

Cu Pt organometallics porphyrines
bio inorganic enantioselective Fe m
yield Li ligand cross coupling
oxidation metathesis Zn reaction
hydrogen Ir Mg efficiency Ag rec
green syn Pd coordination selectivity
chemistry Au environment Ru
phosphine bond Rh photosynthesis



Società Chimica Italiana

Gruppo Interdivisionale
Chimica Organometallica

GICO Awards 2020 ON-LINE EVENT

Friday, 26th February 2021 - 3.00 p.m.

FINAL PROGRAM

3.00 p.m: Welcome and awards ceremony

3.15 p.m.: Prof. **Stephen K. Hashmi** - *Gold Catalysis and Light*

3.50 p.m.: Dr. **Marco Baron** - BONATI Prize 2020 - *A tale on gold complexes with di(N-heterocyclic carbene) (diNHC) ligands*

4.25 p.m.: Prof. **Emanuela Licandro** - GICO Senior 2020 - *An organic chemist's journey into the wonderful world of metals*

5.00 p.m.: Prof. **Gerald F. Manbeck** - *Photo- and electrochemical mechanisms of CO₂ reduction using self-sensitized Ir catalysts*

The event will be free of charge and can be followed at

<https://unicam.webex.com/meet/eventi>

Certificate of participation will be available, upon request and booking on:

cogico.eventi@iccom.cnr.it

You can follow updates at <https://www.soc.chim.it/it/node/2678>

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Gold Catalysis and Light

For a long time the activity of gold in homogeneous catalysis was dominated by π -activation of C-C multiple bonds (alkynes, allenes, olefins). These catalytic cycles did not involve a change of the oxidation state at gold. Now catalytic cycles involving a redox change at the gold center are developed, these reactions often involve light. Latest findings in that sector will be provided.

Prof. **Stephen K. Hashmi**
University of Heidelberg

A tale on gold complexes with di(N-heterocyclic carbene) (diNHC) ligands

Gold complexes have been extensively studied in the last 15 years, since they are promising compounds in homogeneous catalysis, medicinal chemistry and material science. In this frame, N-heterocyclic carbenes (NHCs) are privileged ligands for gold centers as highlighted both from experimental and theoretical studies. We started our investigation on gold NHC complexes by using bidentate ligands (diNHC) that can afford organometallic chelating complexes with enhanced stability, or can act as bridging ligands affording dinuclear complexes with supported aurophilic interaction. We deeply investigated dinuclear gold(I) diNHC complexes of general formula $[\text{Au}_2(\text{diNHC})_2](\text{PF}_6)_2$ with a focus on their photophysical and biological properties, and on their reactivity in the oxidative addition of halogen. We systematically observed that properties and the reactivity of the complexes are strongly influenced by the ability of the employed ligand to support the intramolecular aurophilic interaction.

More recently, we also studied the catalytic behavior of gold(I) diNHC complexes of general formula $[\text{Au}_2\text{Br}_2(\text{diNHC})]$ in the alkyne hydroamination and hydroalkoxylation reactions and investigated on the possible occurrence of cooperative effects. The synthesis of gold(III) diNHC complexes is more challenging compared to the gold(I) corresponding compounds, considering their lower stability. In this regard we successfully reported the first X-ray structure of a gold(III) diNHC complex and the first example of a gold(II) diNHC complex. We also optimized the synthesis of mononuclear gold(III) diNHC complexes of general formula $[\text{Au}(\text{diNHC})_2](\text{PF}_6)_3$ and studied their application as halide sensors in solution.



Dr. Marco Baron
University of Padova

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Prof. Emanuela Licandro

University of Milano Statale

An organic chemist's journey into the wonderful world of metals

Modification of organic molecules with transition metals is a long-standing strategy to obtain organometallic systems with improved reactivity, spectroscopic, and chemico-physical properties. This approach has yielded excellent results in many research fields due to its versatility, with infinite possible combinations of transition metals and organic systems. This lecture will highlight the most interesting and innovative results of the presenter's research in the field of organometallic compounds. Progressing from older studies on Fischer-type carbenes to the most recent research on

metal-conjugates of peptide nucleic acids (PNAs) and 7-thiahelicenes, the presenter will show that, in all cases, the presence of the metal gives the organic molecule specific chemico-physical properties that can be useful in electrochemical and spectroscopic analysis, imaging, and catalysis.

Several illustrative examples will be presented. (1) The conjugation of PNAs with transition metal complexes involving chromium and iron makes possible significant IR and electrochemical detection at a very low concentration without affecting the specificity and efficiency of PNA/DNA binding. (2) The rapid internalization of dinuclear Re-PNA conjugates in different types of cells confirms the fundamental role of the metal in increasing cell uptake of PNAs. (3) In the context of asymmetric catalysis, enantiomerically pure gold complexes of phosphorus-containing 7-thiahelicenes give high enantiomeric excess in a number of asymmetric reactions.

Photo- and electrochemical mechanisms of CO₂ reduction using self-sensitized Ir catalysts.

$\text{Ir}(\text{tpy})(\text{ppy})\text{Cl}$, where tpy = 2,2'-terpyridine and ppy = 2-phenylpyridine and related complexes possess the rare ability to reduce CO₂ photochemically without the necessity of an additional sensitizer. This self-sensitized reactivity with high quantum efficiency can simplify systems for artificial photosynthesis if durability can be improved. In this presentation, I will discuss research efforts at Brookhaven National Laboratory directed toward identification of key reactive species, elucidation of mechanisms, and uncovering non-productive side reactions for $\text{Ir}(\text{tpy})(\text{ppy})\text{Cl}$ and structurally similar complexes. Important discoveries include the roles of isomerization, the identification of Ir-Ir dimers and Ir-H-Ir hydride bridged dimers as deactivation products, and the discovery of many electrochemical mechanisms depending upon applied potential and the role of protons or CO₂ in the rate-limiting C-O bond cleavage step from Ir-CO₂ metallocarboxylate or Ir-CO₂ metallocarboxylic acid intermediates.



Prof. Gerald F. Manbeck

Brookhaven

National Laboratory - NY