, 4, 2969-2975.

[3] K. Wee; B.D. Sherman; M.K. Brennaman; M.V. Sheridan; A. Nayak; L. Alibabaei; T.J. Meyer J. Mater. Chem. A, 2016, 4, 2969-2975.

Poster 80

Novel Activation Mechanisms for Rhodium(III) Cyclopentadienyl Complexes

Edward C. Lant,^a Samya Banerjee,^{a,e} Juliusz A. Wolny,^a Bryan Marzullo,^a Jingsha Xu,^a Marc Walker,^c Christopher A. Wootton,^d Guy J. Clarkson,^a Volker Schünemann,^a Peter B. O'Connor,^a and Peter J. Sadler^{a*}

^aDepartment of Chemistry, Division of Biomedical Sciences, Warwick Medical School, University of Warwick, Coventry CV4 7AL, UK. ^bDepartment of Physics, Technische Universität Kaiserslautern, Kaiserslautern, Germany.

^cDepartment of Physics, University of Warwick, Coventry CV4 7AL, UK. ^dBruker Daltonik GmbH, Bremen, Germany,

^eDepartment of Chemistry, Indian Institute of Technology (BHU), Varanasi, UP-221005, India.

The Cp x C-H protons in certain organometallic RhIII half-sandwich anticancer complexes $[(\eta^5\text{-Cp} \times)\text{Rh}(\text{N},\text{N}')\text{Cl}]^+$, where Cp x = Cp*, phenyl or biphenyl-Me4Cp, and N,N' = bipyridine, dimethyl bipyridine, or phenanthroline, can undergo rapid sequential deuteration of the 15 Cp* methyl protons in aqueous media at

ambient temperature (1,2,4). DFT calculations suggest a mechanism involving abstraction of a Cp* proton by the Rh-hydroxido complex, followed by sequential H/D exchange, with the Cp* rings behaving like dynamic molecular 'twisters' (Fig.1). Calculations show the crucial role of p π orbitals of N,N'-chelated ligands in stabilizing deprotonated Cp x ligands, and the accessibility of RhI-fulvene intermediates (4). We readily trapped and characterized RhI-fulvene intermediates by Diels-Alder [4+2] cyclo-addition reactions with the natural biological dienes isoprene and conjugated (9Z,11E)-linoleic acid in aqueous media, including cell culture medium (Fig.1). These findings will introduce new concepts into the design of organometallic Cp* anticancer complexes with novel mechanisms of action (3,4)

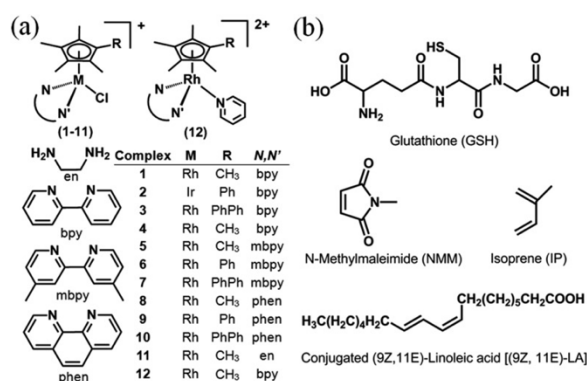


Figure 1

- [1] S. Banerjee, J. J. Soldevila-Barreda, J. A. Wolny, C. A. Wootton, A. Habtemariam, I. Romero-Canelón, F. Chen, G. J. Clarkson, I. Prokes, L. Song, P. B. O'Connor, V. Schünemann, P. J. Sadler, *Chem. Sci.*, 2018, 9, 3177-85. (
- [2] J. Markham, J. Liang, A. Levina, R. Mak, B. Johannessen, P. Kappen, C. J. Glover, B. Lai, S. Vogt, P. A. Lay, *Eur. J. Inorg. Chem.* 2017, 1812-23.
- [3] Wu, H., Y. Han, Y. Rodriguez Sillke, H. Deng, S. Siddiqui, C. Treese, F. Schmidt, M. Friedrich, J. Keye, J. Wan, Y. Qin, A. A. Köhl, Z. Qin, B. Siegmund, R. Glaubien, *EMBO Molecular Medicine* 2019, 11(11), e10698.
- [4] A. Sink, S. Banerjee, J.A. Wolny, C. Imberti, E.C. Lant, M. Walker, V. Schünemann, P.J. Sadler *Dalton Trans* **2022**, 51, 16070 – 16081.