

XIV International School of Organometallic Chemistry

Camerino, Italy

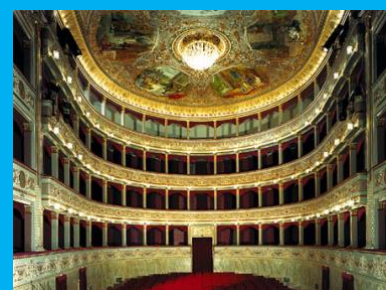
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University of Camerino

School of Pharmacy and School of Science and Technology



Organometallic Chemistry beyond the future

Interdivisional Group of Organometallic Chemistry

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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 XIV 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.



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TIMETABLE

Thursday 07 September	Friday 08 September	Saturday 09 September	Sunday 10 September	Monday 11 September
	7:45-8:45 Breakfast	7:45-8:45 Breakfast	7:30- 8:30 Breakfast	7:45- 8:45 Breakfast
9:00-14:30 Registration	9:00-10:20 Prof. Christophe Copéret <i>NMR chemical shifts beyond numbers: understanding the electronic structure of reaction intermediates</i>	9:00-10:20 Prof. Beatriz Royo <i>Manganese-catalyzed hydrosilylative reduction: ligand design and mechanistic aspects</i>	8:30-9:50 Prof. Igor Larrosa <i>Mechanistic Understanding-Led Transition Metal Catalyzed C-H Functionalization</i>	9:00-10:20 Prof. Bruce A. Arndtsen <i>Alternative Energy Drivers for Palladium Catalyzed Coupling Reactions</i>
14:30 -15:00 Opening Ceremony	10:20-10:40 Coffee Break	10:20-10:40 Coffee Break	9:50-11:10 Prof. Thierry Ollevier <i>Chiral Iron Catalysts for Asymmetric Organic Transformations</i>	10:20-10:40 Coffee Break
	10:40-12:00 Prof. Bill Morandi <i>Recent adventures in catalysis</i>	10:40-12:00 Prof. Matthias Beller <i>The Importance of Organometallic Chemistry in H and Heterogeneous Catalysis</i>	11:10-11:30 Coffee Break	10:40-12:00 Prof. Joaquín García Álvarez <i>Design of hybrid one-pot tandem protocols by using transition-metal or s-block organometallic chemistry under greener reaction conditions</i>
15:00-16:20 Prof. Odile Eisenstein <i>The chemistry of the Grignard systems: a cold case now open to computational studies</i>	12:00-12:15 Elsevier Presentation	12:00-12:15 OLON Presentation	12:50 -15:00 Lunch	12:00-12:30 Closing Ceremony
16:20-16:40 Coffee Break	12:30-14:40 Lunch	12:30-14:40 Lunch		
16:40-18:00 Prof. Johannes G. de Vries <i>Use of homogeneous catalysis for the conversion of renewable resources to chemicals</i>	14:40-16:00 Prof. Franc Meyer <i>Merging Organometallic and Bioinorganic Chemistry: N-Heterocyclic Carbene Ligands in Bioinspired Model Studies</i>	14:40-16:00 Prof. Dorota Gryko <i>Vitamin B12 catalysis – lessons learned from nature</i>	15:00-20:00 Social Tour	12:30-15:00 Lunch
18:00-19:20 Prof. Alessandro Mordini <i>The Organometallic Chemist's Toolbox to Access New Molecules for Sustainable Energy and Fuels Production</i>		16:00-17:20: Prof. Eva Hevia <i>Tailoring organosodium reagents for new stoichiometric and catalytic reactions</i>		
20:30-22:00 Welcome Dinner	16:00-17:00 Flash-presentations	17:20-18:30 Flash-presentations	20:00 Social Dinner	
	17:00-19:00 Coffee Break with Poster Session	18:30-20:00 Coffee Break with Poster Session		
	20:00 Dinner	20:00 Dinner		

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Prof. Bruce A. Arndtsen



McGill University, Montreal, Canada

“Alternative Energy Drivers for Palladium Catalyzed Coupling Reactions”



Biography: Bruce Arndtsen was born in Minnesota in 1966. He did his undergraduate studies at Carleton College (B.A. in Chemistry, 1988). He received a Ph.D. in Chemistry (1993) at Stanford University, under the direction of Prof. Lisa McElwee-White. His thesis research probed the synthesis and reactivity of low valent metal-nitrene complexes. He was a postdoctoral fellow with Prof. Robert Bergman at the University of California, Berkeley from 1993-1995, working in the area of iridium mediated alkane C-H bond activation. In 1995, he accepted his faculty position at McGill University, was promoted to associate professor in 2001 followed by full professor in 2010. Research in his group focuses on the discovery and mechanistic understanding of new approaches to chemical synthesis by

transition metal catalysis. Their work has demonstrated that transition metal-based reactions can be used to design efficient, one step syntheses of a range of important core structures directly from available building blocks, as an alternative to classic multistep protocols. His group has also developed the general concept of using ion pairing with chiral anions as an alternative to chiral ligands in asymmetric transition metal catalysis. More recently, his lab has discovered new classes of 1,3-dipoles for use in cycloaddition reactions (phospha-Münchnones), as well as approaches to polymer synthesis based upon metal catalyzed multicomponent reactions and developed mechanistic insights into each of these metal catalyzed processes. Professor Arndtsen is the recipient of a DuPont Aid in Education Award (2000), and one of only a handful in Canada to be awarded an NSERC Accelerator Grant for Exceptional New Opportunities (2004). He was his department's nominee for a Leo Yaffe Teaching award in 1998, and in 2005 was named a William Dawson Scholar at McGill University. In 2011 he was named a James McGill Professor of Chemistry; a Canadian Research Chair Tier I equivalent at McGill University.

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Prof. Joaquín García Álvarez

Universidad de Oviedo, Oviedo, Spain



Universidad de Oviedo

" Design of hybrid one-pot tandem protocols by using transition-metal or s-block organometallic chemistry under greener reaction conditions "



Biography: Joaquín García Álvarez studied chemistry at the University of Oviedo and received his PhD degree in 2005 under the supervision of Prof. J. Gimeno and Dr. Victorio Cadierno, studying the coordination of iminophosphorane ligands in arene-Ru(II) fragments. Then, he joined the group of Prof. Robert E. Mulvey at the University of Strathclyde in Glasgow (Scotland, UK) working for two years and a half in the field of main group chemistry (alkali-metal-mediated-metallation). In 2008, he returned to the University of Oviedo as a postdoctoral researcher, thanks to the award of a contract from the regional program "Clarín" of the Principado de Asturias. The current focuses of his research are: *i*) the study of metal-catalyzed (Ru, Cu, Pd, Au) and metal-mediated (Li, Mg) organic reactions using

environmentally friendly solvents [water and Deep Eutectic Solvents (*DESs*)] as reaction media; and *ii*) the design of *one-pot* processes combining both metal- and bio-catalysis. This research has been recognized over the last years with the award of a postdoctoral contract "Juan de la Cierva" in 2009, and more recently (2012), with a postdoctoral contract "Ramón y Cajal". In 2018, he was promoted to an Associate Professor position. He has published a total of 60 scientific articles and is co-author of nine book chapters on Organometallic Chemistry and Catalysis in unconventional reaction media. In 2016, he received the Prize "GEQO-Young scientist Award"; in 2017 the "Beca Leonardo a Jóvenes Investigadores y Creadores Culturales" from the BBVA foundation; and in 2018 the "PHOSAGRO/UNESCO/IUPAC Research Grant In Green Chemistry".

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Prof. Matthias Beller



Leibniz-Institut für Katalyse e.V. (LIKAT), Rostock, Germany

“The Importance of Organometallic Chemistry in Homogeneous and Heterogeneous Catalysis”



Biography: Matthias Beller, born 1962 in Gudensberg (Germany), studied chemistry at the University of Göttingen, Germany, where he completed his PhD thesis in 1989 in the group of L.-F. Tietze. As recipient of a Liebig scholarship, he then spent a one-year with K. B. Sharpless at MIT, USA. From 1991 to 1995, Beller worked in industry. Then, he moved to the Technical University of München as Professor for Inorganic Chemistry. In 1998, he relocated to Rostock to head the Institute for Organic Catalysis, which became in 2006 the Leibniz-Institute for Catalysis. The work of his group has been published in >1075 original publications, reviews and >150 patent applications have been filed (H-index: 142). 2014 – 2021: Web of Science “Highly Cited Researcher” (among the top 1% of

researchers with most cited documents in a specific field). He has received a number of awards including the Otto-Roelen Medal and the Leibniz-Price of the DFG. In 2006, he was also awarded “Entrepreneur of the Year” of Rostock and he received the German Federal Cross of Merit. Since then, he received the first “European price for Sustainable Chemistry”, the “Paul-Rylander Award” of the Organic Reaction Catalysis Society of the USA, the Gay-Lussac-Alexander-von-Humboldt-Prize of the French Academy of Sciences and the Emil Fischer Medal of the German Chemical Society. In 2015, he was awarded an honorary doctoral degree from the University of Antwerp, Belgium and received the Wöhler price for Sustainable Chemistry from the German Chemical Society as well as an ERC Advanced grant from the European Commission. In March 2016, he received the honorary doctorate of the University of Rennes 1. In 2017, Matthias Beller has received the Karl Ziegler Prize from GDCh, (German Chemical Society) and the Karl Ziegler Foundation - the award is one of the highest honors in the field of chemistry in Germany – and he was awarded as the first European chemist with the ACS Catalysis Award Lectureship. Most recently, he was selected as the prestigious “Hassel Lecturer 2018” from the University of Oslo, Norway and for the “Gordon Stone Lectureship” of the University of Bristol, UK. Matthias Beller is Vice President of the Leibniz Society – one of the major science organizations in Germany and a member of the German National Academia of Science “Leopoldina” and three other Academies of Sciences.

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Prof. Christophe Copéret

ETH zürich

Laboratory of Inorganic Chemistry, ETH Zürich, Switzerland

“The Importance of Organometallic Chemistry in Homogeneous and Heterogeneous Catalysis”



Biography: Prof. Christophe Copéret (CCH) was trained in chemistry and chemical engineering in CPE Lyon (France) and then undertook a PhD in chemistry at Purdue University (USA), where he studied the development of highly efficient synthesis of complex molecules via Pd-catalyzed carbonylation reactions in the group of Prof. E. Negishi (1991-1996). After a postdoctoral stay at the Scripps Research Institute (La Jolla, USA) in the group of Prof. K.B. Sharpless (1996-1997), where he developed oxidation reactions, CCH was offered in 1998 a permanent research position in CNRS in C2P2 (at the time LCOMS, directed by Dr. Jean-Marie Basset), a laboratory devoted to catalysis, chemistry of surfaces and polymers, and was promoted CNRS Research Director in 2008. Since Nov, 1st 2010, CCH is

Professor in the Department of Chemistry and Applied Biosciences at ETH Zürich. His scientific interest lies at the frontiers of molecular, material and surface chemistry, with the aims to design functional materials with applications in catalysis (sustainable chemistry and energy), molecular recognition, imaging and microelectronics. CCH is Editor in Chief of *Helvetica Chimica Acta*. Besides scientific activities, CCH enjoys literature, history, cooking and wine tasting, probably a reminiscence of his childhood spent in the vineyards in Fleuri, one of the famous crû of Beaujolais (La reine) just 50 km North of Lyon.

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SPEAKERS

Prof.ssa Odile Eisenstein



University Montpellier; CNRS, ENSCM, Montpellier, France.

Hylleraas Centre for Quantum Molecular Sciences and Department of Chemistry, University of Oslo, Norway

“The chemistry of the Grignard systems: A cold case now open to computational studies”



Biography: Odile Eisenstein was born near Paris from Jewish parents from Lithuania and Romania. After a PhD with Nguyen Trong Anh and Lionel Salem at the University of Paris-Sud at Orsay, she went for post-doc with Jack Dunitz at the ETH Zurich and then with Roald Hoffmann at Cornell. She also was assistant professor at University of Michigan. In France, she was a CNRS research professor. She started at University Paris-Sud and in 1996 she moved to the University of Montpellier. Since 2012, she is adjunct professor at the University of Oslo. She also held several visiting professor positions in the US (Indiana, Texas A&M, Berkeley), in UK (Nottingham, York), in Israel (Technion). She holds several honorary doctorates. She is a member of the French Academy of Science, a foreign member of

the Norwegian Academy for Science and humanities, a foreign member of North-Westphalia Academy. She is a member of the International Academy of Quantum Molecular Science and has been president since 2018. She was elected to the American Academy of Arts and Science a few days before being elected to the US National Academy of Science. She is officier de l'ordre du Mérite et de l'ordre la Légion d'Honneur.

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Prof.ssa Dorota Gryko



Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

“Vitamin B12 catalysis – lessons learned from nature”



Biography: Bruce Dorota Gryko obtained her Ph.D. degree from the Institute of Organic Chemistry of the Polish Academy of Sciences in 1997 under the supervision of Professor J. Jurczak. After a postdoctoral stay with Professor J. Lindsey at North Carolina State University (1998–2000), she started her independent career in Poland. In 2009 she received the prestigious TEAM grant from the Foundation for Polish Science. She became Full Professor in 2015.

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Prof.ssa Eva Hevia

Department für Chemie und Biochemie, University of Bern, Switzerland



“Tailoring organosodium reagents for new stoichiometric and catalytic reactions”



Biography: Originally from Gijón (Spain), Eva received both her MSci degree in Chemistry and her Ph.D. degree from the Universidad de Oviedo (Spain) in 1998 and 2002 respectively. The latter under the supervision of Victor Riera and Julio Perez. After a three-year postdoctoral period at the University of Strathclyde working with Robert Mulvey, as a Marie Curie Fellow, in 2006 she took up a Royal Society University Research Fellowship and Lectureship there. Subsequently she was promoted to Senior lecturer in 2010, Reader in 2011 and as a Professor in 2013. In 2019 Eva moved to the University of Bern where she is currently a Professor in Inorganic Chemistry at the at the Department of Chemistry and Biochemistry. She has published over 140 peer-reviewed papers in the area and to date

her research has been recognised with several prestigious prizes including the 2016 SRUK Emerging Talent Award, which honours the most promising Spanish scientist in the UK under 40, and more recently by the 2017 RSC Corday-Morgan Prize awarded to the most meritorious contributions to Chemistry. An elected Fellow of the Royal Society of Edinburgh (RSE) and the European Academy of Sciences her research has been supported by the SNF, EPSRC, UK Charities, EU (ERC-Stg-2011), industry and governmental bodies. She sits on the International Advisory Boards of Eur. J. Inorg. Chem, Organometallics, Chem Catalysis, Chemistry Open and Asian J. Org. Chem and she has presented over 100 invited lectures worldwide.

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Prof. Igor Larrosa



School of Chemistry, University of Manchester, United Kingdom

“Mechanistic Understanding-Led Transition Metal Catalyzed C-H Functionalization”



Biography: Igor was born in Barcelona, Spain. He received his undergraduate education at the Universitat de Barcelona (1999) where he also underwent M.Sc. and Ph.D. studies with Felix Urpi and Pere Romea. A fellowship from Ministerio de Educacion y Ciencia supported three month's research in Professor Erick M. Carreira's laboratories at ETH Zurich, Switzerland. With a second fellowship he started postdoctoral research in Professor Anthony G. M. Barrett's group at Imperial College London, UK, where he was appointed group leader. In September 2007 he started his independent career as a Lecturer in synthetic organic chemistry at Queen Mary University of London and was promoted to Senior Lecturer in 2011 and to Reader in Catalysis in 2012. In 2014 Igor moved to the University of Manchester to take up the position of

Professor of Organic Chemistry. Igor received an ERC Starting Grant in 2011 and currently holds an ERC Advanced Grant. In 2019, Igor was selected for the UK Blavatnik Award for Young Scientists as a Chemistry finalist.

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Prof. Franc Meyer



Institut für Anorganische Chemie Georg-August, University of Göttingen, Germany

“Merging Organometallic and Bioinorganic Chemistry: N-Heterocyclic Carbene Ligands in Bioinspired Model Studies”



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.

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Prof.ssa Barbara Milani



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Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy

“A tour around the late transition metal catalysts for polymerization reactions”



Biography: Barbara Milani is Associate Professor of General and Inorganic Chemistry at the University of Trieste. Since October 2022 she is the Rectoral Delegate for Internationalization and International Mobility @ UniTS. She received her PhD degree at University of Trieste in 1994. After a post-doctoral period, she became assistant professor in 1998 and in 2014 she was promoted associate professor. She was visiting professor at Institut National Polytechnique in Toulouse in 2010 and at Université Pierre et Marie Curie in Paris in 2014. In 2017 she got the National Abilitation to Full Professor of General and Inorganic Chemistry. She was member of the Advisory Board of European Journal of Inorganic Chemistry (2007-2009). Currently, she is member of the Advisory Board of Dalton

Transactions, and of the International Advisory Board of the International Symposium on Homogeneous Catalysis (ISHC). She was the coordinator of the PhD School Doctorate in Chemistry (joint PhD School between University of Trieste and Ca' Foscari University Venice; 2017-2019). She is the ERASMUS coordinator for chemistry for the Department of Chemical and Pharmaceutical Sciences @UniTS. Her main research interests focus on organometallic chemistry and on development of homogeneous catalysts, based on late transition metals, for polymerization reactions.

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Prof. Bill Morandi



Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland

“Recent adventures in catalysis”



Biography: Professor Bill Morandi studied at ETH Zürich (2003–2008), receiving a BSc in Biology and a MSc in Chemical Biology. From 2008 to 2012, he pursued his PhD in organic synthesis at the same institution in the labs of Professor Erick M. Carreira. Afterwards, he moved to the California Institute of Technology (Pasadena, CA) for a postdoctoral stay with Professor Robert H. Grubbs. From 2014 to 2018, he was an independent Max Planck Research Group Leader at the Max-Planck-Institut für Kohlenforschung (Mülheim, Germany), before subsequently returning to ETH Zürich as a Professor in 2018. He is currently Full Professor of Synthetic Organic Chemistry and heads the Institute of Organic Chemistry (Laboratorium für Organische Chemie) at ETH Zürich.

His research program targets the design and development of new catalytic reactions for the synthesis of small molecules and materials, as well as the valorization of renewable feedstocks and waste material. He has received numerous awards, among them a Novartis Early Career Award in Organic Chemistry, the Carl Duisberg Memorial Prize from the German Chemical Society and a selection as a C&EN's Talented 12. He is currently an Associate Editor for Organic Chemistry Frontiers, a journal from the Royal Society of Chemistry.

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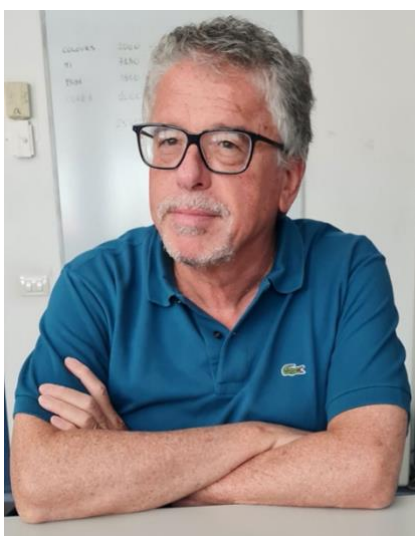
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Prof. Alessandro Mordini



Istituto di Chimica dei Composti Organometallici, CNR, Sesto Fiorentino, Italy

“The Organometallic Chemist's Toolbox to Access New Molecules for Sustainable Energy and Fuels Production”



Biography: Alessandro Mordini received his degree in Chemistry (with honors) in 1983 from the University of Firenze (Italy), where he also completed his PhD in 1987. The same year he became CNR researcher at the CNR Center on Heterocyclic Chemistry – University of Firenze joining the group of Prof. Alfredo Ricci where he was involved in the chemistry of Silicon and Tin organometallic derivatives. He spent three research periods in the group of Prof. Manfred Schlosser at the University of Lausanne in 1984-1985 (during the PhD course), in 1988-1989 as post doctor and in 1992 as instructor. In Lausanne he worked on the synthesis and reactivity of polar organometallic compounds and, in particular, on superbasic reagents. In 1999 he was appointed CNR Senior Researcher at the same CNR research Center in Florence

which later, in 2001, became Institut on the Chemistry of Organometallic Compounds (ICCOM). In 2001 he spent three months as invited professor at the University of Kyoto. Dr. Mordini has been the Director of the NATO – ASI School “New Methodologies and Techniques in Organic Chemistry” (Certosa di Pontignano, Siena, 2005); the chairman of the “IX International Symposium on Carbanion Chemistry” (Firenze, 2010) and of the “IX Congress of the Interdivisional group of Organometallic Chemistry of the Italian Chemical Society” (Firenze, 2010). He will be the chairman of the next “Spanish-Italian Symposium on Organic Chemistry” (Firenze, 2014) and of the “XXVII International Conference on Organometallic Chemistry” (Firenze, 2018). He is Member of the Executive Board of the Interdivisional Group of Organometallic Chemistry of the Italian Chemical Society; of the Executive Board of the Tuscan Section of the Italian Chemical Society and of the Technical and Scientific Board of Polo delle Energie Rinnovabili della Regione Toscana. He is reviewer for several journal in the field of organic and organometallic chemistry and referee for some European Research Agencies. He has been the responsible of bilateral international projects and COST networks as well as responsible of research contracts with several Italian companies. He is the author of about 10 monographies and book chapter's, 90 articles in peer-reviewed international journals mainly dealing with the synthesis and application of organometallic reagents, synthesis of new heterocyclic scaffolds, and, more recently, design and synthesis of new materials for energy.

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Prof. Thierry Ollevier



Département de chimie, Université Laval, Québec, Canada

“Chiral Iron Catalysts for Asymmetric Organic Transformations”



Biography: Prof. Dr. Thierry Ollevier obtained his B.Sc. in Chemistry at the University of Namur, Belgium, in 1991. He obtained his B.Sc. (1991) and Ph.D. (1997) at the Université de Namur, Belgium. After an Assistant Professor appointment (2001) at Université Laval, Québec (Canada), he became Associate Professor (2006) and is currently a Full Professor. Current research in his group aims at designing novel catalysts, developing catalytic reactions and applying these methods to chemical synthesis. He is active in the areas of Lewis acids, asymmetric catalytic synthesis, and organic chemistry in aqueous conditions, metal chemistry, and green synthetic chemistry. He has 75 publications (53 research articles, 20 encyclopedia articles, 2 conference proceedings), 3 book chapters, and 1 book to his credit. He is a member of the Canadian Society of Chemistry, American Chemical

Society (Organic Division), Société française de chimie, and European Chemical Society. Synthetic organic chemistry, homogeneous catalysis.

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Prof. ssa Beatriz Royo

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

“Manganese-catalyzed hydrosilylative reduction: ligand design and mechanistic aspects”



Biography: Beatriz Royo is Principal Investigator and Head of the Organometallic Catalysis Group at ITQB NOVA, University Nova of Lisbon (Portugal). She graduated with honours in Chemistry at University of Alcalá (Madrid, Spain), and obtained her PhD in 1993 at the University of Sussex, UK, where she worked on main group chemistry under the supervision of Prof. Michael F. Lappert. After her PhD, she spent four years at University of Alcalá working on early transition metals in the group of Prof. Pascual Royo, and in 1997 she moved to Lisbon to join the group of Prof. C. Romão at ITQB. In 2004, she started her independent career at ITQB as Head of the Organometallic Catalysis group. Her research spans the areas of synthetic organometallic chemistry and catalysis. Royo's group has

developed sustainable catalytic methods for a range of organic transformations using Earth-abundant metals and N-heterocyclic carbene ligands. Her research interests include hydrosilylation, hydrogen borrowing processes, oxidative coupling reactions and catalytic methods for the activation of CO₂ mediated by 3d metals.

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Prof. Dr. Johannes G. de Vries



Leibniz Institute for Catalysis (LIKAT), Rostock, Germany

“Use of homogeneous catalysis for the conversion of renewable resources to chemicals”



Biography: Johannes G. de Vries received his PhD from the University of Groningen in 1979. After a postdoc at Brandeis University, Waltham, USA, his first job was as a medicinal chemist with Sandoz in Vienna and in London. From 1988–2013 he worked for DSM in Geleen, The Netherlands, lastly as a Principal Scientist in the area of Homogeneous Catalysis. From 1999–2018 he was part-time professor at the University of Groningen. In 2014 he became Department Head Catalysis with Renewables at the Leibniz Institute for Catalysis in Rostock, Germany. In 2013 he received the Paul N. Rylander Award for outstanding contributions in the field of catalysis as it applies to organic synthesis.

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LECTURES

Lecture 1, September 7, 15:00 - 16:20

The chemistry of the Grignard systems: a cold case now open to computational studies

Odile Eisenstein,^{a,b*} Michele Cascella^b

^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.

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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

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LECTURES

Lecture 2, September 7, 16:40 - 18:00

Use of homogeneous catalysis for the conversion of renewable resources to chemicals

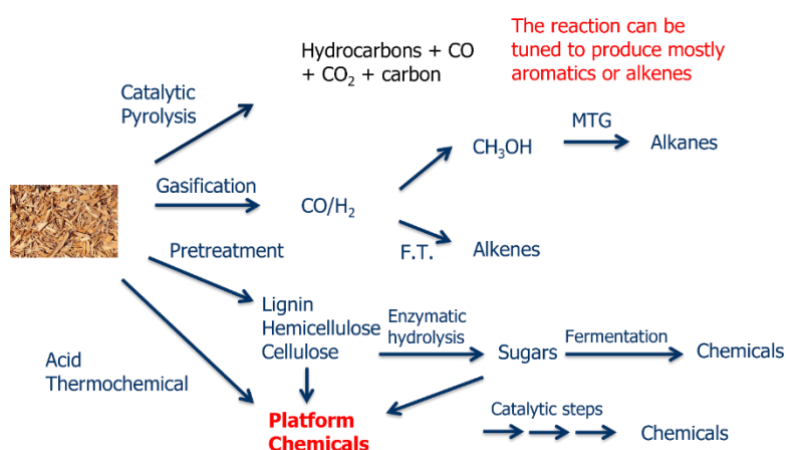
Johannes G. de Vries

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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.

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The Organometallic Chemist's Toolbox to Access New Molecules for Sustainable Energy and Fuels Production

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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).

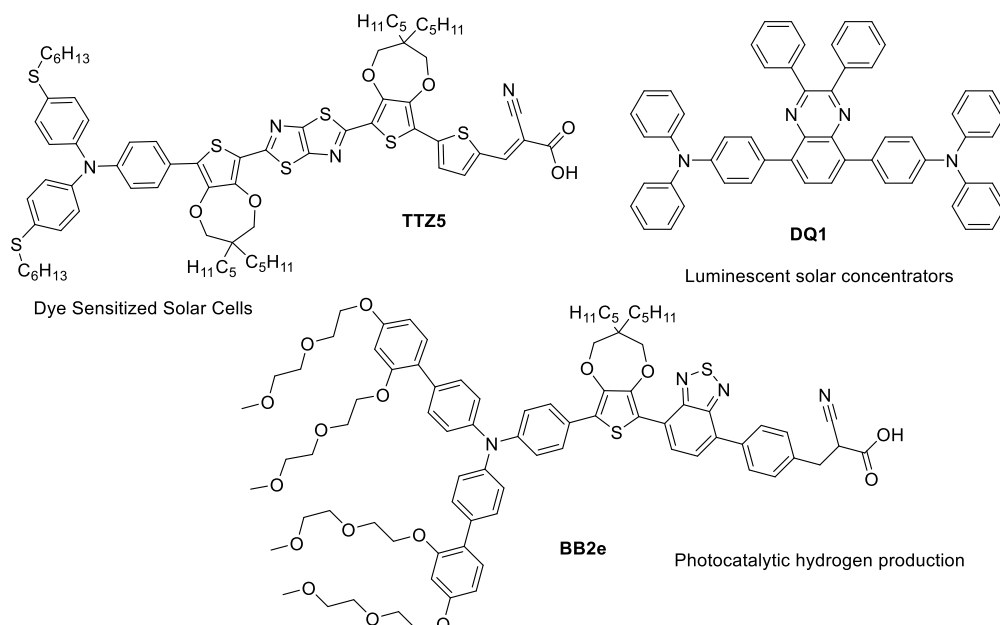


Figure 1: Structures of selected organic compounds recently applied in solar energy conversion devices

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.

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LECTURES

Lecture 4, September 8, 09:00 - 10:20

NMR chemical shifts beyond numbers

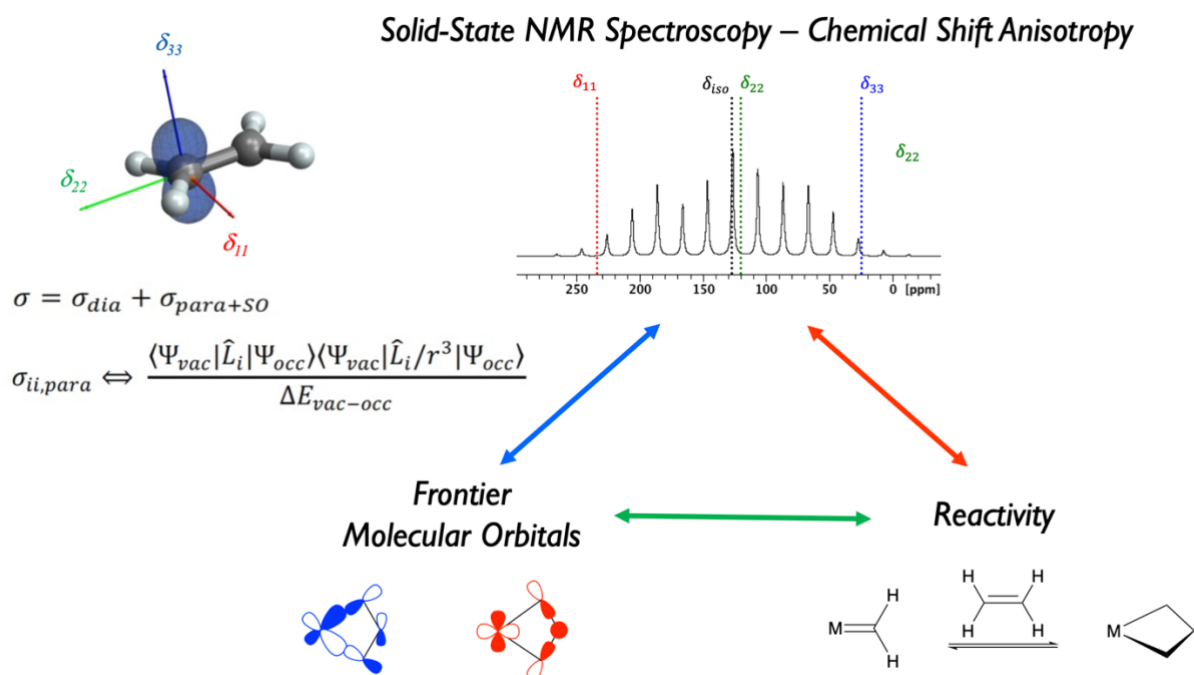
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Chemical shift has been successfully used since the beginning of NMR to identify the signature of molecules (and materials) making NMR an invaluable tool of characterizations. Because of its power to elucidate molecular structure, NMR interpretation 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.



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[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.

LECTURES

Lecture 5, September 8, 10:40 - 12:00

Recent adventures in catalysis

Prof. Bill Morandi

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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.

Lecture 6, September 8, 14:40 - 16:00

Merging Organometallic and Bioinorganic Chemistry: N-Heterocyclic Carbene Ligands in Bioinspired Model Studies

Franc Meyer

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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.

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LECTURES

Lecture 7, September 9, 09:00 - 10:20

Manganese-catalyzed hydrosilylative reduction: ligand design and mechanistic aspects

Prof. Beatriz Royo

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

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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.

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Lecture 8, September 9, 10:40 - 12:00

The importance of organometallic chemistry in homogeneous and heterogeneous catalysis

Prof. Matthias Beller

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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

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

Vitamin B₁₂ catalysis – lessons learned from nature

Prof. Dorota Gryko

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“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.



<https://www.beckylaroc.co.uk/b12-injections-in-bromley/>

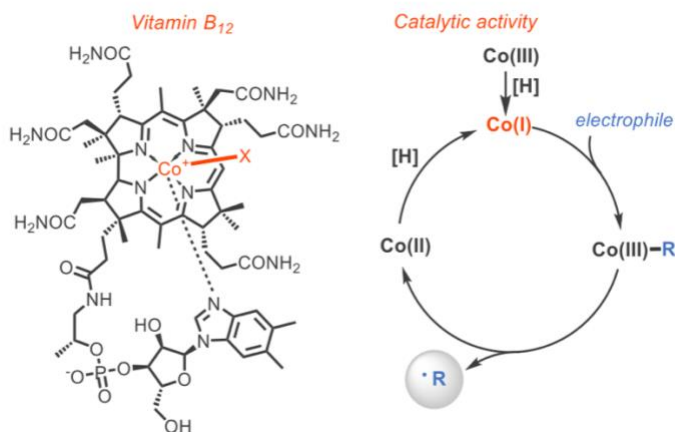


Figure 1. Vitamin B₁₂ not only a medicine

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- [4] Giedyk, M.; Gryko, D.; *Chem Cat.* **2022**, *2*, 1534.
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- [10] Potrzęsaj, A.; Ociepa, M.; Chaładaj, W.; Gryko, D. *Org. Lett.* **2022**, *24*, 2469.
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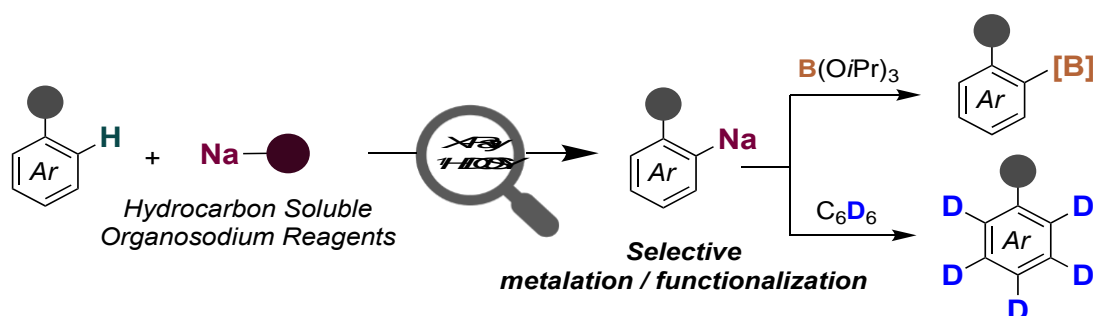
Lecture 10, September 9, 16:00-17:20

Tailoring organosodium reagents for new stoichiometric and catalytic reactions

Prof. Eva Hevia

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.



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Lecture 11, September 10, 08:30 – 9:50

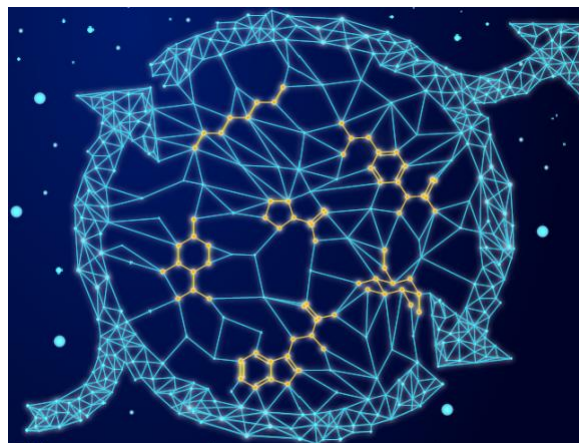
Mechanistic understanding-led transition metal catalyzed C-H functionalization

Prof. Igor Larrosa

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



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Lecture 12, September 10, 09:50 – 11:10

Chiral Iron Catalysts for Asymmetric Organic Transformations

Prof. Thierry Ollevier

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The objective of our research program is the development of new synthetic methods, with emphasis on catalytic and enantioselective procedures for the simple preparation of biologically and commercially important molecules.

Various iron-derived Lewis acids have been developed as green catalysts in asymmetric synthesis. Chiral iron complexes have been employed in selected asymmetric C–C, C–N, and C–S bond-forming reactions, such as the Mukaiyama aldol, epoxide opening, thia-Michael and Diels–Alder reactions.^{1–5} As part of our ongoing interest in ligand design, we report the fine-tuning of alternate designer ligands toward higher chiral inductions. Iron coordination chemistry will be discussed in the context of the enantiocontrol of selected reactions. We developed an efficient chiral C_2 -symmetric 2,2'-bipydiol ligand possessing an adamantyl or a CF_3 group in the a,a'-positions. A highly enantioselective method for the catalytic addition of thiols to a,b-unsaturated oxazolidinones was developed using Fe^{II} salts with the (S,S)-2,2'-bipyridine-a,a'-tBu-diol ligand (Bolm's ligand, up to 86% *ee*)⁵ and the analogue ligand possessing 3,3'-dimethyl substituents (up to 90% *ee*).² The Fe^{III} -catalyzed asymmetric Diels–Alder reaction of various dienes with a,b-unsaturated oxazolidinones was performed using Bolm's ligand (up to 98% *ee*)⁴ and the adamantyl-variant (S,S)-2,2'-bipyridine-a,a'-1-Ad-diol (up to > 99.5% *ee*).¹ Another new 2,2'-bipydiol ligand possessing CF_3 groups in the a,a'-positions was prepared and used in the asymmetric addition of Et_2Zn to aldehydes (up to 95% *ee*).³ Overall, we developed 4 new asymmetric reactions: Fe^{II} -catalyzed thia-Michael (up to 90% *ee*),⁵ Fe^{II} -catalyzed Mukaiyama aldol (up to 98% *ee*),^{1,2} Fe^{III} -catalyzed Diels–Alder (up to > 99.5% *ee*),^{1,4} and Zn^{II} -mediated Et_2Zn addition to aldehydes (up to 95% *ee*).³

These results will contribute to the development of greener iron-derived acid catalysis for asymmetric synthesis.

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LECTURES

A tour around the late transition metal catalysts for polymerization reactions

Prof. Barbara Milani

Lecture 13, September 10, 11:30 – 12:50

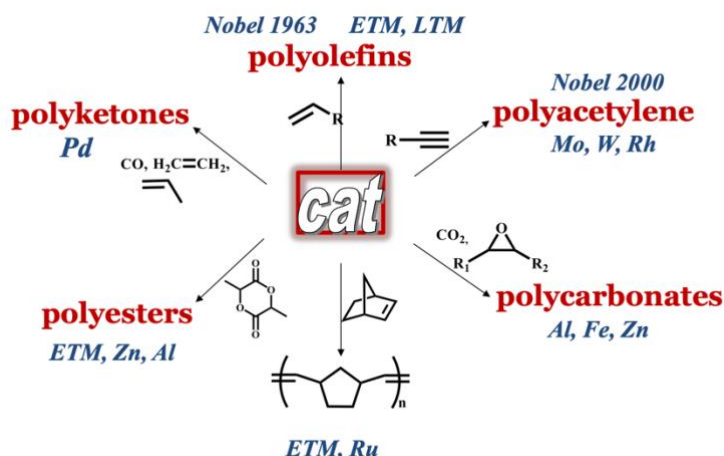
Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, 34127 Trieste, Italy.

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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.



LECTURES

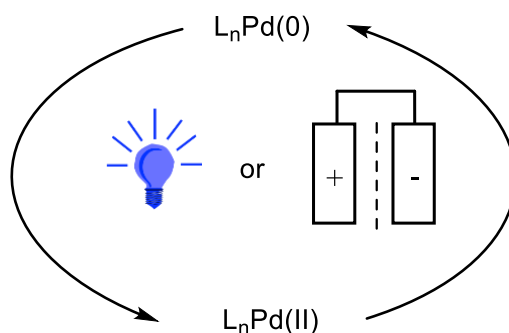
Alternative energy drivers for palladium catalyzed coupling reactions

Prof. Bruce A. Arndtsen

Lecture 14, September 11, 09:00 – 10:20

Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal QC H3A 0B8 Canada

The ability of transition metal catalysts to mediate new bond forming reactions has had a dramatic impact on modern molecular synthesis. Nevertheless, a central feature in these reactions is need to balance of reverse operations on the catalyst so it is regenerated at the end of each cycle of product formation, which can limit catalytic activity and the scope of many transformations. This talk will describe our efforts to address these challenges by introducing alternative, often renewable, energy sources into catalysis, and from this create new bond forming reactions. These include using visible light excitation directly on active palladium catalysts to drive the oxidative addition/reductive elimination cycle in coupling reactions independent of the classical limits in thermal catalysis, or the use of electrochemistry to change the nature of the metal throughout the cycle.^[1] Combining these with the favored energetics of carbon monoxide conversion to carboxylic acid derivatives can be used to drive the build-up of reactive products from stable reagents. The use of this chemistry to create ambient temperature and general catalysts for carbonylation reactions, multicomponent transformations, acyl halide or even super-electrophile formation, or new avenues to C-H bond functionalization, will be discussed, as will the mechanistic origins of these influences, and their ability to enable the use of earth abundant catalysts in traditionally precious metal catalyzed reactions.



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LECTURES

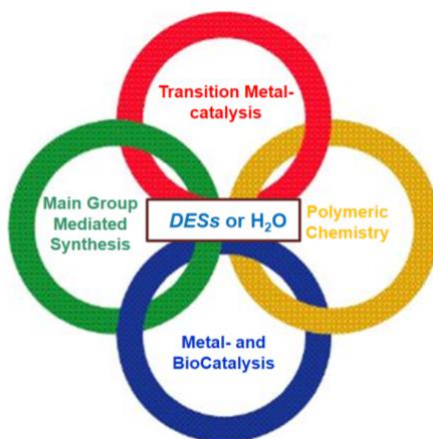
Lecture 15, September 11, 10:40-12:00

Design of hybrid one-pot tandem protocols by using transition-metal or s-block organometallic chemistry under greener reaction conditions

Joaquín García Álvarez

Universidad de Oviedo, Oviedo, Spain

Due to the increasing rate of production of the *Chemical Industry* it is necessary to look for new alternative and greener ways that attempt to minimize the undesired side effects caused to the environment.^[1] In this sense, considerable attention has been recently focused on *Deep Eutectic Solvents (DESs)* as an alternative to conventional volatile organic compounds (*VOCs*) in many fields of science.^[2] Our group has had an ongoing interest in the study of both transition-metal-catalysed^[3] or main-group-mediated^[4] organic transformations using biorenewable and biodegradable *DESs* as reaction media. The implementation of these neoteric solvents has allowed us to work under bench-type reactions (room temperature, under air/moisture) even in the case of highly reactive *s*-block reagents (*RLi/RMgX*). Relatedly, we are pursuing the design of new hybrid one-pot tandem protocols in sustainable solvents and under bench-type reactions conditions which combine different instruments from the traditional organic synthetic toolbox (transition metals, main-group elements, enzymes or organocatalysts),^[5] circumventing the need of tedious and time-consuming intermediate purification and separation processes, therefore minimizing the generation of residues and simplifying practical aspects, being therefore in agreement with the Principles of *Green Chemistry*.



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[5] a) N. Ríos-Lombardía, C. Vidal, E. Liardo, F. Morís, J. García-Álvarez, J. González-Sabín, *Angew. Chem. Int. Ed.* **2016**, 55, 8691; b) M. Ramos-Martín, R. Lecuna, L. Cicco, P. Vitale, V. Capriati, N. Ríos-Lombardía, J. González-Sabín, A. Presa-Soto, J. García-Álvarez, *Chem. Commun.* **2021**, 57, 13534.

Poster 1

Comparative synthesis methods for novel, air-sensitive, antimony(III) aryloxides

Maria Caterina Afloarei,* Cristian Silvestru

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Organoantimony(III) compounds have attracted considerable attention in recent years, with significant achievements in both fundamental and applied chemistry. Applications in a wide range of topics were observed, in fields such as CO₂ fixation by organoantimony(III) oxo-species, C-H bond activation, as well as catalysis. However, relatively few examples of organoantimony(III) alkoxides and aryloxides have been published so far.¹⁻⁴

We proposed the syntheses of a series of novel organoantimony(III) aryloxides, [2-(Me₂NCH₂)C₆H₄]₂Sb(OAr) (2), [2-(Me₂NCH₂)C₆H₄]Sb(OAr)₂ (6), [2-(Me₂NCH₂)C₆H₄]Sb(OAr)Cl (9), [(2-(Me₂NCH₂)C₆H₄)Sb(OAr)]₂O (10), using several synthetic pathways (Figure 1).⁵⁻⁷ Different synthetic approaches were employed, due to the air- and moisture-sensitive nature of the compounds. A comparison between the different methods was drawn, and the practical challenges and advantages of each method were discussed.

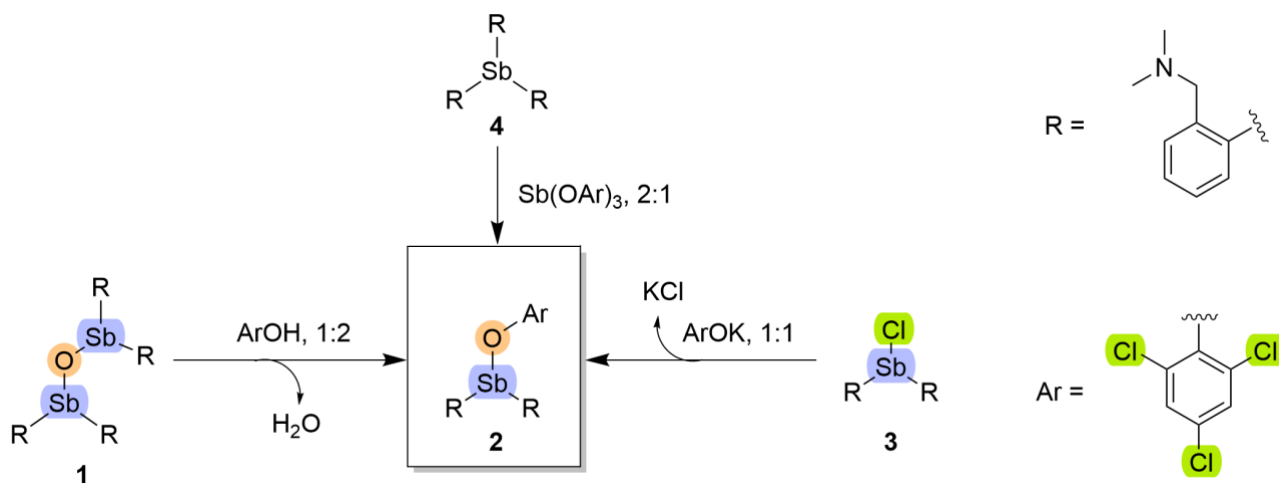


Figure 1

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Poster 2

Ion exchange resin supported tetrahalo-metallates as efficient catalysts for the synthesis of cyclic carbonates and carbamates from CO₂

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

Ammonium tetrahalo-metallates of the first transition series elements combine ease of preparation and storage, excellent catalytic activity and extremely low production costs.¹ Recently we showed that ammonium ferrates and zincates are active catalysts in the cycloaddition of CO₂ to aziridines and epoxides to yield carbamates and carbonates, respectively.^{2 3 4} These reactions display interesting features in terms of eco-sustainability, since the coupling occurs with 100% of atom-economy, valorizing waste CO₂ to yield value-added products. Additionally, metallates can be easily anchored on anionic exchange resins, such as Amberlyst[®] and Amberlite[®] (Figure 1).

A simple and efficient protocol to functionalize Amberlyst[®] ionic exchange resins with ferrate and zincate complexes was thus developed. The obtained materials can be finely tuned both by choosing the preferred metallic halide and resin reticular size, effectively controlling the productivity of the reaction and pave the way for a future flow implementation.

We present our recent progress in this field of chemistry, highlighting both the benefits and the challenges encountered in the functionalization of ion exchange resins with tetrahalo-metallates.

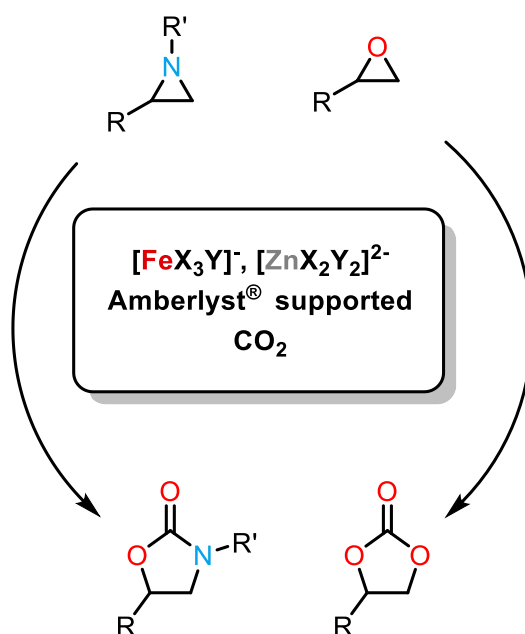


Figure 1

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Poster 3

Cyclometalated C[^]N diphosphine ruthenium catalysts for Oppenauer-Type Oxidation / Transfer Hydrogenation Reactions and Cytotoxic Activity

Matteo 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; ^b Dipartimento di Area Medica, Università di Udine, Via Colugna 50, I-33100 Udine, Italy,

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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.

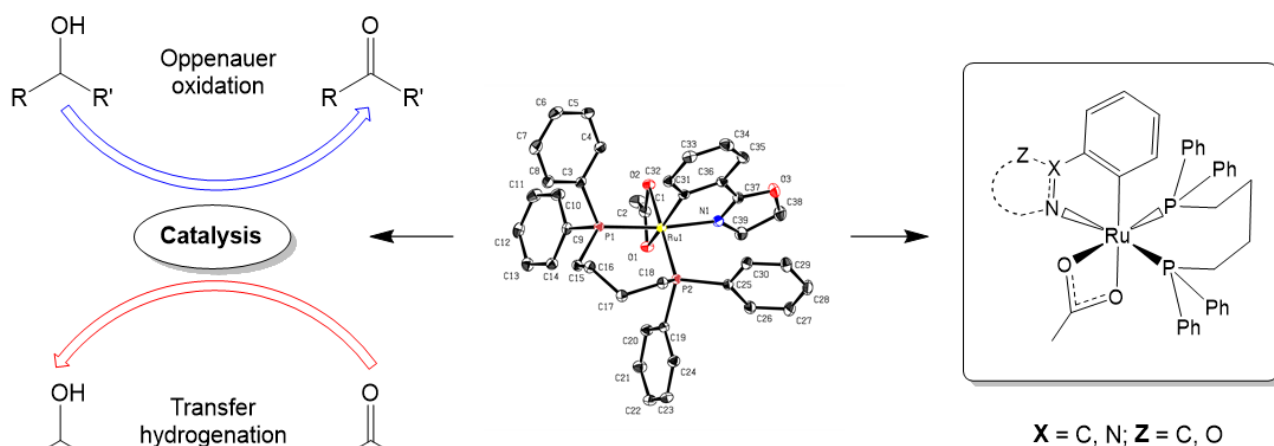


Figure 1

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Poster 4

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

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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 (R = Me, Et, Pr, 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 result in a drastic increase in the cytotoxicity and possible related anticancer potential of these type of complexes.

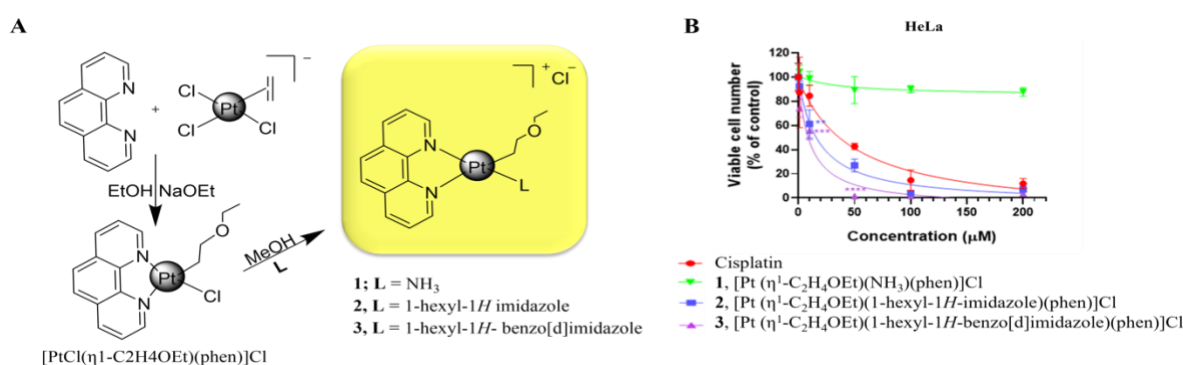


Figure 1: Showing the synthesis and cytotoxic activity of newly synthesized platinum(II) complexes

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

Poster 5

Expanding the scope of allylic C–H alkynylations via copper-photocatalyzed cross-dehydrogenative coupling

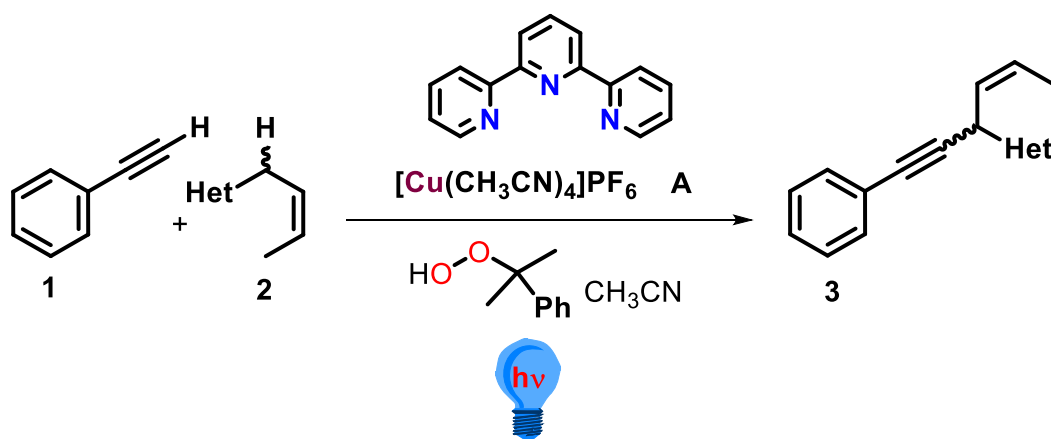
Gustavo Álvarez,* and Esteban Mejía.

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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.



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Poster 6

Strategies in Photoredox Catalysis for the Synthesis of Unnatural Amino Acids

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Photoredox catalysis has emerged as one of the fastest-growing fields in organic synthesis over the past decade because it provides a mild and non-toxic entrance to one-electron reaction manifolds. A milestone in this renaissance was the development of organic photoredox catalysts and their application to synthetic methodology.^[1-3] Here, we have developed a convenient protocol for constructing unnatural α -amino acids from feedstock chemicals, allowing quick access to diverse derivatives. An N-sulfinyl-imine is employed as the α -amino acid precursor and is used as the radical acceptor to which radicals can be appended, forming the amino acid sidechain. This radical is generated from a native functionality, either carboxylic acid, alcohol, or α -amino C–H bond.

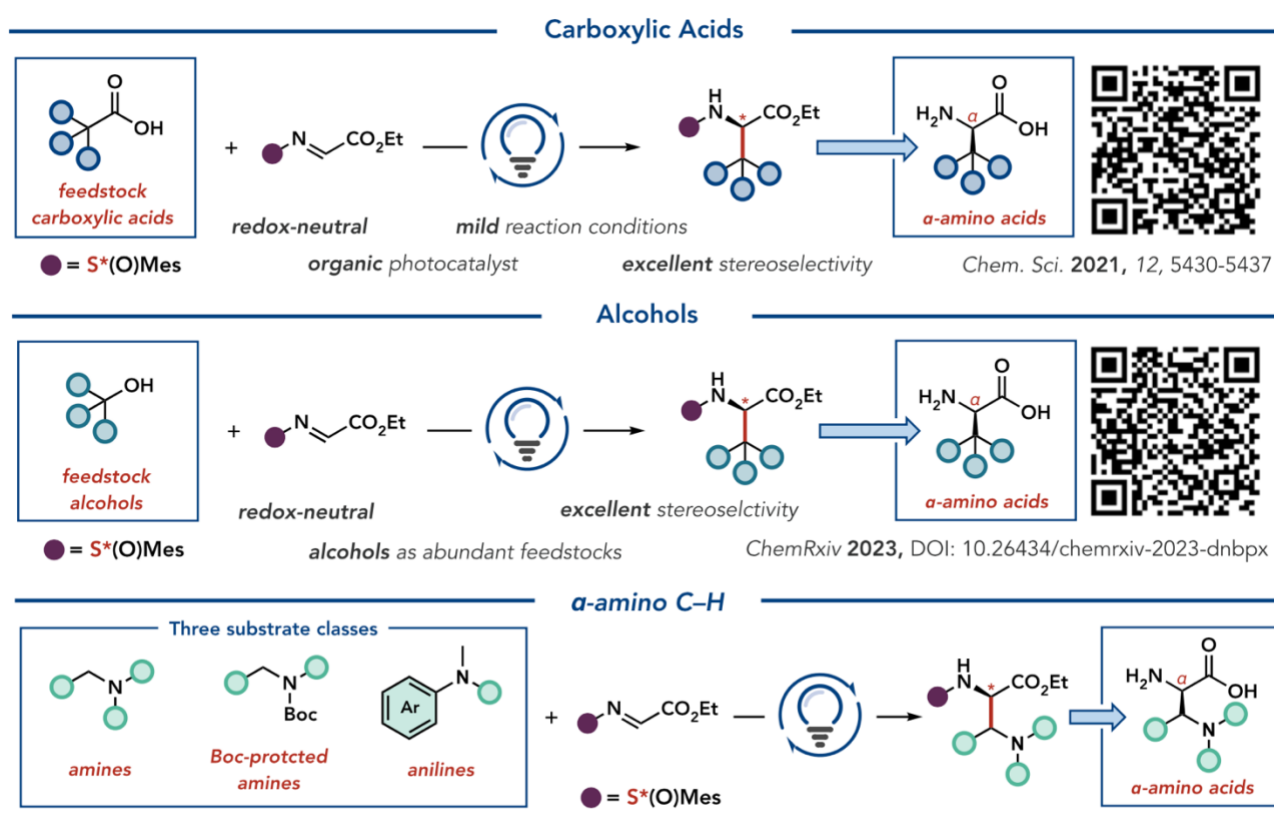


Figure 1

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[2] M. H. Shaw, J. Twilton, D. W. MacMillan, *J. Org. Chem.* **2016**, 81, 6898-6926.

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Poster 7

Iridium-based luminescent sensors for barium tagging

Ane I. Aranburu,^{a,b*} Pablo R.G. Valle,^{a,b} Virginia San Nacienceno,^a Ariadna Pazos,^a Juan J. Gómez-Cadenas,^{b,c} and Zoraida Freixa,^{a,c} On behalf of the NEXT Collaboration.

^a Department of Applied Chemistry, University of the Basque Country (UPV/EHU), Donostia, 20018, Spain

^b Donostia International Physics Center DIPC, Donostia, 20018, Spain

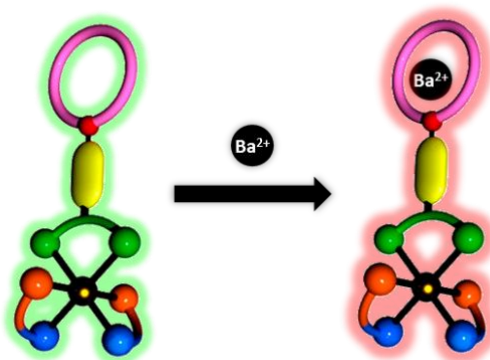
^c Ikerbasque, Basque Foundation for Science, Bilbao, 48009, Spain

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When considering luminescent sensors for cations, organometallic luminescent probes present outstanding properties due to the variety of energetically accessible excited states of different nature, permitting the color and intensity tuning of the emission by a rational design of the ligands, and an educated selection of the metallic center. Additionally, due to spin-orbit coupling induced by the heavy atom, transitions are possible from/to both singlet and triplet excited states. Compared with pure fluorescence, the long-lived nature of these emissions presents an advantage for specific applications, as it permits distinguishing their emission from the autofluorescent background (i.e. in biosensing) or from the scattered light, by applying a time-gated acquisition (time-resolved spectroscopy).

In the last years, in our group, we have been developing iridium(III)-based sensors as ratiometric and time-resolved probes for Ba²⁺-sensing. These compounds are relevant in the context of Ba²⁺-tagging in ¹³⁶Xe double-beta radioactive decays, where ultra-low background detection is imperative.^{1,2} In this context, this work is part of the R&D chemical effort of the NEXT Collaboration.

In this communication, a new family of iridium complexes for Ba²⁺-sensing will be presented. Their photophysical characterization together with their luminescent response to Ba²⁺ will be discussed.



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Acknowledgements: This work is funded by Spanish Ministry of Science and Innovation (PID2019-111281GB-I00 funded by MCIN/AEI/10.13039/501100011033), Basque Government (IT1880-19 and IT1553-22) and European Research Council (ERC) under the European's Union Horizon 2020 research and innovation programme (Grant agreement ERC-2020-SyG 951281).

Poster 8

A Mild, Efficient and Sustainable Tetrahydropyranylation of Alcohols Promoted by Acidic Natural Deep Eutectic Solvents

Davide Arnodo,^a Eugenio De Nardo,^a Simone Ghinato,^a Salvatore Baldino,^a Marco Blangetti,^{a,*} and Cristina Prandi^a

Dipartimento di Chimica, Università degli Studi di Torino, Via Pietro Giuria 7, 10125 Torino (Italia).
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The development of novel methodologies for the introduction/removal of protecting groups which ideally fulfill the sustainability requirements (quantitative yields, use of environmentally responsible solvents, low E-factor and high atom economy) is of great significance and represents nowadays an urgent challenge for industrial research.¹ The introduction of an -OH protecting group is often essential to avoid undesired reaction pathways induced by the acidic and nucleophilic character of the hydroxyl functionality.² In this framework, a straightforward protocol to promote the tetrahydropyranylation of alcohols, using for the first time bioinspired acidic natural deep eutectic solvents (NADESs) as non-innocent reaction media under mild reaction conditions, was investigated (Figure 1).³ This approach enables the preparation of several tetrahydropyranyl- (THP) ethers starting from primary, secondary and tertiary alcohols in short reaction times and with high levels of chemoselectivity, working under air and without the need of additional catalysts. The sustainability of the methodology was further highlighted by its scalability and the easy recyclability of the NADES, allowing multigram preparations of THP ethers without any loss of the catalytic activity of the reaction media up to ten recycling steps. Telescoped, one-pot tetrahydropyranylation/nucleophilic acyl substitution transformations with the use of highly polar organometallic reagents (RLi) were also demonstrated using the same acidic eutectic mixture.

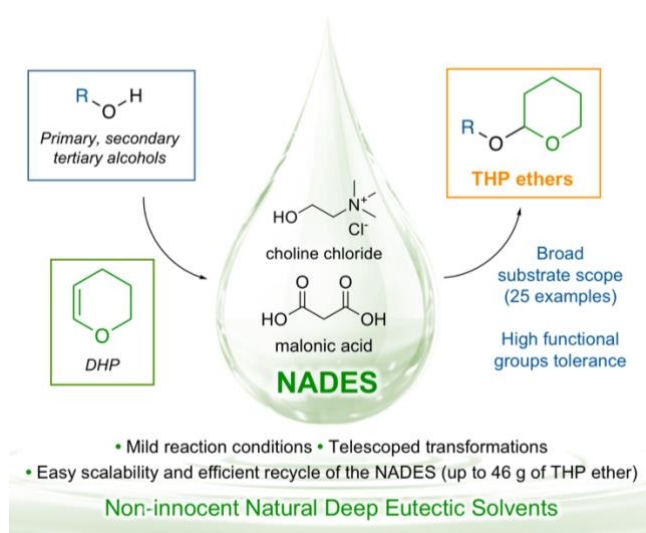


Figure 1

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Poster 9

Lanthanide metallo-ligands for the synthesis of heteronuclear Pt₂Eu₂ luminescent arrays

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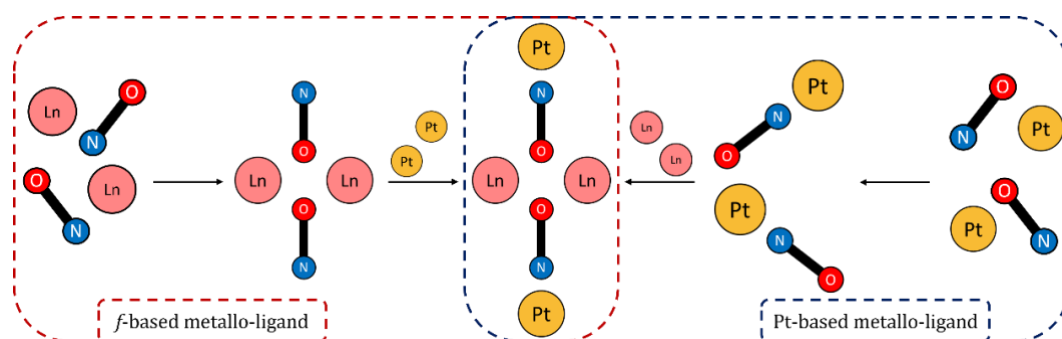
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In the last decades rare-earth complexes have been highly studied due to their luminescent properties, exploitable in many different fields.^[1] Many research efforts have been devoted to the design of innovative lanthanide-based luminescent thermometers.^{[2],[3]} A family of homodinuclear Ln³⁺ (Ln: Gd, Eu) luminescent complexes with general formula [Ln(β -diketonato)₃(μ -N-oxide)]₂ has been recently developed to study the effect of the β -diketonato and N-oxide ligands on their thermometric properties.^[3] We report here that [Ln(tta)₃(μ -pyrzNO)]₂^[3] (Ln: Eu, Gd, Htta: thenoyltrifluoroacetone, pyrzNO: pyrazine N-oxide) presenting a pending nitrogen donor functionality, can behave as a ligand for an open site platinum coordination sphere in the reaction with [Pt(μ -Cl)Cl(EPh₃)₂] (E: P, As). New heterometallic complexes with formula [Ln(tta)₃(μ -pyrzNOPtCl₂EPh₃)]₂ (Ln: Eu, Gd; E: P, As) have been isolated and crystallographically characterized. The dinuclear lanthanide unit [Ln(tta)₃(μ -pyrzNO)]₂ is sufficiently inert to be used as a *f*-based metallo-ligand but it is also sufficiently stable to be formed in mild conditions starting from a *d*-based metallo-ligand [PtCl(ppy)pyrzNO] (Hppy: 2-phenylpyridine) with a pending oxygen donor functionality and the [Ln(tta)₃] fragment (**Scheme 1**). Also the heterometallic complexes [Ln(tta)₃(μ -pyrzNOPtCl(ppy))]₂ (Ln: Eu, Gd) present a dinuclear lanthanide core bridged by two oxygen atoms. In all molecular complexes, platinum is bonded to the nitrogen functionality of pyrzNO.



Scheme 1: The two synthetic pathways for the synthesis of the Ln/Pt heterometallic arrays

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Poster 10

Alkali-Metal Silyl Zincates: Synthesis, Structure and Reactivity

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The high natural abundance of silicon and its non-toxic nature are just some of this element's advantages, strengthened by the popular use of organosilicon compounds within cross-coupling reactions.^[1] Therefore, there stands a natural drive to easily access such useful organosilicon building blocks. While numerous pathways for the silylation of organic molecules have been designed using electrophilic silicon species (mainly using transition metals and/or harsh conditions), the use of nucleophilic silicon reagents is a lesser-employed alternative.^[2] Current methods that have emerged within the past decade include nucleophilic addition or substitution reactions *via* silylmetalation,^[3a] silylboration,^[3b] defluorosilylation^[3c] or nucleophilic silyl substitution^[3d] using monometallic-silyl reagents. Despite these advances, a gap in the knowledge still exists with regards to (i) fundamental characterisation and understanding of these bimetallic reagents employed and (ii) the *modus operandi* which they follow.

In an effort to bridge this gap, this work exploits the high reactivity of alkali-metals (e.g. K) combined with the better selectivity of a lower-polarity metal (Zn) as a platform for accessing novel, nucleophilic silyl complexes. The results presented include X-ray crystallographic characterisation of these bimetallic silyl reagents, and our preliminary understandings surrounding their nucleophilic capabilities in the direct silylation of haloarenes or the silylzincation of phenylacetylene (Figure 1).

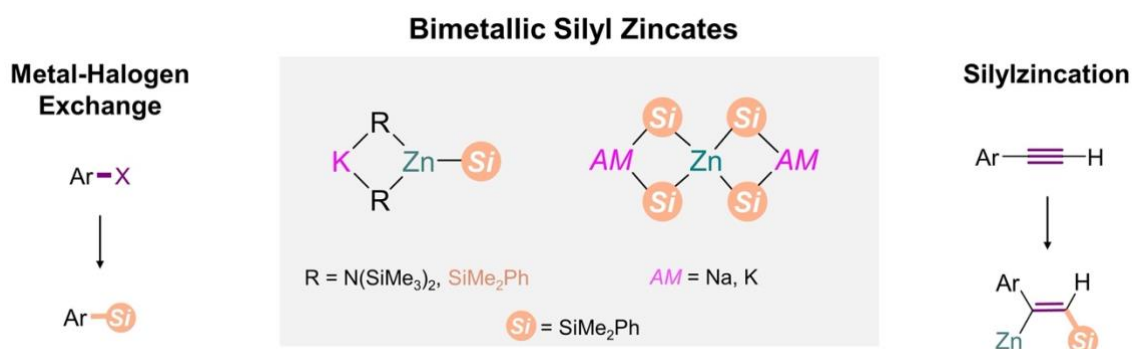


Figure 1

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Poster 11

A New Class of Ferrabenzenes Obtained from Diiron precursors

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Metallabenzenes have been widely studied over the years for their unique properties and reactivity associated with their aromatic character^{1,2}. While a variety of, inter alia, ruthenabenzenes and osmabenzenes have been reported, displaying in some cases a coordinating behaviour towards an external metal centre, a very limited number of ferrabenzenes are known³. By exploiting the advantages provided by dimetallic complexes⁴, we synthesised a new class of functionalized Fe-coordinated ferrabenzenes (**1**) via unusual three-component reaction (Figure 1). Complexes **1** are prone to alkylation giving the cationic derivatives **2**. The identification of **1** and **2** relied on analytical and spectroscopic techniques, and single crystal X-ray diffraction studies.

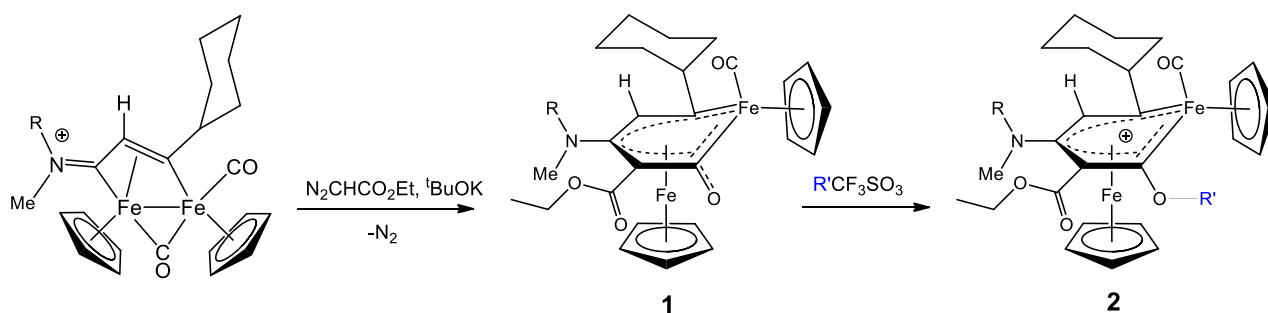


Figure 1. Synthesis of iron-coordinated ferrabenzenes via carbene-aminocarbene-CO coupling. R = Me, 4-MeOC₆H₄, 2-naphthyl; R' = Me, Et.

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Poster 12

Palladium Imidoyl complexes as antiproliferative agents

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The first metal based anticancer drug discovered was cisplatin, which, despite its effectiveness, presents dangerous side effect such as significant neuro and nephrotoxicity. In order to limit these problems researchers are began to investigate complexes with metal center other than Platinum; among these palladium derivatives have taken on a certain importance.

During the last years, the research activity carried out by group of prof. Visentin developed some classes of Palladium organometallic compounds equipped with a wide range of ancillary ligands and with the metal center in different oxidation states. Some of these compounds have shown an interesting antiproliferative activity on different tumor cell lines.

Palladium imidoyl organometallic complexes will enhance the panel of new palladium molecules which can be “killers” for cancer cells. In particular, *trans* complexes with PTA and DAPTA water soluble phosphines and *cis* DPPF derivatives were synthesized and fully characterized. In this contribution we also propose the investigation of the cytotoxic activity and the activation of apoptotic pathway. (Figure 1)

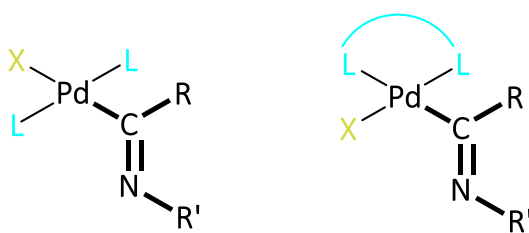


Figure 1

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Poster 13

Lignin Carbonyl Derivatives as Substrates for Transfer Hydrogenation Reactions Catalyzed by Diphosphine Ruthenium Complexes

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Carbonyl compounds derived from biomass are becoming extremely important in green chemistry, although their valorization still poses difficult challenges.^[1,2] The use of diphosphine ruthenium complexes for the transfer hydrogenation of lignocellulose platform aldehydes and ketones has been previously reported.^[3] Herein we present the synthesis and catalytic studies of $[\text{Ru}(\text{X})(\text{dpe})(\text{CO})(\text{phen})]\text{X}$ ($\text{X} = \text{AcO}^-$, PivO^- , Cl^- , I^- ; phen = 1,10-phenanthroline) compounds on several biomass-derived substrates, in H_2O -MeOH media, using a $\text{HCOONa}/\text{HCOOH}$ mixture (Figure 1). Among these compounds, $[\text{Ru}(\text{AcO})(\text{dpe})(\text{CO})(\text{phen})]\text{AcO}$ displays catalytic activity towards lignin derived carbonyl compounds via transfer hydrogenation, through the formation of a water-stable ruthenium hydride species. Interestingly, preliminary findings suggest that phenolic aldehyde substrates, such as vanillin, can be subjected to a thermally controlled hydro-deoxygenation reaction that converts the CH_2OH moiety into a methyl group.

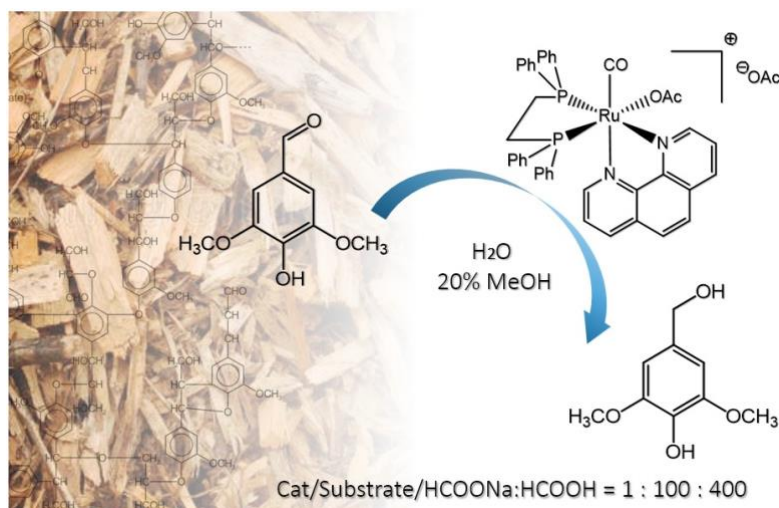


Figure 1

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Poster 14

Assessing the ion-pairing effect in gold(I) catalyzed alkyne hydroalkoxylation, a DOSY NMR approach

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Metallic In recent years, homogeneous gold(I) catalysis caught attention as a growing field in the development of organic chemistry reactions promoted by L-Au-X compounds (L = an ancillary ligand, and X- = a counterion), which mainly involve nucleophilic additions to carbon-carbon unsaturated bonds.¹ The alkyne hydroalkoxylation reaction is among the most studied gold(I)-catalyzed reactions, as it provides an excellent framework to develop a robust complex by tuning the ligand (L) and studying the counterion (X-) effect²⁻³. Indeed, the counterion, usually regarded as a spectator, here instead plays a pivotal role in the reaction mechanism. Optimizing the choice of the counterion becomes hence crucial because of its involvement in the reaction's key steps: 1) the pre-equilibrium, 2) the nucleophilic attack and 3) the protodeauration.⁴ In the hydroalkoxylation reaction, where the rate-determining step (RDS) is the nucleophilic attack, the p-toluenesulfonate anion (OTs-) provides the best compromise for achieving an efficient catalyst, thanks to its intermediate coordinating ability, basicity, and hydrogen bond acceptor property.⁵ These properties are assumed to affect the actual ion-pairing ratio during catalysis between the cation (L-Au-S+, S = substrate) and the counterion (X-), but the ion-pairing ratio constitutes an elusive and complex quantity to assess experimentally, particularly under catalytic conditions. Taking advantage of diffusion-ordered spectroscopy (DOSY) NMR, we measured the average hydrodynamic volumes of different L-Au-X catalysts under catalytic conditions, which from the ion-pairing ratio of each species was obtained (**Figure 1**).⁶⁻⁷ The experimental results highlighted how the ion-pairing ratio is a fundamental parameter to consider, but also that the basic properties of the anion matter, as the trifluoromethanesulfonate (OTf-) and OTs- anions displayed the same average ion-pairing ratio despite different catalytic performances.



Figure 1: Flow diagram depicting the experimental approach used to observe the ion-pairing effect

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Poster 15

Synthesis and characterization of water-soluble silver nanoparticles stabilized by *N*-heterocyclic carbenes derived from amino acids

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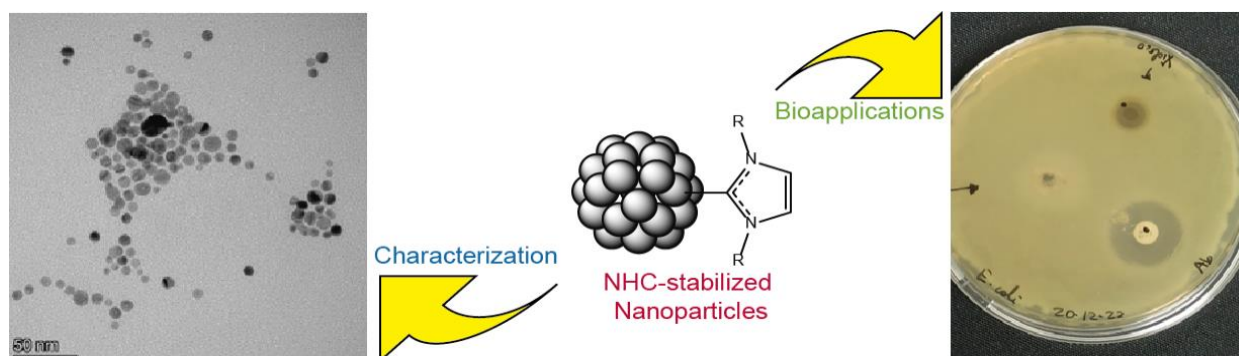
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Metallic nanoparticles (MNPs) have attracted much interest in the last few decades in a wide range of applications in the fields of materials, catalysis, and medicine. In many cases, stabilization of MNPs is required to prevent agglomeration processes, which can be achieved by interaction with stabilizing substances such as polymers, dendrimers, surfactants or coordinated ligands. In recent years, the use of *N*-heterocyclic carbenes (NHCs) has become an alternative as stabilizing ligands for MNPs [1]. On the other hand, silver nanoparticles (AgNPs) have been extensively exploited in a variety of biological and biomedical applications due to their superior physicochemical properties, higher stability, and excellent biocompatibility [2].

Following our recent research on amino acid derived NHC metal complexes and their biological applications [3], we have selected imidazolium-based zwitterionic dicarboxylate, [HIm^{aa}], and monocarboxylate, [Im^{X,aa}], to produce silver NHC-complexes soluble in aqueous media. These complexes have been used as precursors of new AgNPs that incorporate NHC as a stabilizing ligand. The NHC-functionalized AgNPs have been characterized by using different techniques, including dynamic light scattering (DLS) and Transmission Electron Microscopy (TEM). They were found to be highly stable in water, under air, remaining fully dispersed without agglomeration or Ag precipitation for a long time. Furthermore, these nanomaterials were found to have effective antimicrobial activity.



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Poster 16

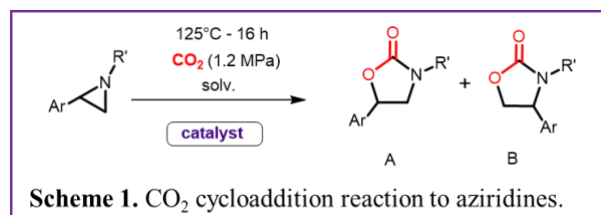
Hematin@ColorCatcher®: a Sustainable Catalyst for Oxazolidinones Synthesis

Caterina Damiano, Matteo Cavalleri,* and Emma Gallo

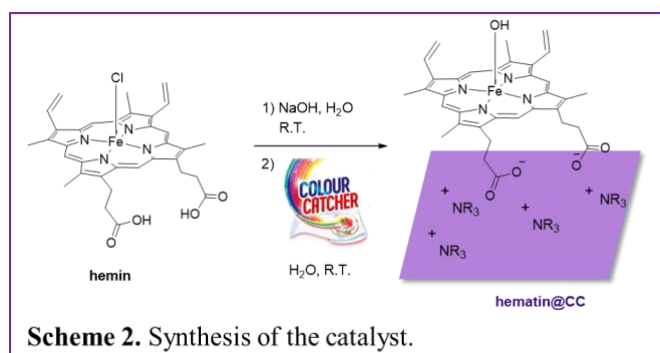
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Oxazolidinones play a significant role as intermediates and chiral auxiliaries in organic synthesis¹ and they also belong to a class of active antibacterial and antibiotic compounds². An intriguing approach for synthesizing oxazolidinones involves 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.

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Poster 17

An Adaptive Rhodium Catalyst to Control the Hydrogenation Network of Nitroarenes

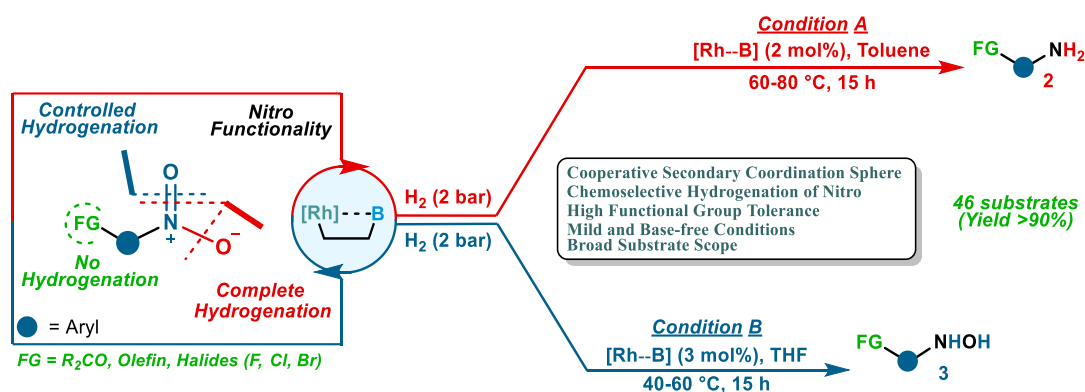
V. Chugh,^{a,b*} B. Chatterjee,^{a,b} W.C. Chang,^{a,b} H. H. Cramer,^a H. Randel,^{a,b} C. Hindemith,^{a,b}
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Catalysts and catalytic systems are typically used to transform substrates selectively into a single product.¹ Alternatively, one could imagine 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

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Ruthenium(II) arene complexes containing dioxime ligands: catalysts for one-pot transfer hydrogenation/N-methylation of nitroarenes with methanol

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This study focuses on the development of novel ruthenium(II) η^6 -arene complexes (Figure 1) as efficient catalysts for the reductive N-monomethylation of nitroarenes using methanol as a reductant, methylating agent, and solvent. We used commercially available and inexpensive dioxime ligands, $\{RC=N(OH)\}_2$, to synthesize the ruthenium(II) arene complexes. The complexes were obtained as nitrate or hexafluorophosphate salts in high yields and were characterized using analytical techniques such as CHN content, conductivity measurements, and spectroscopic techniques like IR and NMR. After optimizing the reaction conditions for the one-pot reduction/N-methylation using nitrobenzene as a benchmark substrate, we evaluated the catalytic activity of the dioxime complexes and other selected ruthenium(II) compounds. The catalysts successfully promoted the conversion of various aromatic nitrocompounds into their respective N-methyl anilines. To gain insights into the reaction mechanism and intermediates, we conducted NMR and MS experiments on a model catalytic system involving nitrobenzene and the most promising catalyst. The main observed results will be showed during this presentation. Overall, this study presents the development of efficient ruthenium(II) η^6 -arene complexes as catalysts for the reductive N-monomethylation of nitroarenes using methanol as a reductant and methylating agent. The findings provide valuable insights for further investigations in the field of metal–ligand cooperative catalysis.

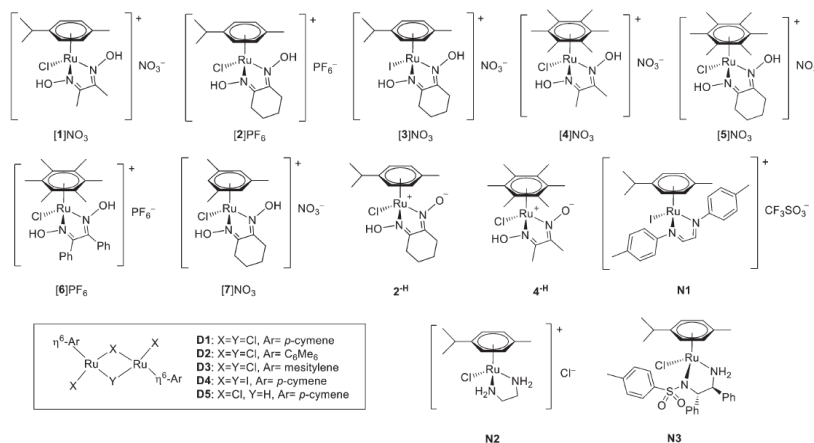


Figure 1

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Poster 19

An investigation of Miyaura borylation and *one-pot* Suzuki–Miyaura cross-coupling reaction under air in sustainable Deep Eutectic Solvents

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Within the framework of green chemistry, the solvent's choice is strategic in the design of a new chemical process: an alternative solution to common organic solvents is represented by deep eutectic solvents (DESs).¹ The straightforward zero-waste synthesis, the possibility of using inexpensive and environmentally benign components, and their unique physicochemical properties like low volatility and high thermal stability make these solvents extremely appropriate for many applications. In this work, DESs have been employed as green solvents for both Miyaura borylation and Suzuki-Miyaura cross-coupling reactions.² To the best of our knowledge, no examples of such comprehensive protocols in DES are reported in the literature so far.

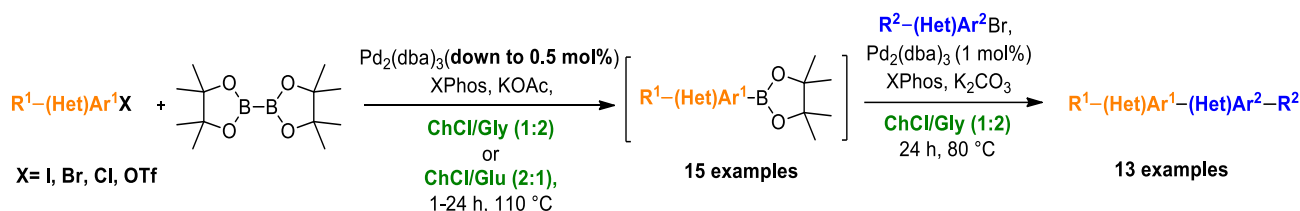


Figure 1: Generic scheme of Miyaura borylation and *one-pot* Suzuki-Miyaura cross-coupling in Deep Eutectic solvents.

Herein, an optimized protocol for the Pd-catalyzed Miyaura borylation and the resulting *one-pot* Suzuki-Miyaura cross-coupling reaction of (hetero)aromatic iodides, bromides, chlorides, and triflates in Deep Eutectic Solvents made of choline chloride/glycerol (1:2) and choline chloride/glucose (2:1) DES is presented. The fine-tuning of each reaction component led to robust conditions for the borylation of both electron-poor and electron-rich (hetero)aryl substrates with moderate-to-high yields. This protocol allowed us to reduce the Pd-loading down to 1%, without the need for an inert atmosphere. The so-obtained boronic esters were isolated and characterized or directly employed for Suzuki-Miyaura cross-coupling in a *one-pot* fashion to introduce different bromides. The optimized protocol was successfully applied for the simple preparation of conjugated organic compounds with potential application in optoelectronics. The sustainability of the protocol was established through calculations of green metrics, such as Eco-scale and E-factor, and compared with the literature, when possible.

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Acknowledgments: The authors would like to thank the Ministero dell'Università e della Ricerca (MUR) within the National PRIN program (project "NATUREChem-Unlocking Sustainable Technologies Through Nature-inspired Solvents", grant number: 2017A5HXFC_002) and Consiglio Nazionale delle Ricerche (CNR) for financial support.

Poster 20

A green approach to Wittig olefination in Deep Eutectic Solvents

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The Wittig reaction¹ is one of the most strategic, widely applicable carbon–carbon bond forming processes available in organic synthesis. This reliable strategy allows the chemo-, regio- and stereoselective preparation of alkenes from carbonyls and it is widely used both in academia and on industrial scale.² This transformation requires the use of a phosphorus ylide that can react with a carbonylic compound via an oxaphosphetane intermediate. Traditionally the Wittig olefination is carried out in dry and aprotic solvents, under homogeneous conditions, using an organometallic base to generate a stabilized or semistabilized phosphonium ylide.³ In recent years, the Wittig reaction has been studied in many variations, including catalytic versions and MW-assisted processes.⁴ In order to improve the sustainability of the reaction, an aqueous environment⁵ has been used to perform Wittig olefination. However, many organic molecules are not soluble in water or may undergo undesired chemical transformations in a protic environment.

In this context, owing to our interest in the development of sustainable synthetic strategies,⁶ we decided to investigate *Deep Eutectic Solvents* (DESs) as green reaction media to promote the Wittig olefination under sustainable reaction conditions starting from carbonylic compounds and phosphonium salts. Our findings in terms of reactivity, reaction conditions and substrate scope will be presented.

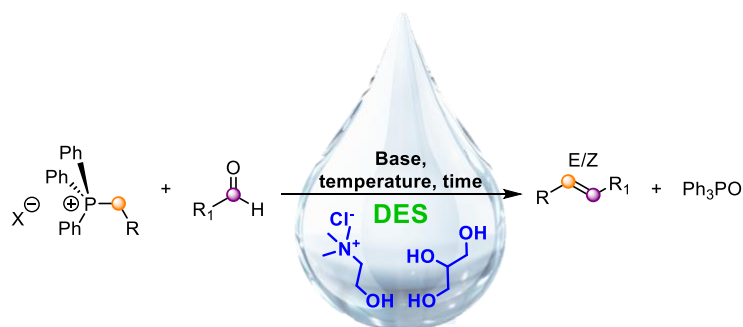


Figure 1: Wittig olefination in Deep Eutectic Solvents.

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Poster 21

New and efficient copper(II) complexes as catalysts for allylic oxidation and Ullman-type reactions

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In the last decade, to meet the needs of the circular economy, efforts have been made to reuse alkenes in a green methodology, trying to transform them into new raw materials useful from an industrial point of view. One of the processes that could lead to the synthesis of highly functionalized materials is represented by the allylic oxidation of alkenes. The most important allylic radical oxidation reaction is the Kharasch-Sosnovsky, that originally involved the chemistry of Se, Cr, Pd, Rh. We focused on copper species due to their versatile properties, cost-effectiveness, easy-accessibility, and environmentally friendly properties. In recent studies, the attention has been given to heteroscorpionate ligands due to their coordination ability; in particular, transition metal complexes supported by bis(pyrazol-1-yl)carboxylate ligands have shown their potential as catalysts. Based on these experimental data, we designed and synthesized hexyl and isopropyl ester derivatives of bis(pyrazol-1-yl)- and bis(3,5-dimethyl-pyrazol-1-yl)-acetic acids (L^{OHex} , L^{iPr} , L^{2OHex} and L^{2iPr} , respectively). The related monomeric or dimeric copper(II) complexes were obtained starting from $CuCl_2 \cdot 2H_2O$ or $CuBr_2$ acceptors, and tested as catalysts in the allylic oxidation of alkenes.^{1,2} The Cu(II) complexes showed a very promising catalytic activity in allylic oxidations avoiding the use of any external agents and superstoichiometric amounts of reagents, preventing the generation of excessive waste (Figure 1). In addition, studies related to new copper complexes supported by the anions of the sterically hindered β -diketone ligands, 1,3-dimesitylpropane-1,3-dione (HL^{Mes}), 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one (HL^{CF_3}) and the parent 1,3-diphenylpropane-1,3-dione (HL^{Ph}) are ongoing,³ with special attention to their potential catalytical activity on Ullman-type reaction for the coupling of two aryl and heteroaryl halides.

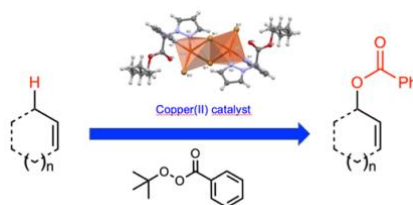


Figure 1 Kharasch-Sosnovsky reaction catalyzed by copper catalysts.

Acknowledgements: NextGenerationEU - D.M. 737/2021 "INVIRCuM" University of Camerino FAR 2022 PNR

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

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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.

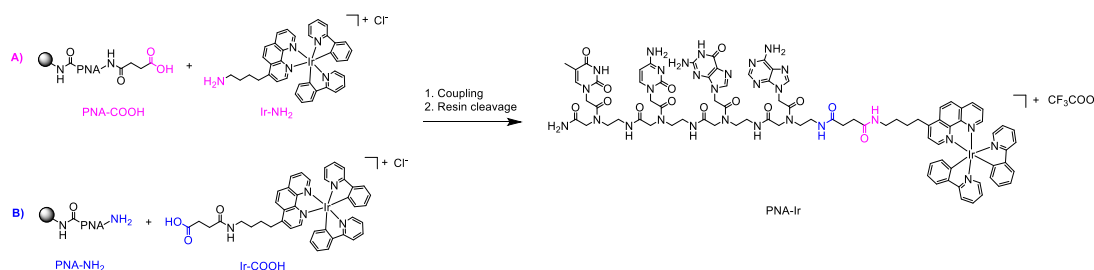


Figure 1. Conjugation of Ir(III) complexes to PNAs.

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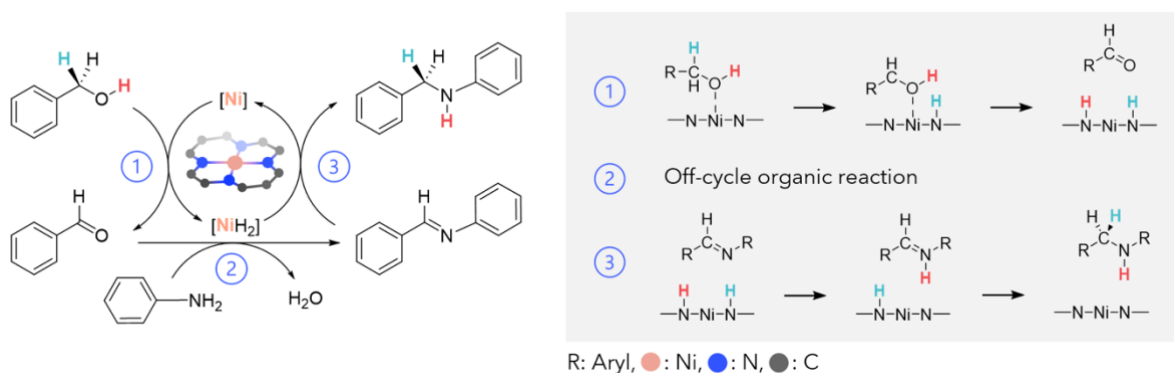
Poster 23

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

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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 H_2 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.

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Poster 24

Synthesis and Antiproliferative study of Ru(II) - Hydroxy Stearic Acids

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Prospectives on Ruthenium anticancer agents are encouraging since Ru(II) can directly interact on tumor cells via multiple mechanisms provoking their death. The selection of ligands plays a key role in anticancer activity, the addition of hydrophobic species such as PPh₃ to a metal center increases drug uptake in cancer cells and could allow the intercalation in DNA nucleobases pairs. Metallodrugs often show an enhanced anticancer activity compared to free ligands.¹

In this context, ligands with well-established antitumor activity as 7- and (R)-9-Hydroxy stearic acid (HSA) were selected and reacted with *mer*-[Ru(H)₂(CO)(PPh₃)₃] to give Ru(II) anticancer species.² The anticancer *in vitro* properties of this class of metallo-prodrugs could be ascribed to synergistic effects between the metal center and bioactive ligands. The results have been compared with the analogously coordinated innocuous 12-HSA (figure 1).

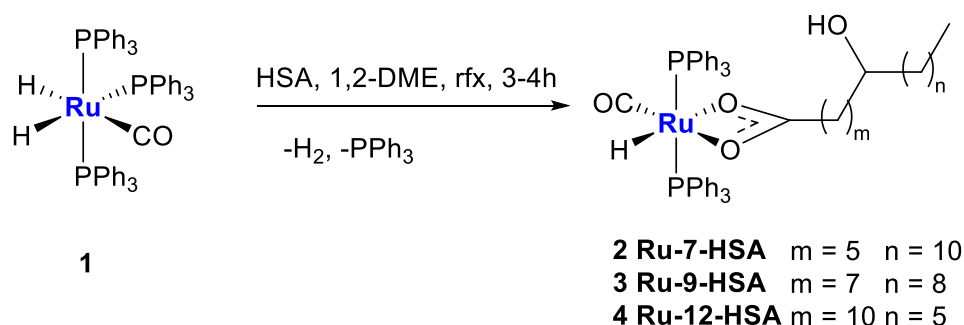


Figure 1

The three novel Ru(II)-HSA complexes were fully characterized spectroscopically by using ESI-MS, IR, UV-Vis, and NMR techniques. The nature of Ru-12-HSA was also determined by single crystal X-ray diffraction. Cytotoxicity, cell proliferation, and DNA damage tests were performed demonstrating the biological activity of Ru-7-HSA and Ru-9-HSA.

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Synergy between Homogeneous and Heterogeneous Catalysis: A Novel Approach to Multifunctional Catalytic Systems

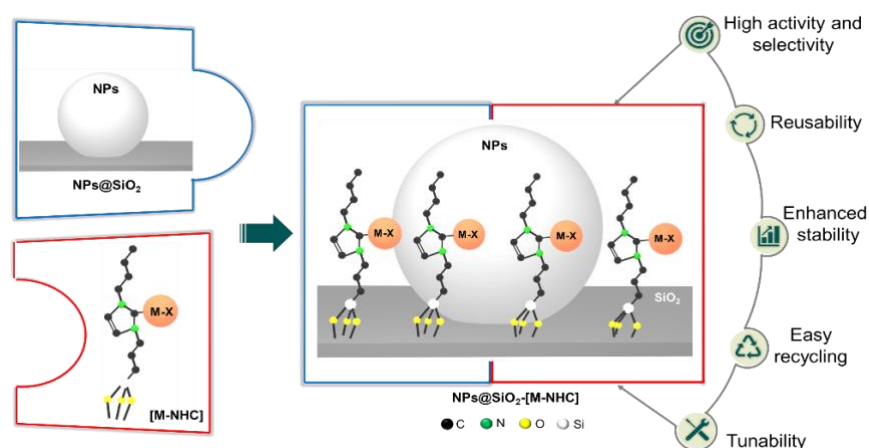
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The immobilization of homogeneous complexes on solid supports has been gaining attention to facilitate the catalyst recovery and recyclability.^[1] This innovative yet challenging synthetic methodology aims at bridging the positive aspects of both molecular and material catalysts which abide by the rubrics of green and sustainable chemistry. As a further development of this strategy, we have rationally designed a multifunctional catalytic system that contains a joint assembly of molecular and nanoparticle (NP) sites on a single support (Scheme 1). Since such materials possess two different active centers dispersed on the support surface, they have the potential of performing complex reaction sequences in one-pot. To stabilize and preserve the activity of organometallic complex in a heterogeneous environment, functionalized *N*-heterocyclic carbenes have been employed as potential ligand candidates considering their easy accessibility, tunability, and pronounced influence on the electronic properties of metal centers.



Scheme 1. Approach to design a Multifunctional catalytic system and the advantages of this strategy.

As a proof of concept for this catalyst design, ruthenium nanoparticles were immobilized on a silica support functionalized with Copper *N*-heterocyclic carbene complexes to act as multifunctional catalysts for the one-pot synthesis of allyl and alkyl amines from phenylacetylene, paraformaldehyde, and piperidine derivatives.^[2] The characterization, flexibility, synergistic effect, and challenges of this novel catalytic system will be presented.

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Poster 26

Synthesis and Application of Rhodium Complexes Bearing Novel Helically Chiral Indenyl Ligands

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Direct functionalization through asymmetric C-H activation is a versatile and powerful strategy, which allows selective and efficient access to complex molecules with high optical purity. In recent years, rhodium complexes of chiral cyclopentadienyl ligands emerged as a privileged class of catalyst for these transformations.¹ Surprisingly, little development has been made in the field of chiral indenyl ligands, which remain significantly underexplored – even though they may offer interesting differential reactivity.²

Herein we present our work on the development of a novel class of helically chiral indenyl ligands based on helicenes, which can be synthesized optically pure on a gram scale. The coordination to rhodium(I) yields air and moisture-stable complexes, which can be readily oxidized and employed as catalysts in asymmetric C-H activations. We also present their application in the C-H activation of benzo[h]quinolines followed by arylation with diazonaphthoquinones to obtain axially chiral biaryls in excellent yield and enantioselectivity.³

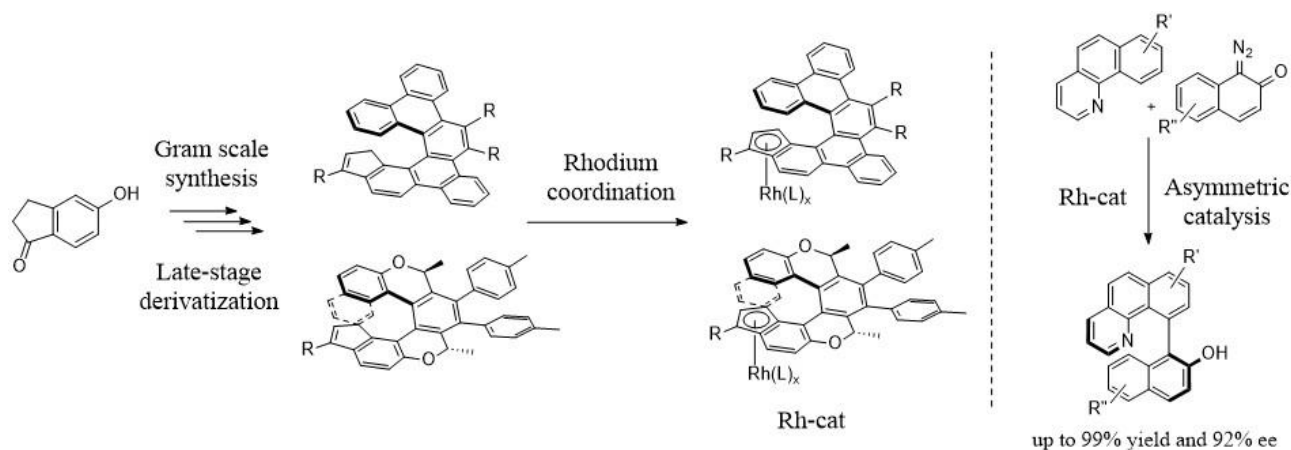


Figure 1 Scheme of the presented work

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Poster 27

Structural-activity relationship in homogeneous catalysis: the case of dimeric iron(III) salen complexes in methyl levulinate transesterification.

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Biomass is a renewable source of raw materials that can be efficiently converted into intermediate and base chemicals. Among these, levulinic acid has garnered considerable attention due to its direct derivation from lignocellulosic biomass, as well as its versatile structure which enables diverse transformations into valuable products. Levulinic acid esters have already found applications in various industrial sectors such as cosmetics, plasticizers, and solvents.¹ In this study, a wide range of alkyl levulinates has been successfully prepared by Lewis acid-catalyzed homogeneous transesterification. A systematic screening approach was employed, examining a library of μ -oxo-dinuclear Fe(III) salen complexes² (Figure 1), with the aim of elucidating the impact of substituents on steric and electronic properties. A complementary computational study unraveled the correlation between the structures of the catalysts and their corresponding activities, providing insights into the key factors that influence their performance.

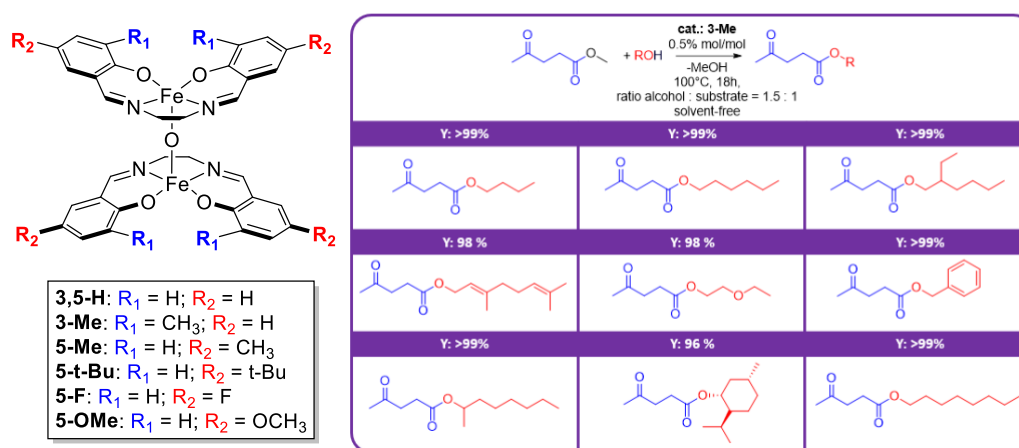


Figure 1 - Transesterification of methyl levulinate catalyzed by μ -oxo-dinuclear iron(III) salen complexes.

R.E and V.R. are grateful to Italian Ministero dell'Istruzione dell'Università e della Ricerca for the financial support provided through the LEVANTE project "LEvulinic acid Valorization through Advanced Novel Technologies", Progetti di Ricerca di Rilevante Interesse Nazionale -Bando 2020, Prot. 2020CZCJN7.

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Poster 28

Reactivity of *N,C*-chelated bismuth(I) compounds towards different organic substrates

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Recently, bismuth compounds have drawn a particular interest due to their possible application in catalysis and for the activation of small molecules. Among those, bismuth(I) hypervalent compounds have proven to be really efficient in catalytic hydrodefluorination reaction or in the catalytic activation of N_2O , other than its potential in CO and CO_2 activation.^{1,2} This reactivity is ascribable to the lone pair of bismuth(I) in a $6p^2$ orbital, which has been proven to be nucleophilic and readily oxidized, in comparison with the nonbonding lone pair in bismuth(III) compounds which is low in energy and rather inert. The reactivity of different *N,C,N*-chelated bismuth(I) compound towards different $C-X^3$ and $E-E$ ($E=O, S, Se, Te$)⁴ bonds have been evaluated; the main objective of this work is to evaluate differences and similarities in the reactivity of less stabilized *N,C*-chelated bismuth(I) homocycles.

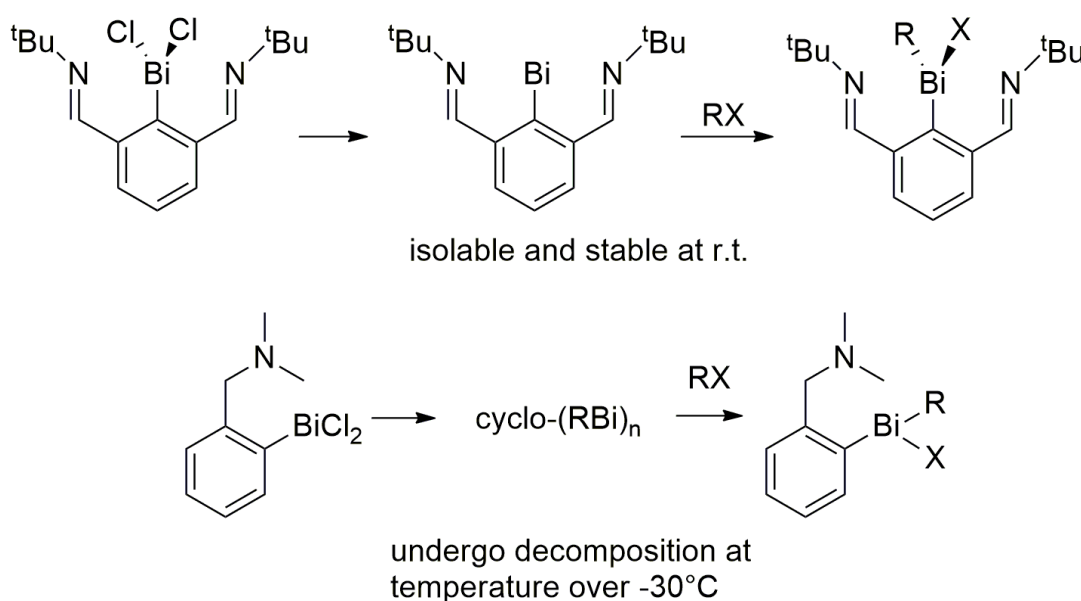


Figure 1

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Poster 29

Synthesis and characterization of chiral $[(\mu\text{-H})_3\text{Os}_3\text{Rh}(\text{CO})_{10}(\text{diphosphine})]$ clusters and study of their catalytic activity in asymmetric hydrogenation

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Four new osmium-rhodium tetranuclear chiral clusters of the general formula $[(\mu\text{-H})_3\text{Os}_3\text{Rh}(\text{CO})_{10}(1,1\text{-P-P}^*)]$ (P-P* = chiral diphosphine of the ferrocene-based Walphos family) have been synthesized and characterized. The phosphorus atoms of the diphosphine ligands were found to be coordinated in a chelating mode to the rhodium atom.¹ The clusters have been tested as catalysts for asymmetric hydrogenation of tiglic acid [trans-2-methyl-2-butenoic acid] (Figure 1 b).² The catalytic reactions gave conversion rates of 45-57% and enantiomeric excesses of 11-39% under mild catalytic reaction conditions. The crystal structures of $[(\mu\text{-H})_3\text{Os}_3\text{Rh}(\text{CO})_{10}(1,1\text{-W002})]$ **2** and $[(\mu\text{-H})_3\text{Os}_3\text{Rh}(\text{CO})_{10}(1,1\text{-W009})]$ **4** are presented (Figure 1 a).

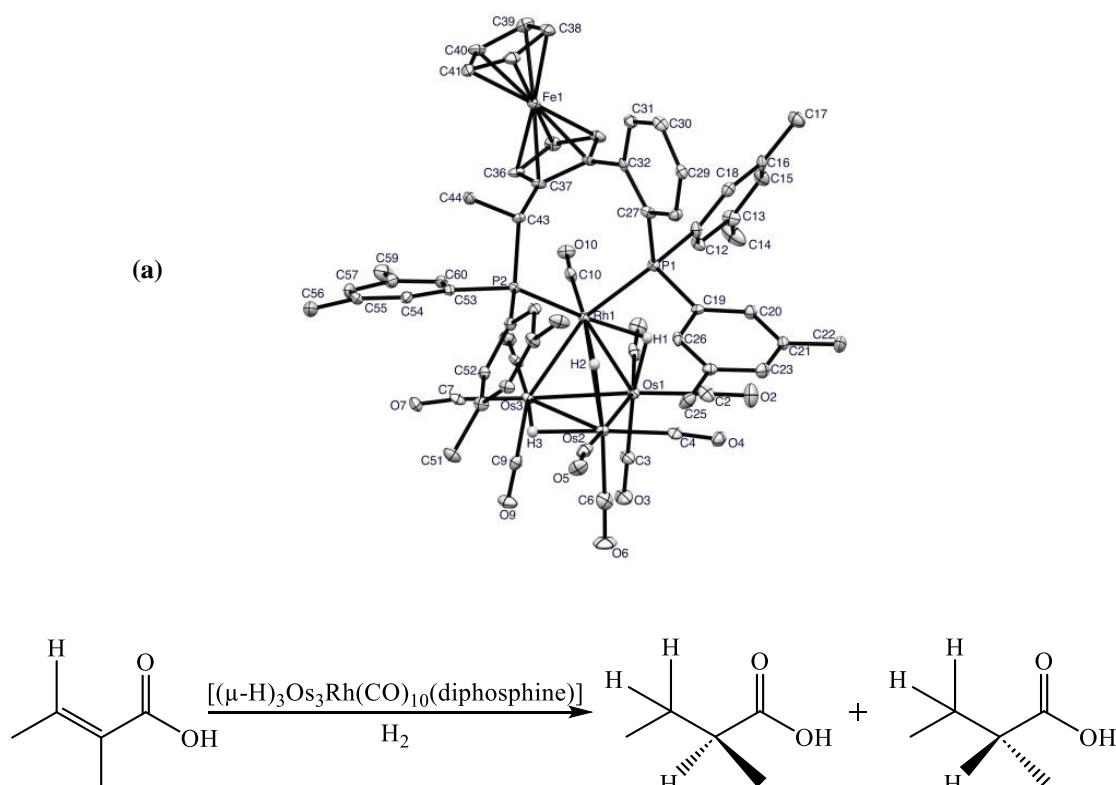


Figure 1. (a) XRD-SC structure of compound **4**; (b) catalytic hydrogenation of tiglic acid.

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Poster 30

Formic Acid as Carbon Monoxide Source: A two-steps Synthesis of 2,5-unsubstituted *N*-Arylpyrroles from Nitroarenes and Dienes

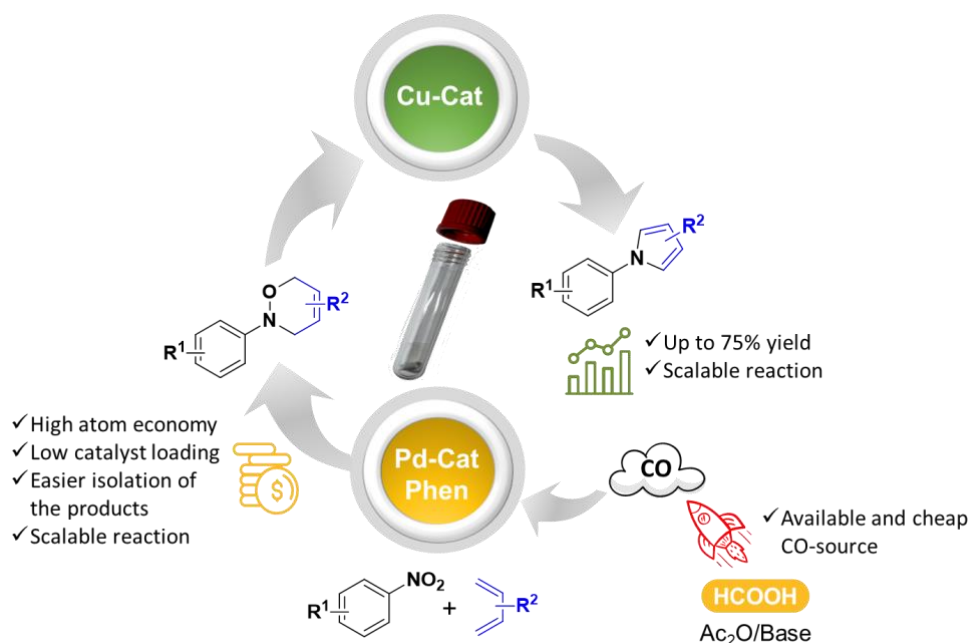
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Working with pressurized CO requires high-pressure equipment and safety measures, thus the development of alternative methods exploiting the role of the so-called “CO surrogates” is a noteworthy issue in the field of reactions involving carbon monoxide. In this perspective, we recently reported that phenyl formate performs as an excellent CO source in the reductive cyclization of various nitro compounds.^{1,2} An improvement of this strategy has been achieved by employing an equimolar mixture of formic acid, acetic anhydride and a base:³ in this way we are able to prevent the formation of phenol from the decomposition of phenyl formate, which may be annoying in the isolation step. This methodology has been applied in this work for the reduction, by carbon monoxide, of nitroarenes to nitrosoarenes, which are quickly trapped by conjugated dienes in an hetero-Dies-Alder reaction to give 3,6-dihydro-2*H*-[1,2]-oxazines. The initial reduction requires only a low loading of a palladium/phenanthroline complex as a homogeneous catalyst, while the hetero-cyclization takes place “off-metal”. In the second step, oxazines conversion to 2,5-unsubstituted *N*-arylpyrroles is achieved with yields up to 75% employing CuCl as the catalyst.



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Poster 31

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

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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.

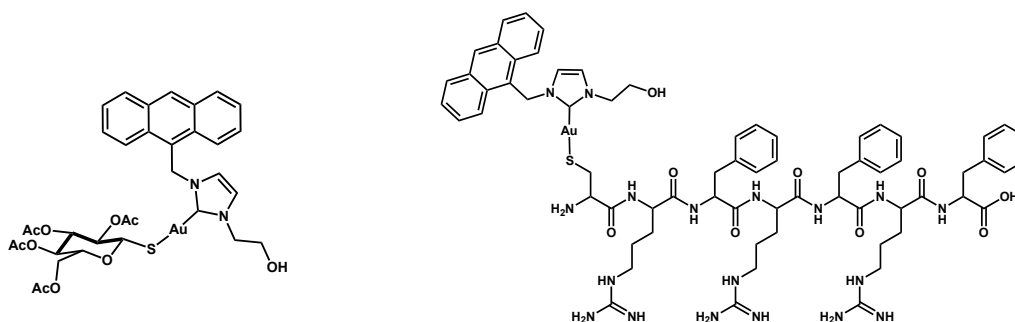


Figure 1: Two examples of the synthesized conjugates. The 2,3,4,6-tetra-O-acetyl-1-thio- β -D-glucopyranose conjugate (left) and the CrFrFrF peptide conjugate (right).

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Poster 32

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

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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.

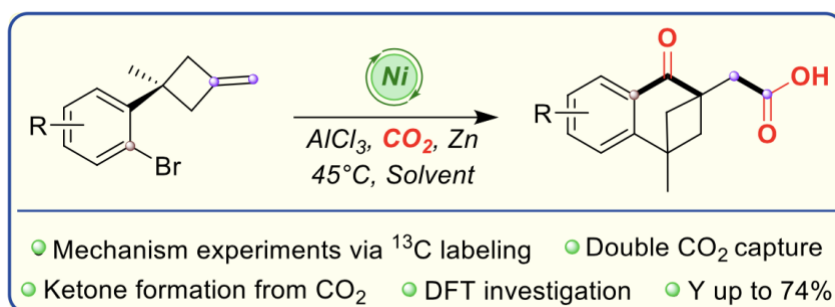


Figure 1 Nickel catalyzed XEC for sequential carbonylation/carboxylation

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Poster 33

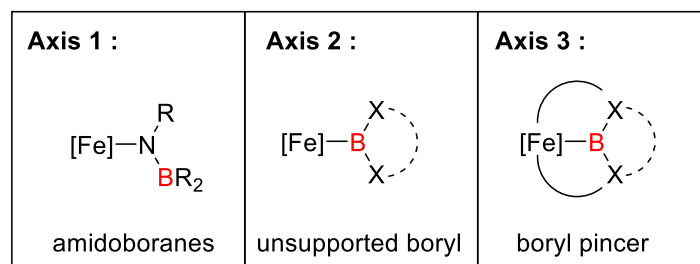
Synthesis and reactivity of low valent open-shell Iron complexes with Boron-containing ligands

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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.



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Poster 34

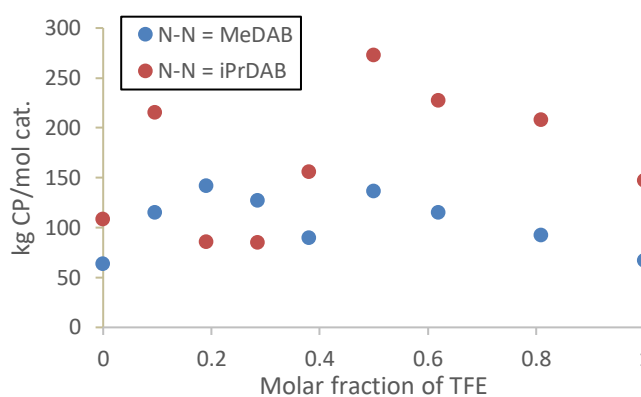
The unprecedented role of solvent in Pd-catalysis for the synthesis of functionalized polyolefins

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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.



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Poster 35

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

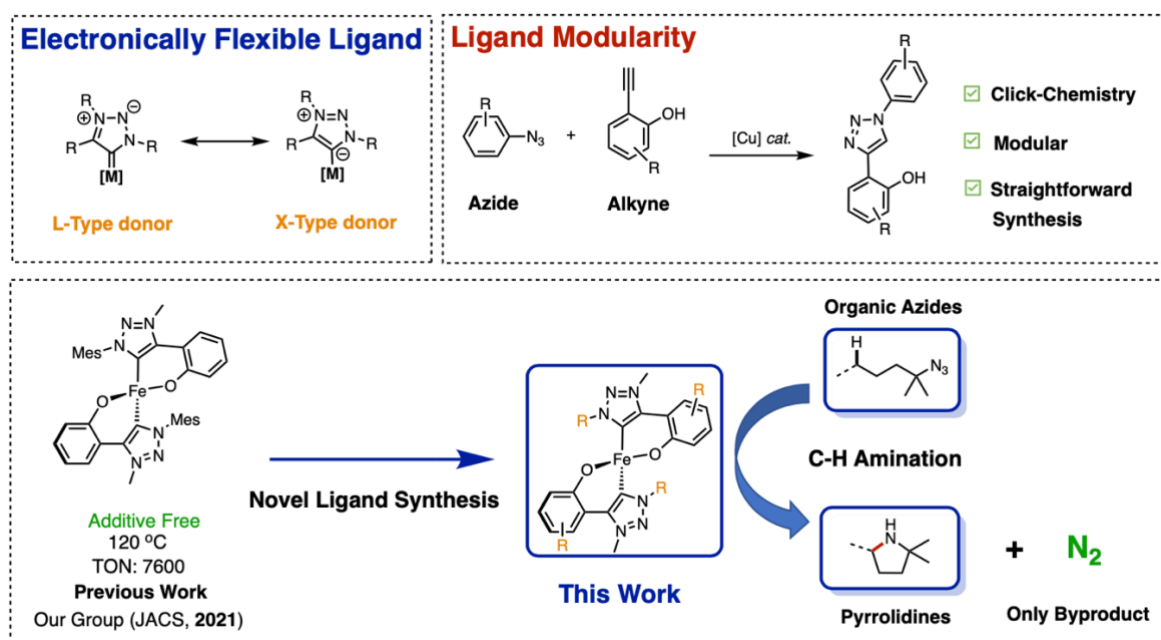
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Nitrogen containing heterocycles are ubiquitous across nature and industry with C-N bonds being found in numerous natural products and pharmaceutically relevant molecules.^{1,2} Therefore carbon-nitrogen bond formation is of utmost importance with 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.



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Poster 36

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

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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).

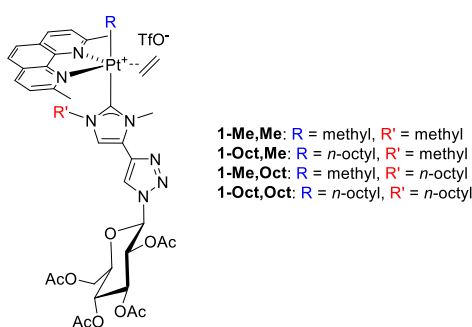


Figure 1

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.

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Poster 37

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

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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-assembly 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.

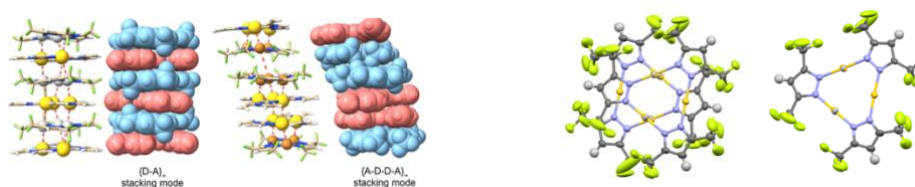


Figure 1

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).

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Poster 38

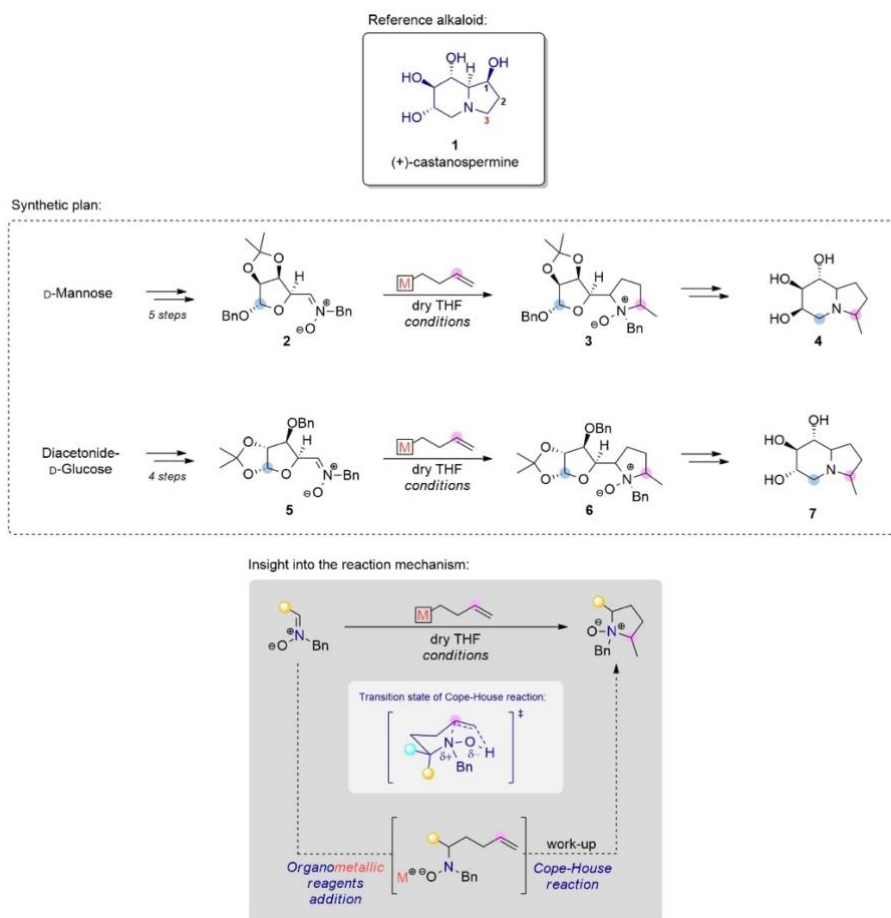
A domino organometallic addition/Cope-House rearrangement to nitrones affords novel 3-methylindolizidines related to Castanospermine.

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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).



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

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H₃salmp, H₂salben and H₂salmen (**Figure 1**) are oligodentate Schiff bases derived from the condensation of two salicylaldehydes (salH) with arylmethanediamine or methanediamine. 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), salben 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.

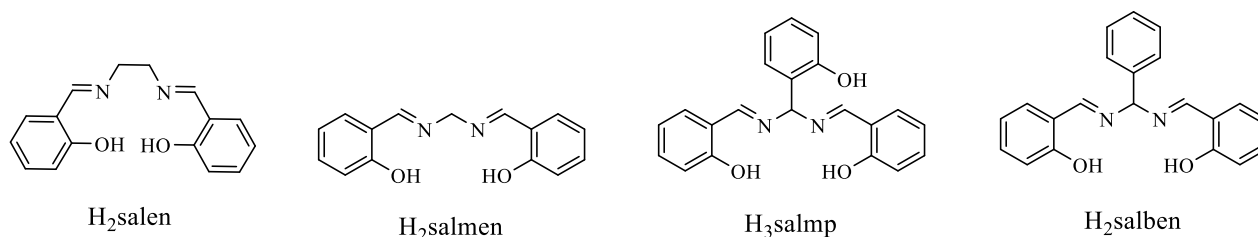


Figure 1 Molecular schemes of H₂salen, H₂salmen, H₃salmp and H₂salben.

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Ir-NHC Catalysts for Selective Glycerol Oxidation through Acceptorless Dehydrogenation

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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.

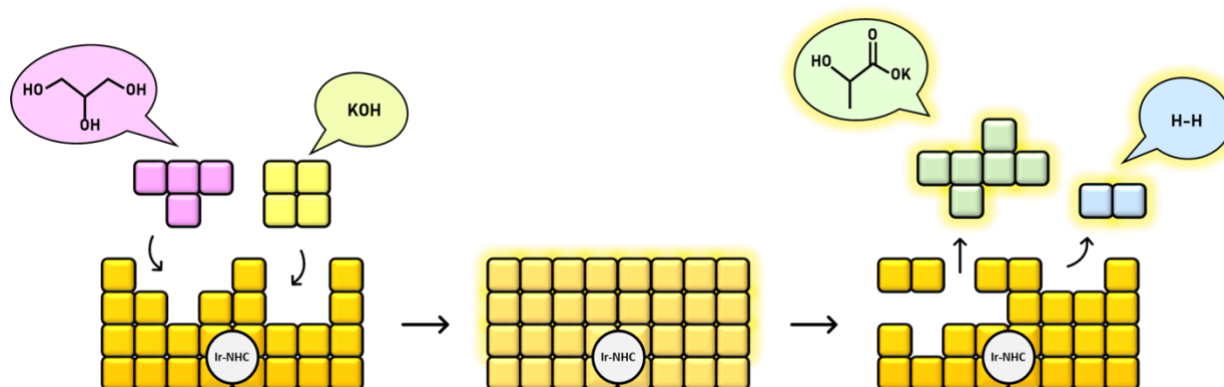


Figure 1. Glycerol transformation into LA and H₂ through Ir-NHC-catalyzed ADH.

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Poster 41

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

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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.

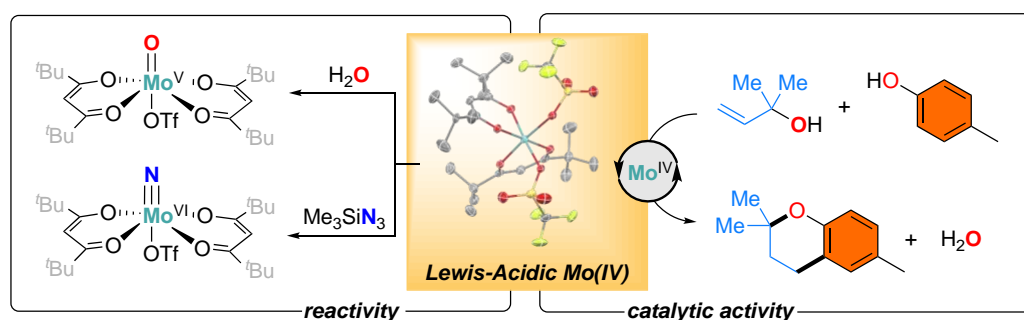


Figure 1

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Poster 42

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

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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.

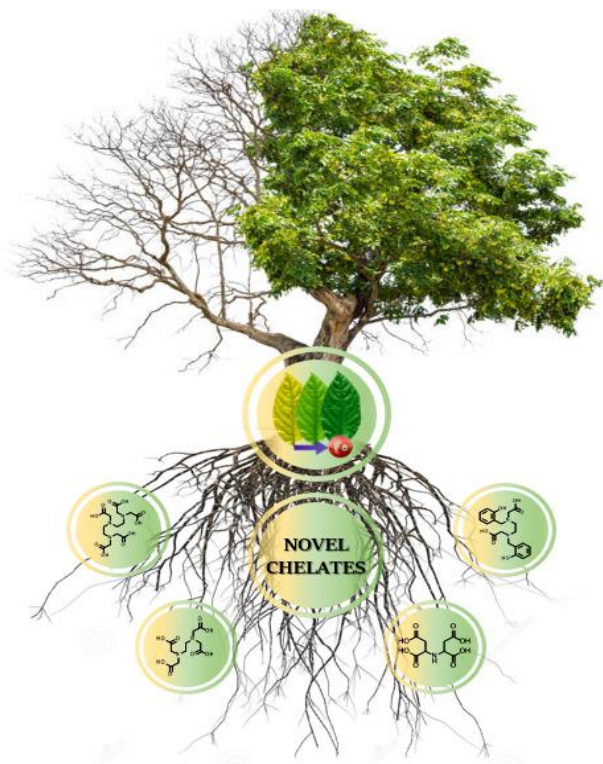


Figure 1: Fe chelates for iron chlorosis treatment.

Poster 43

Homogeneous salophen Fe(III) catalysts and heterogenization strategy for biodiesel synthesis from waste cooking oils

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Maria E. Cucciolito,^{a,c} and Francesco Ruffo^{a,c}

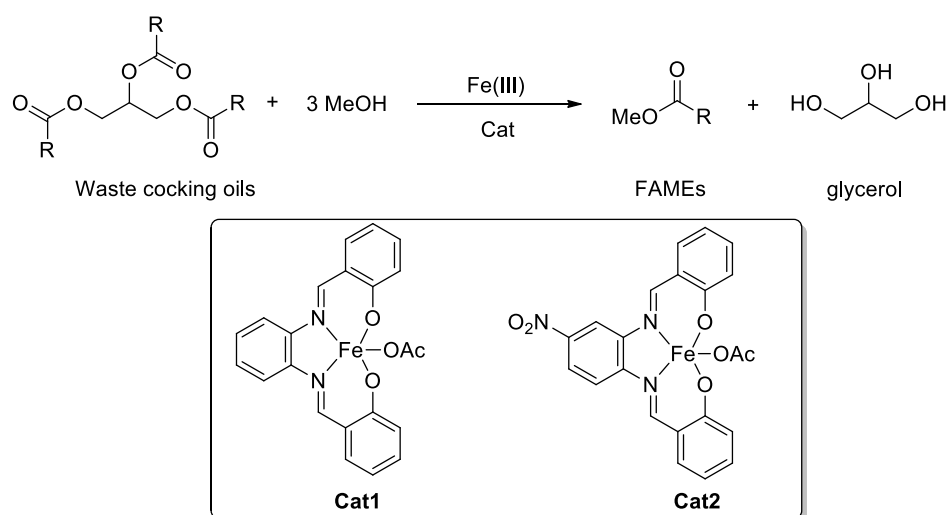
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The increasing demand for energy, along with the depletion of fossil feedstocks, has led academic and industrial research to the development of sustainable products, processes, and technologies. In this context, vegetable oils and lignocellulosic materials are relevant renewable feedstocks for the production of biochemicals and biofuels.¹ Through the methanolysis of triglycerides is possible to obtain a mixture of fatty acid methyl esters (FAMES) that can be used as biodiesel fuel.² Recently we reported catalytic transesterification of vegetable oils promoted by a panel of salen Fe(III) complexes with different substituents and counterions, achieving high FAMES yield (90 %) even with waste cooking oils (WCOs).³

Here we report preliminary results for FAMES synthesis promoted by Fe(III) salophen catalysts (Scheme 1), achieving excellent performance (yield 98 %) in homogeneous conditions (T= 160 °C, t= 2 h, MeOH/oil molar ratio: 20, **Cat1** loading 0.1 % mol_{Fe}/mol_{oil}). Moreover, phenolic moiety in the ligand backbone allows the use of functionalized diamine synthon to introduce a nitro group (**Cat2**), suitable for successive modification and heterogenization strategies. Further details will be presented at the conference.



Scheme 1 – Salophen Fe(III) catalyst for biodiesel synthesis

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Poster 44

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

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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).

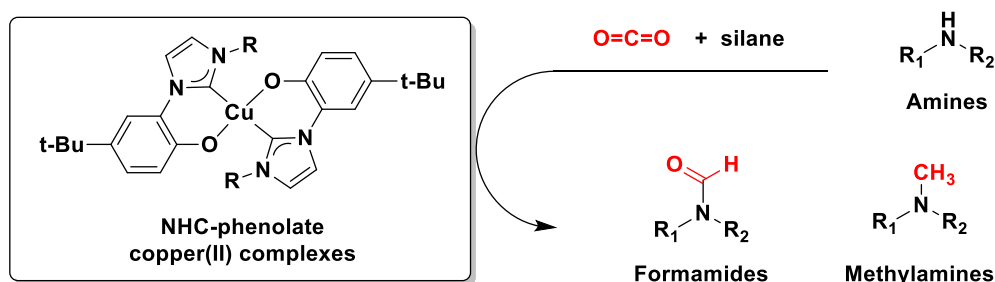


Figure 1

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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

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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.

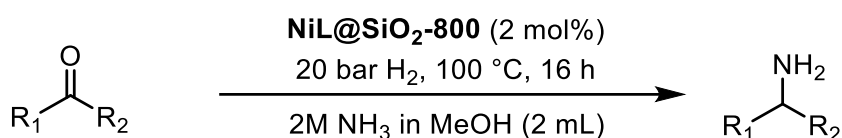


Figure 1: Reductive amination of ketones with the NiL@SiO₂-800 catalyst in 2 M NH₃ in methanol solution, yielding the corresponding primary amine.

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Poster 46

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

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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.

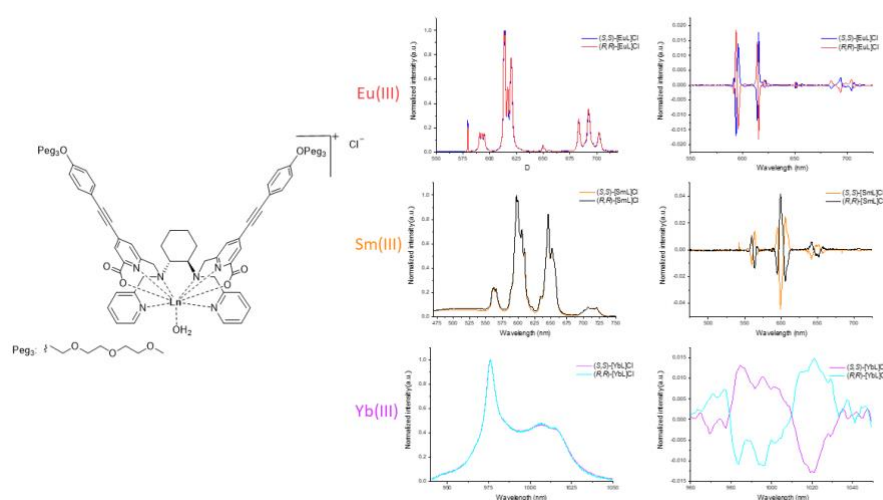


Figure 1 (Left) Structure of (*S,S*)-[LnL]Cl complex presented. (Middle) Normalized PL and (Right) CPL spectra of both enantiomers of [LnL]Cl in aqueous solution at room temperature. λ_{exc} at 336 nm.

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Poster 47

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

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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.

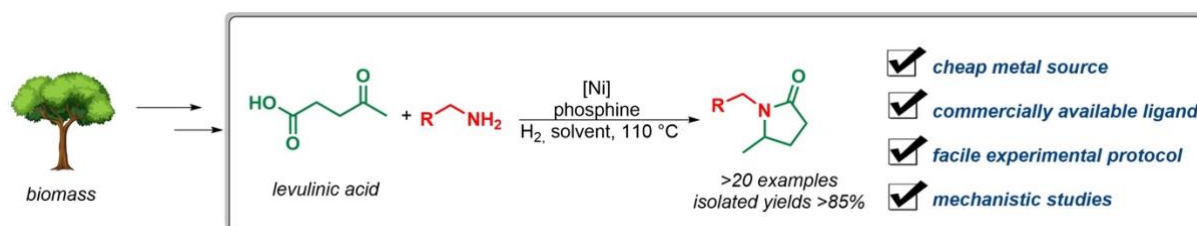


Figure 1 Synthesis of *N*-functionalized pyrrolidones from levulinic acid.

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Poster 48

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

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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.

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Poster 49

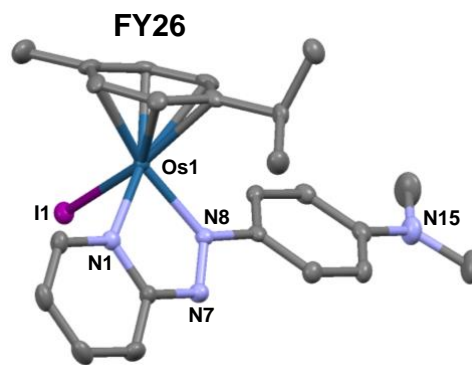
New Insights into the Chemistry of Organo-osmium Anticancer Complexes

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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 >10⁴-fold by changing X from PF₆ to Cl, enabling better formulation for clinical use. The ^{187}Os isotopically enriched bromido analogue, $^{187}\text{Os}(\eta^6\text{-}p\text{-cym})(\text{AZPY-NMe}_2)\text{Br}]\text{PF}_6$, was synthesised. The ^{187}Os spin 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.

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Poster 50

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

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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.

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Poster 51

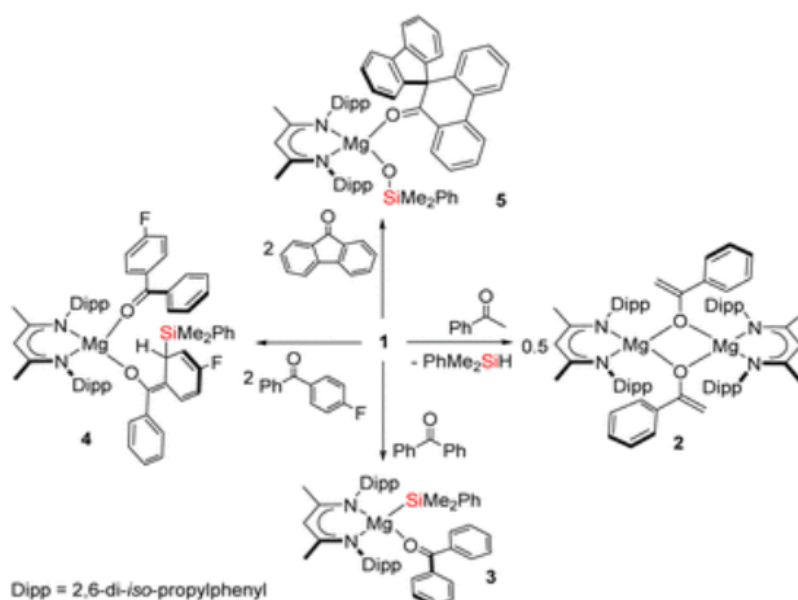
Diverse reactivity of β -diketiminato magnesium silyl towards ketones

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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.

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Poster 52

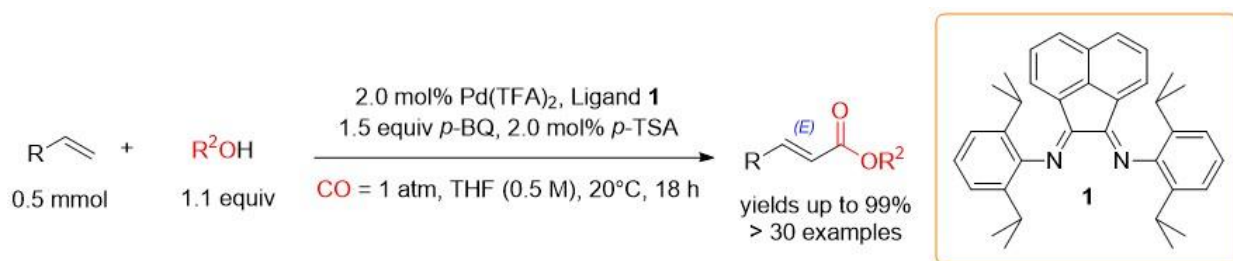
Oxidative Alkoxy carbonylation of Olefins Catalyzed by Aryl α -diimine/Palladium(II) Complexes

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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

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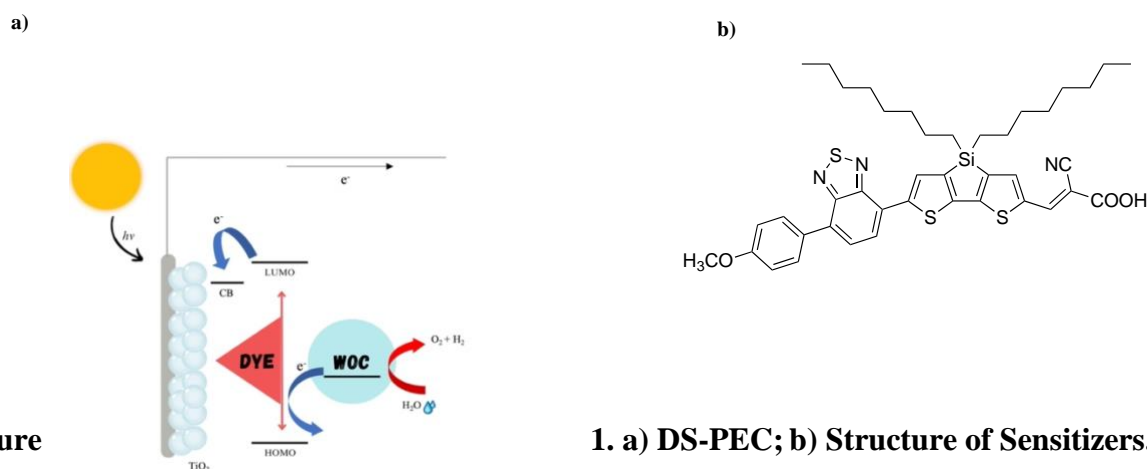
Poster 53

Synthesis of organic sensitizers for water splitting in DS-PEC

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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.



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

In this study, we report the synthesis of the dye **1** (figure), based on a diethyl-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.

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Poster 54

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

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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 de-acetalization or oxidation reactions (Figure 1).

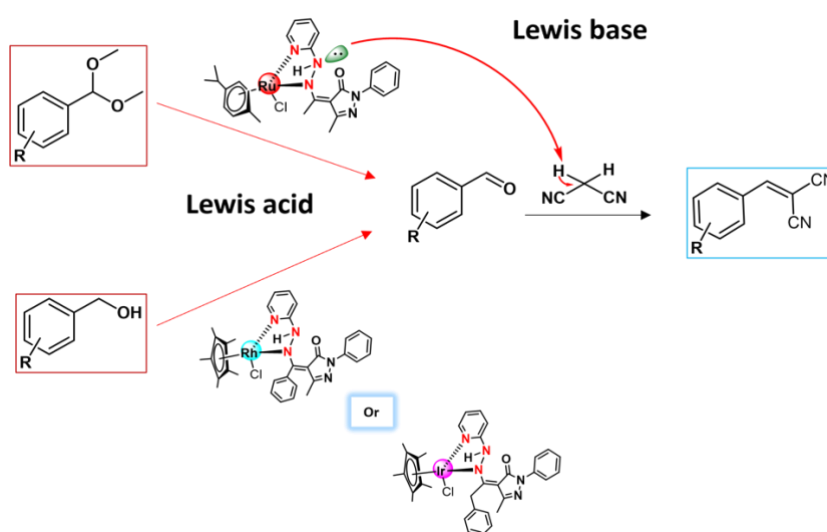


Figure 1 – One-pot tandem reaction catalyzed by Ru(II), Rh(III) and Ir(III)

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Poster 55

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

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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.

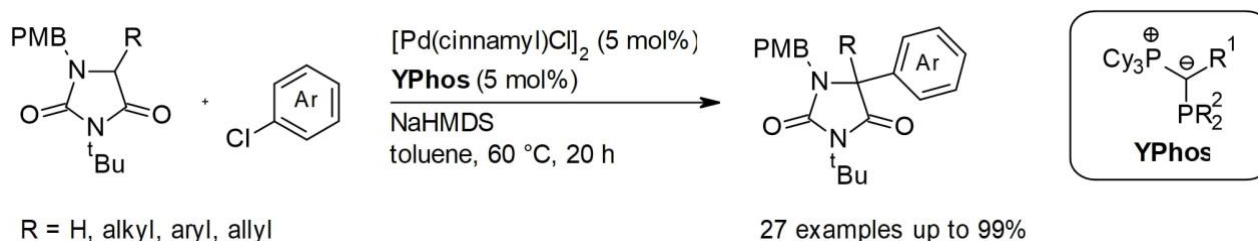


Figure 1. Pd-catalyzed arylation of hydantoins with aryl chlorides.

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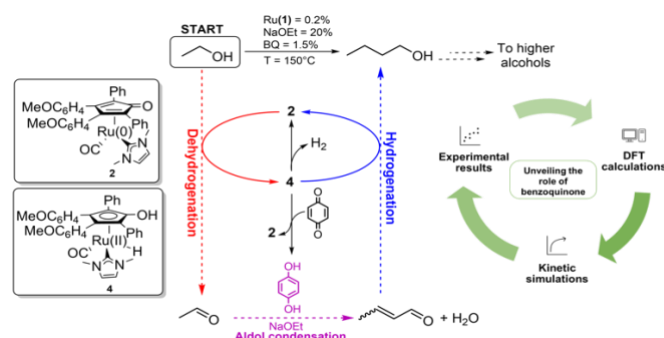
Poster 56

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

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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.

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

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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

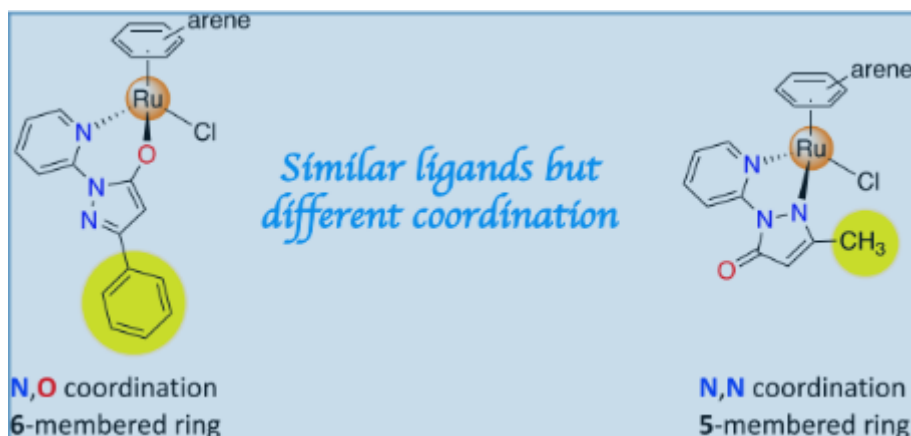


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Poster 58

Continuous organometallic reactions in flow assisted by Deep Eutectic Solvents

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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

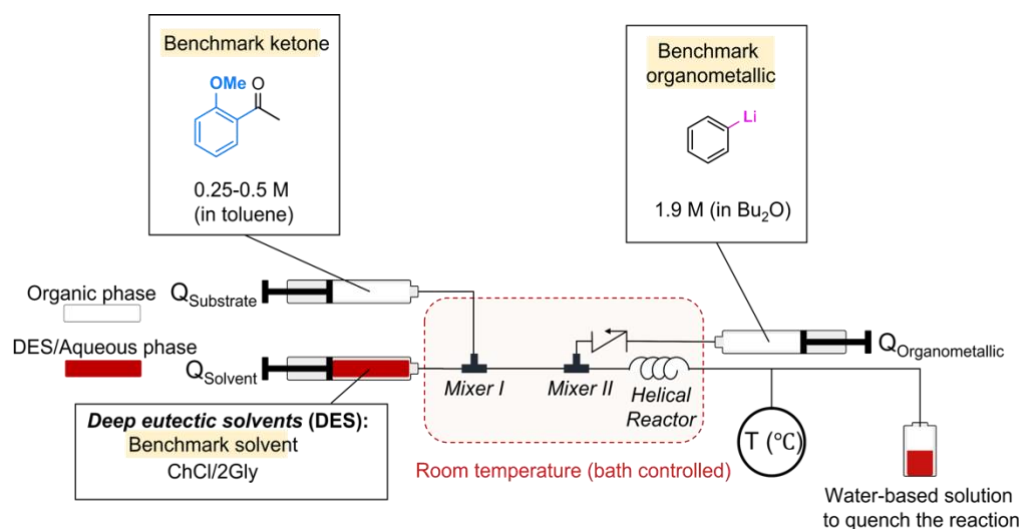


Figure 1

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Poster 59

Hydrogenation of esters promoted by phosphine-NHC manganese catalyst

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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.

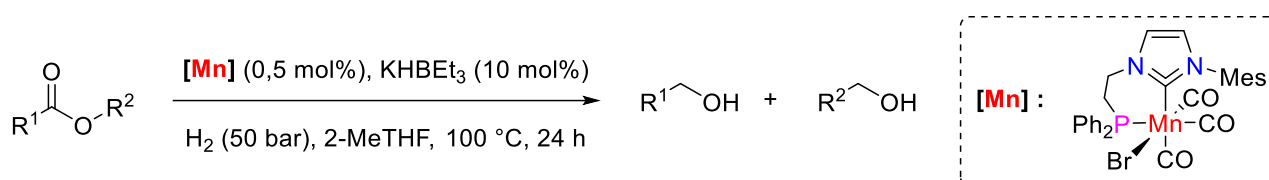


Figure 1

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Poster 60

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

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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.

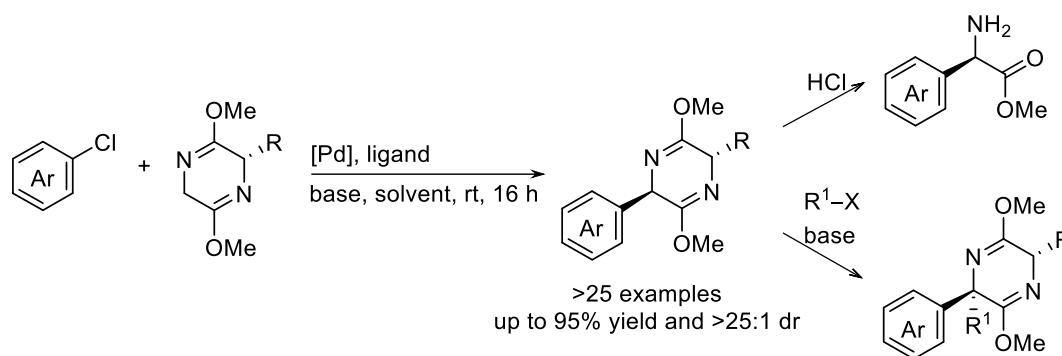


Figure 1: Pd-catalyzed asymmetric arylation of the bis-lactim ether with aryl chlorides.

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Poster 61

Designing polymerizable ligands for luminescent metallapolymers

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Luminescent metallapolymer 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 metallapolymer 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.

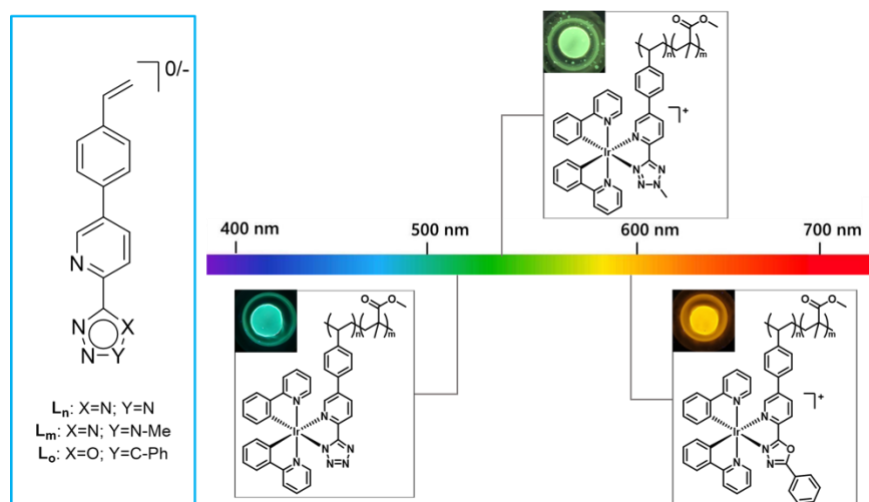


Figure 1

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Poster 62

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

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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.

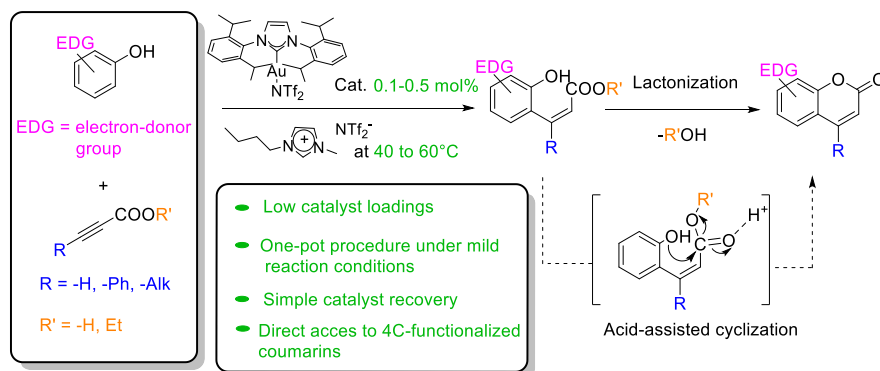


Figure 1 One-pot/two steps synthesis of 4C-functionalized coumarins via intermolecular hydroarylation of electron-rich phenols with propiolic acid derivatives

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Poster 63

Synthesis and characterization of luminescent copper(I) complexes

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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 [Cu(N[^]N)(P[^]P)]⁺ complex which can be used in this kind of application. This heteroleptic copper(I) complex is based on Xantphos as P[^]P ligand and on a pyridine-pyrazole as N[^]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 N[^]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.

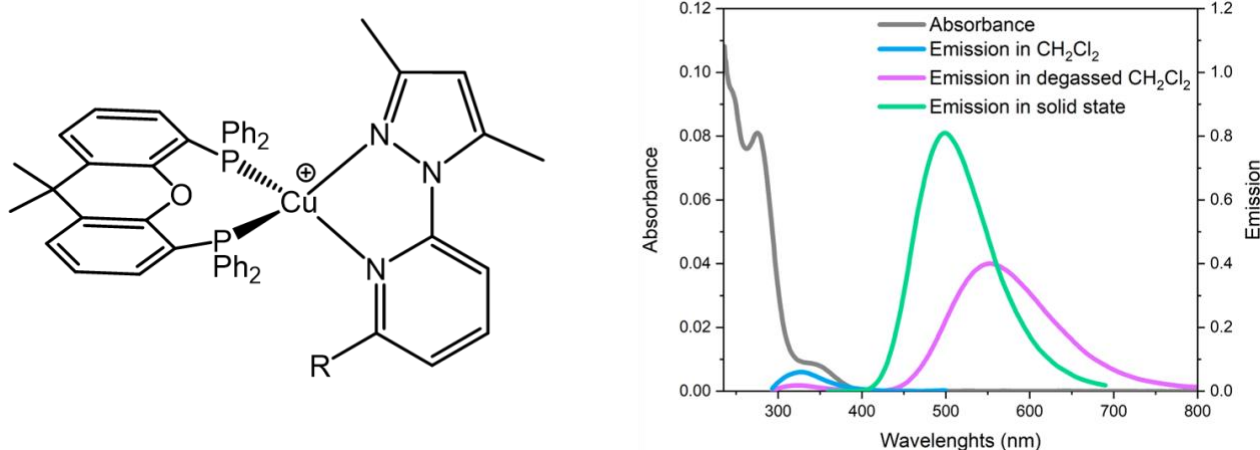


Figure 1. Chemical structure and photophysical properties of synthesized complexes

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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

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$\text{Ru}(\eta^5\text{-cyclopentadienyl})$ 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.

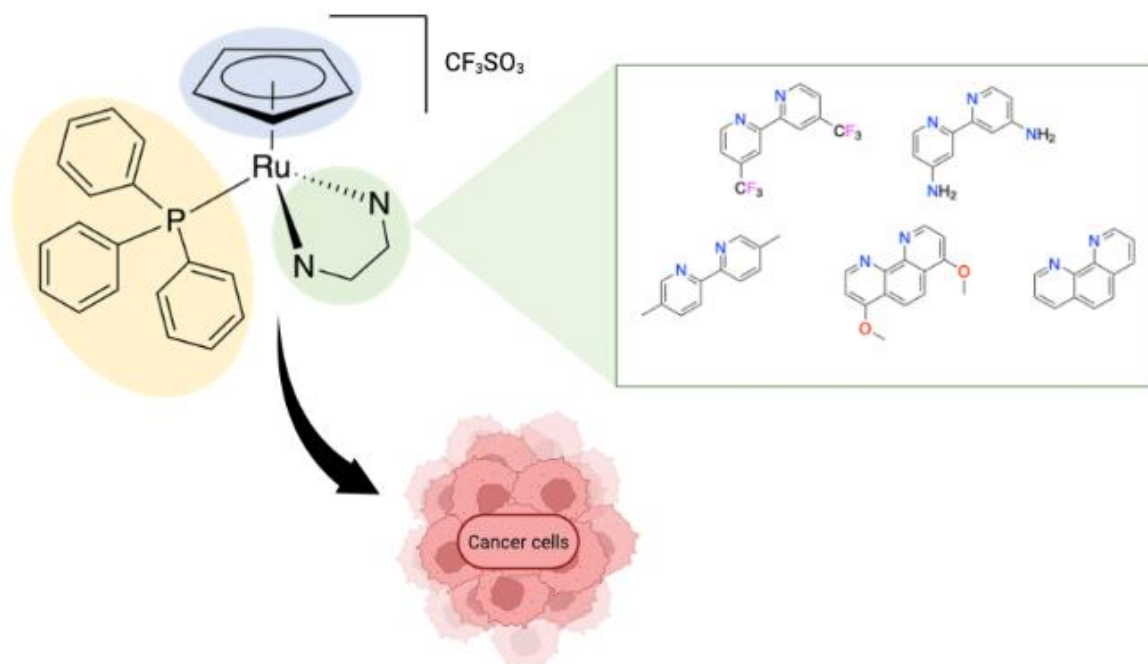


Figure 1

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Poster 65

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

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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.

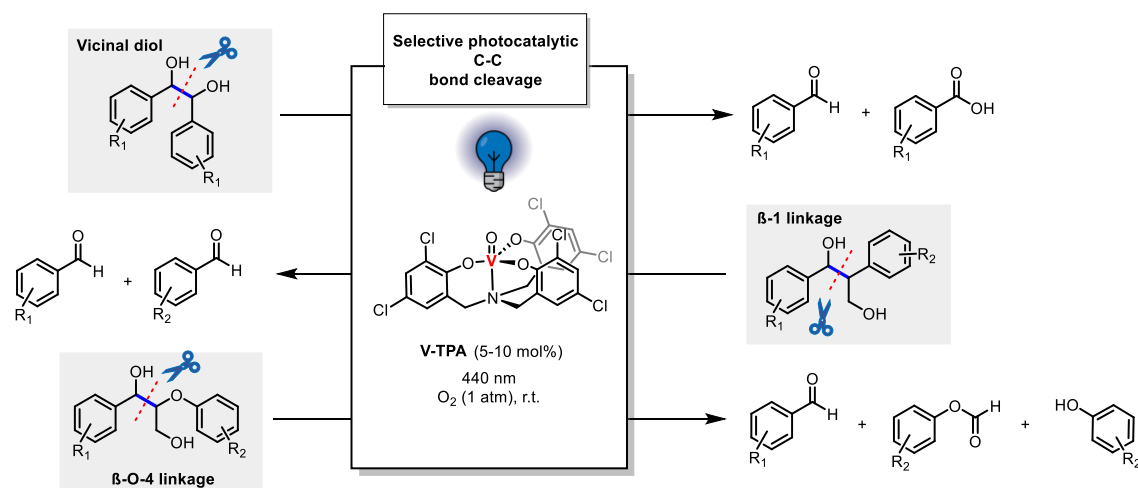


Figure 1. Photocatalytic aerobic C-C bond oxidative cleavage of lignin models.

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Acknowledgement: The project has been carried out in the frame of the project PON "Ricerca e Innovazione" 2014-2020 Azione IV.5 – Dottorati su tematiche green (FSA fellowship).

Poster 66

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

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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.

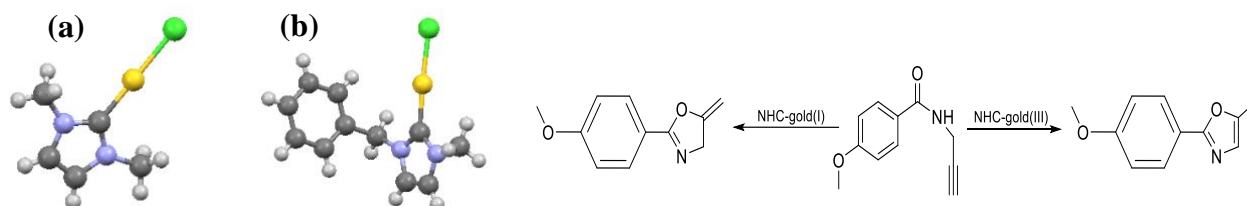


Figure 1: Left: Starting carbene complexes [AuCl(IME₂)] (**a**) and [AuCl(IBnMe)] (**b**); Right: Gold-catalyzed cyclization of N-propargyl amide as benchmark reaction to test the gold catalysts.

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Poster 67

New N-Ferrocenyl Aminocarbonyne Iron Complexes

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Since the former work of Pombeiro and Fischer, aminocarbonyne 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) aminocarbonyne complex (**1**) was achieved on a diiron bis-cyclopentadienyl scaffold via incorporation of isocyanoferrrocene (Figure 1). The {CN(Fc)Me} fragment possesses a hybrid aminocarbonyne-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.

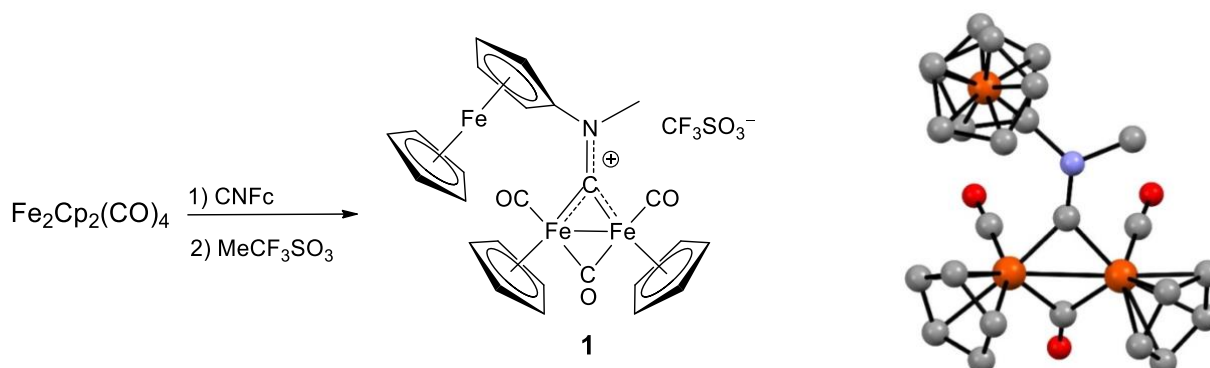


Figure 1. Triiron complex with bridging N-ferrocenyl aminocarbonyne ligand: synthesis and DFT-optimized structure of the most stable isomer.

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

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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 place (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

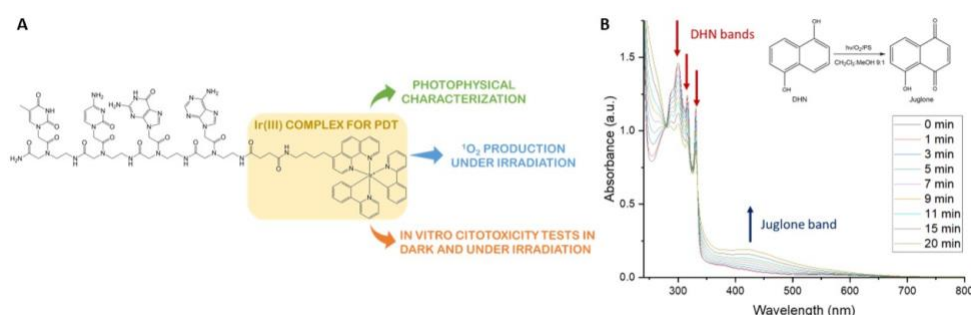


Figure 1: (A) The Ir(III) complex-PNA conjugate; (B) UV-vis spectra of DHN+PS mixture irradiated by a 400 nm LED.

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Poster 69

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

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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 H₂.¹ The most renowned complex of this kind is Wilkinson's catalyst (RhCl(PPh₃)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(PPh₃)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(PPh₃)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(C₂H₄)(PPh₃)₂ and will provide new insights into the reactivity of Wilkinson's catalyst and related complexes (Figure 1).

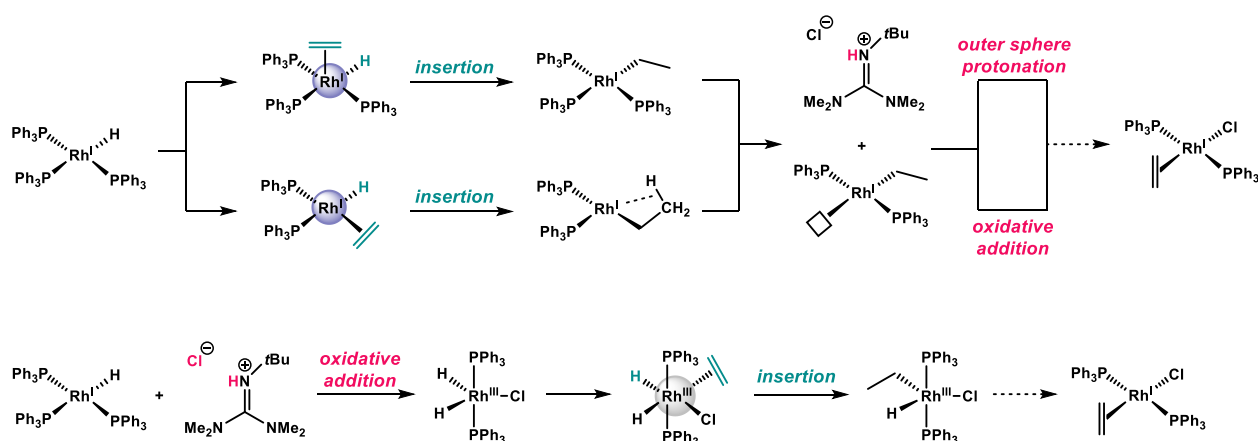


Figure 1

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Poster 70

Influence of CAAC-Triazene Ligands on Rhodium Complexes

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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.

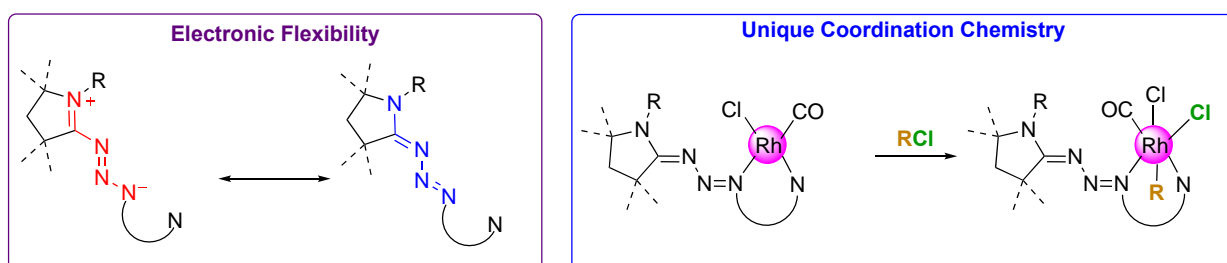


Figure 1: (right) CAAC-triazene ligand electronic flexibility and (left) coordination to rhodium and reactivity towards alkyl chloride.

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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

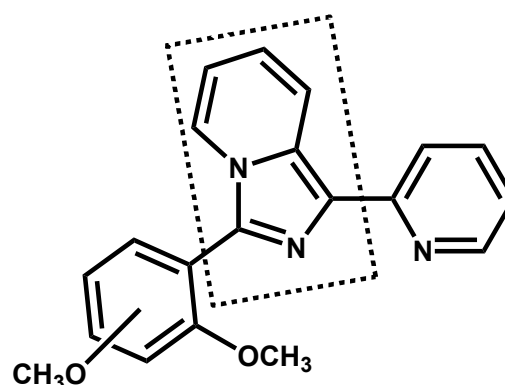
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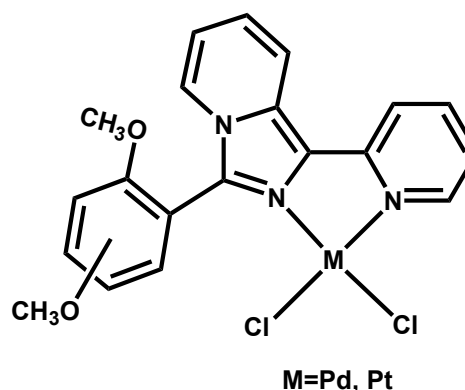
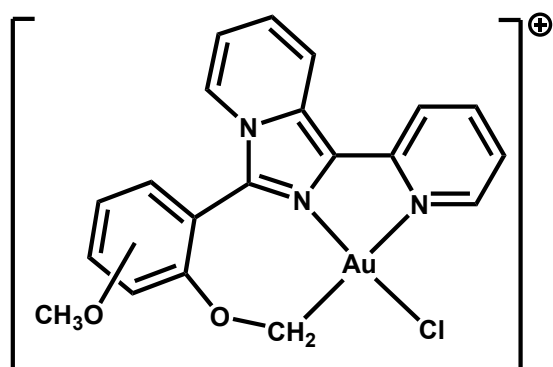
giacomo.senzacqua@gmail.com

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.



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Poster 72

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

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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.

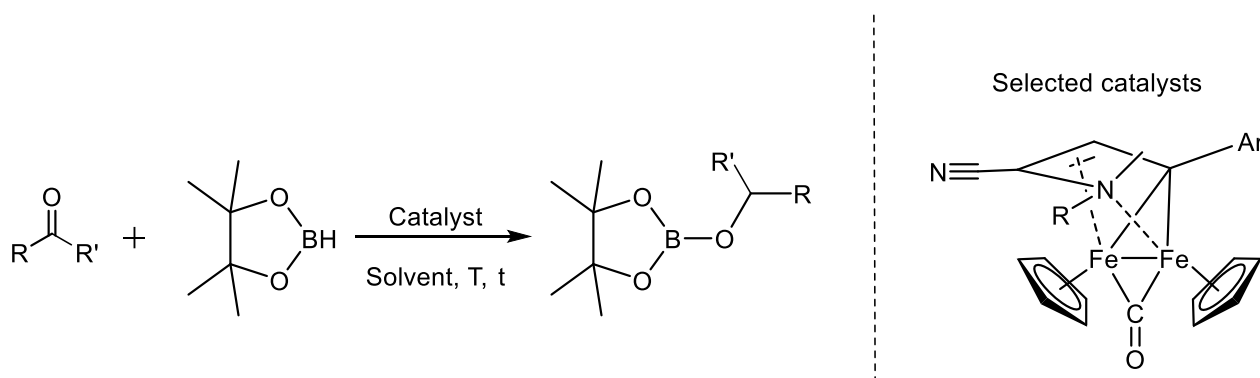


Figure 1

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Poster 73

Design of Hydrophobic Bimetallic MOFs for Application in Heterogenous Catalysis

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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.

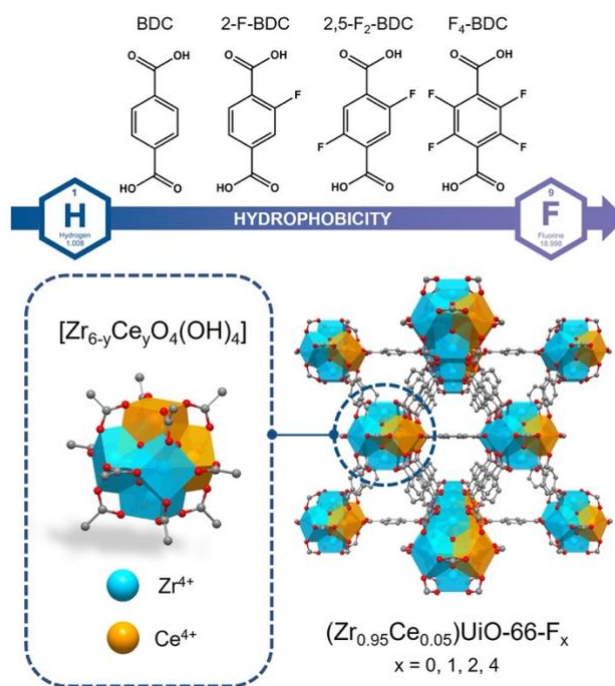


Figure. Representation of linkers, bimetallic clusters, and 3D structure of the synthesized MOFs.

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Poster 74

Zr(IV)-catalyzed Reductive Depolymerization of Polycarbonates

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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 Cp₂Zr(H)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).

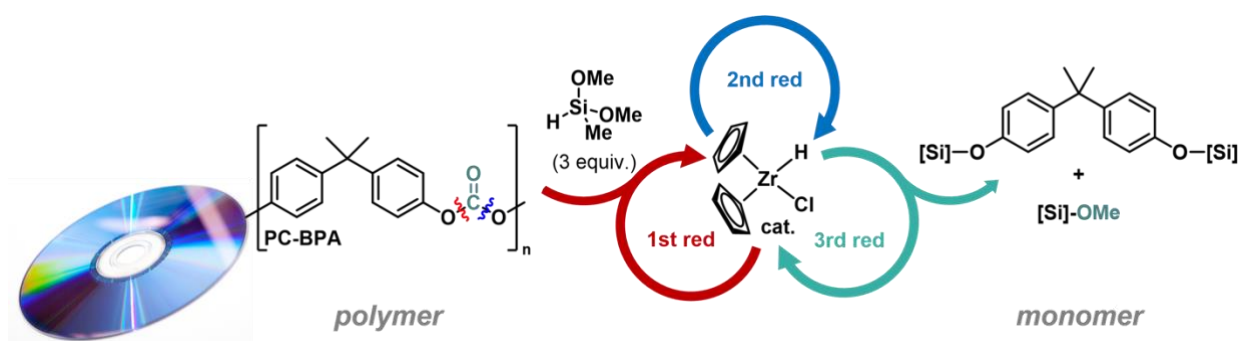


Figure 1

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Poster 75

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

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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

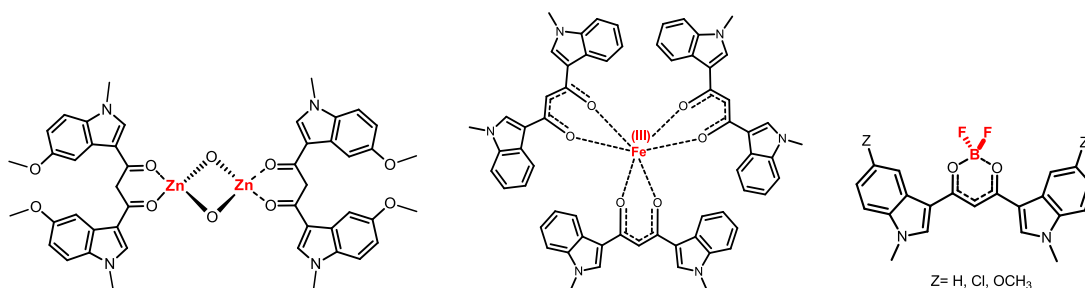


Figure 1

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Poster 76

Ligand Enabled Oxidation: New Avenues in Gold Chemistry

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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.

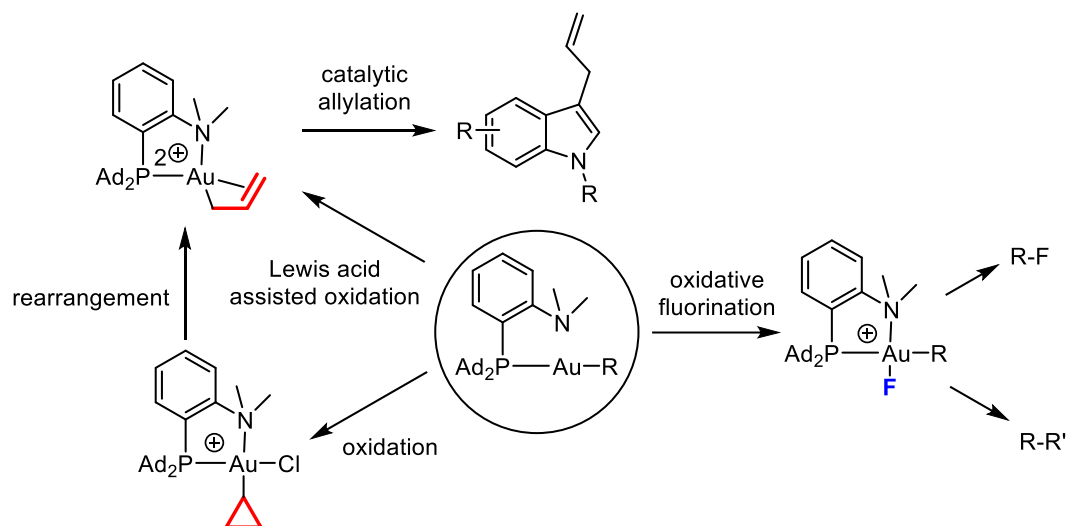


Figure 1

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Poster 77

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

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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.

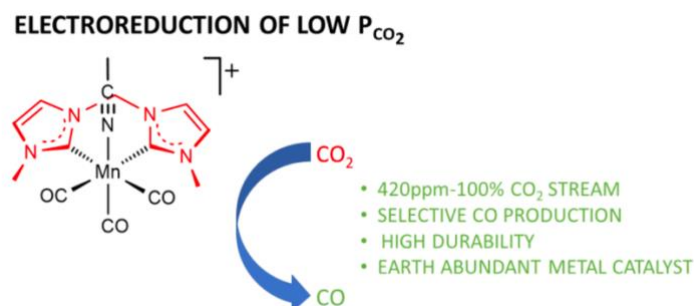


Figure 1

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Poster 78

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

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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-1*H*-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).

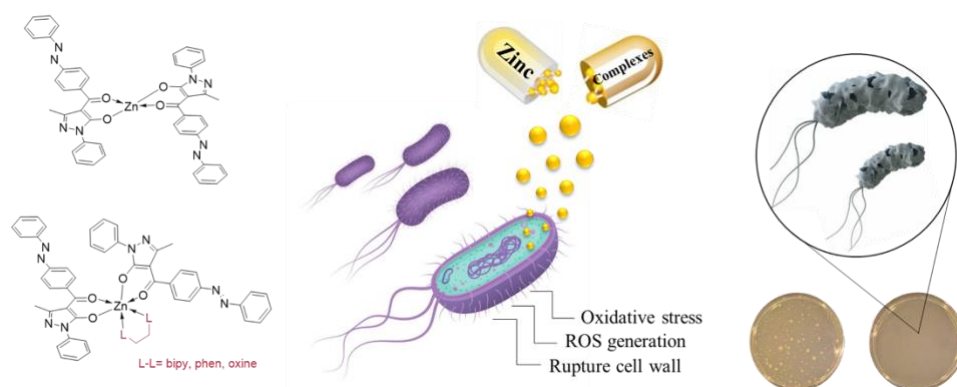


Figure 1. Zn(II) complexes of pyrazolone-based ligands and their biological activities.

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

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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.

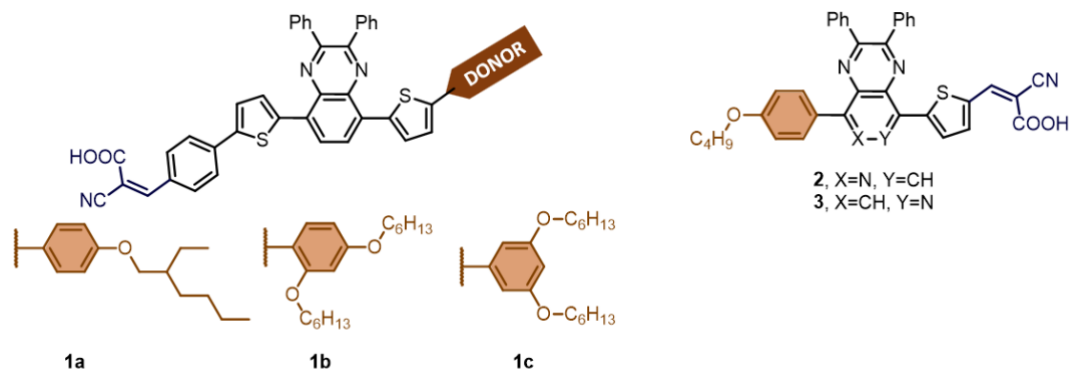


Figure 1 Structure of compounds **1a-c**, **2** and **3**.

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 to evaluate their photoelectrochemical properties and applicability in the device.

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Poster 80

Novel Activation Mechanisms for Rhodium(III) Cyclopentadienyl Complexes

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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)

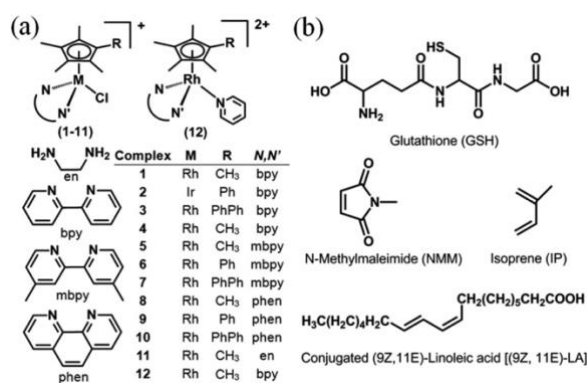


Figure 1

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