

The use of transition metal complexes, for which it is possible to modulate the sphere of coordination around the metal center, allowed to take a decisive step in catalysis in many types of reactions. However, there are still many areas to explore. In order to increase the number of applications in the industrial environment, inexpensive, clean, environmentally friendly processes must be developed. *Within this proposal, we plan to develop two important processes as part of eco-efficiency and energetic transition, that are the reduction reactions of carbonic compounds (CO₂ and derivatives), and reactions of hydrogen autotransfer/borrowing hydrogen catalyzed by cyclopentadienone iron(0) tricarbonyl and triaminocyclopentadienyl iron(II) tricarbonyl complexes under light irradiation.*

1. State of the Art and scientific objectives

1.1 Reduction of CO₂

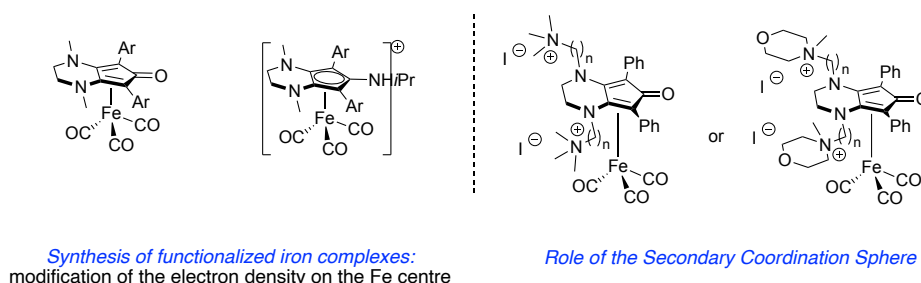
Face to the societal demand, and to the rapid depletion of fossil resources, the recycling of the CO₂ is of utmost importance. Two main strategies have been targeted. The first one is its use (or more generally the use of carbonic derivatives) as C₁ or C₂ carbon source to produce chemical platforms (CO, methanol, formic acid, etc...). The second approach focuses on its utilization as energy storage technology to substitute the fossil fuel base energy feedstock. We have introduced the tricarbonyl iron complex bearing a diaminocyclopentadienone ligand in catalysis. This complex displays the highest activities for an iron complex without any air-sensitive pincer ligand or polydentate phosphine ligand and is competitive with some of the currently reported phosphine-based iron complexes. While these results open new avenues in catalysis, some drawbacks remain. Due to the chemical inertness and high kinetic and thermodynamic stability, the hydrogenation of CO₂ required harsh reaction conditions (high temperatures and hydrogen pressure). Moreover, hydrogen is mainly produced from non-renewable resources. As Nature converts carbon dioxide in biomass via photosynthetic processes (reactions implying electron transfers), the exploitation of light or electrons as an energy source, to activate CO₂ reduction and transform CO₂ into a source of C₁ carbon such as formic acid or carbon monoxide (CO), could be a desirable alternative. Two approaches can then be proposed: (i) either electrocatalytic conversion, (ii) or photocatalytic conversion (to mimic the photosynthesis). In collaboration with Prof. Marc Robert, a preliminary work showed that the triaminocyclopentadienyl iron tricarbonyl complex could selectively reduce CO₂ to CO at a low overpotential. Within this proposal, based on all these results and in the continuity of our work on the reduction of carbonic derivatives, we proposed to study the electro- and photoreduction of CO₂ with cyclopentadienone iron(0) tricarbonyl and triaminocyclopentadienyl iron(II) tricarbonyl complexes (Scheme 1). Both activities and selectivities will be scrutinized and compared. Then, in a second step, because charged groups in the second sphere of coordination could improve the reactivities and selectivities, the iron complexes bearing ammonium groups will be synthesized and evaluated in the electro- and photoconversion of CO₂ into CO (Scheme 1). As perspective, if the photochemical approach is successful, with respect to the economic and ecologic limitations associated with the use of stoichiometric amounts of sacrificial donor, the possibility to transfer the best dual photoredox/organometallic system to a more challenging photoelectrochemical process will be explored. Indeed, such methodology would combine a dual photoredox/organometallic system for the catalytic reduction of CO₂ and electrochemistry to regenerate the electron donor.

1.2 Hydrogen auto-transfer methodology.

Hydrogen auto-transfer methodology or borrowing hydrogen reaction is a thrilling area of research. This process is a greener and safer way to create new C-C or C-N bonds from environmentally benign alcohols. A second research area to get rid of petrochemicals or non-renewable resources is the use of biomass, considering that (i) it is not in competition with the food chain, (ii) it is abundant (knowing that the demand of carbon products is increasing) and (iii) it is cheap. The use of lignocellulose could be the solution as it allows the production of alcohols. Among the reported complexes able to catalyze the borrowing hydrogen reaction, the diaminocyclopentadienone iron tricarbonyl complex has demonstrated its potency in the formation of both C-C and C-N bonds. This complex catalyzed not only the alkylation of ketones, indoles, oxindoles and alcohols, but also the *N*-alkylation of amines and amides. Whilst the hydrogen auto-transfer methodology is a successful technology in fine chemistry,

some drawbacks, such as high reaction temperatures (90-150 °C), remain. Consequently, there is still room to improve such technology, to introduce new substrates and to develop unprecedented methodologies. We have recently disclosed a simple and robust visible light-induced iron-catalyzed α -alkylation of a variety of ketones with aliphatic, benzylic, or even more challenging allylic and propargylic alcohols at room temperature. These results tend to demonstrate the versatility of the cyclopentadienone iron complexes, as the borrowing hydrogen strategy can now be applied either under thermal or visible light activation. Within this proposal, one objective will be to develop new alkylation reactions using our new “light-induced hydrogen autotransfer strategy” catalyzed either by cyclopentadienone iron(0) tricarbonyl or triaminocyclopentadienyl iron(II) tricarbonyl complexes in order to widen the application of this methodology in organic synthesis (alkylation of hydrazides with alcohols, dehydrogenative coupling of amido-alcohols, alkylation of amines with epoxides, etc...) and to modify the steric and electronic properties of the cyclopentadienone iron(0) tricarbonyl or triaminocyclopentadienyl iron(II) tricarbonyl complexes. DFT calculations will be used not only to unveil the mechanism involved in such reactions, but also to help for the design of the new iron complexes (Scheme 1).

Scheme 1: Synthesis of functionalized iron complexes



2. Proposed Collaboration

This project will be done in collaboration with Dr. Albert Poater of the University of Girona. Our two groups have been collaborating since 2013 on this chemistry of iron complexes and their application in hydrogenation. This joint work has already been the subject of 14 publications and one co-supervised PhD (see Appendix). The consortium's expertise is based on an approach combining theoretical chemistry, in-silico study (based on the skills of Dr. Albert Poater's group, necessary to design an efficient iron complex and to unveil the catalytic processes) and an experimental approach (based on the skills of the group at ICPM including organic and organometallic synthesis for the development of new organometallic complexes and their applications in chemistry).

The co-supervised thesis will allow the future doctoral student to lead the project from the theoretical study to the synthesis of the complexes (organic and organometallic chemistry) and applications. The project schedule foresees a period in Girona during the second year for training on DFT calculations and in-silico study and application to the complexes envisaged in this study.

Appendix

1 Joint International Supervision of a Doctoral Thesis (Dr. Nicolas Joly, 2020-2023)

Publications in collaboration with Dr. Albert Poater (University of Girona):

- 1) *Piano Stool Iron Complexes Bearing Non Innocent Substituted Cyclopentadienone Ligand: Synthesis, Characterization and Application in Reductive Amination.*
S. Moulin, H. Dentel, A. Pagnoux-Ozherelyeva, S. Gaillard, A. Poater, L. Cavallo, J.-F. Lohier, J.-L. Renaud *Chem. Eur. J.* **2013**, *19*, 17881-17890.
- 2) *Highly Active Phosphine Free Bifunctional Iron Complex for Hydrogenation of Bicarbonate and Reductive Amination.*
T-T. Thai, D. S. Mérel, A. Poater, S. Gaillard, J.-L. Renaud, *Chem. Eur. J.* **2015**, *21*, 7066-7070.
- 3) *Alkylation of Ketones Catalyzed by Bifunctional Iron Complexes: From Mechanistic Understanding to Application.*
C. Seck, M. D. Mbaye, S. Coufourier, A. Lator, J.-F. Lohier, A. Poater, T. R. Ward, S. Gaillard, J.-L. Renaud *ChemCatChem.* **2017**, *9*, 4410-4416.
- 4) *Iron-Catalyzed Chemoselective Reduction of α,β -Unsaturated Ketones.*
A. Lator, S. Gaillard, A. Poater, J.-L. Renaud *Chem. Eur. J.* **2018**, *24*, 5770-5774.
- 5) *Well Defined Phosphine-Free Iron Catalyzed N-Ethylation and N-Methylation of Amines with Ethanol and Methanol.*
A. Lator, S. Gaillard, A. Poater, J.-L. Renaud *Org. Lett.* **2018**, *20*, 5985-5990.
- 6) *Room Temperature Chemoselective Reductive Alkylation of Amines Catalyzed by a Well-Defined Iron(II) Complex using Hydrogen.*
A. Lator, Q. Gaignard Gaillard, D. S. Mérel, J.-F. Lohier, S. Gaillard, A. Poater, J.-L. Renaud *J. Org. Chem.* **2019**, *84*, 6813-6829. (Selected article for the virtual issue "Celebrating Organic Chemistry in France".)
- 7) *Hydrogenation of CO₂, Hydrogenocarbonate and Carbonate to Formate in Water Using Phosphine Free Bifunctional Iron Complexes.*
S. Coufourier, Q. Gaignard Gaillard, J.-F. Lohier, A. Poater, S. Gaillard, J.-L. Renaud *ACS Catal.* **2020**, *10*, 2108-2116.
- 8) *A Phosphine-Free Ruthenium Complex-Catalyzed Synthesis of Mono- or Dialkylated Acyl Hydrazides via the Borrowing Hydrogen Strategy.*
N. Joly, L. Bettoni, S. Gaillard, A. Poater, J.-L. Renaud *J. Org. Chem.* **2021**, *86*, 6813-6825.
- 9) *Ruthenium-Catalyzed Three-Component Alkylation: A Tandem Approach to the Synthesis of Nonsymmetric N,N-Dialkyl Acyl Hydrazides with Alcohols.*
L. Bettoni, N. Joly, J.-F. Lohier, S. Gaillard, A. Poater, J.-L. Renaud *Adv. Synth. Catal.* **2021**, *363*, 4009-4017.
- 10) *Iron-Catalyzed Chemoselective Hydride Transfer Reaction.*
S. Coufourier, D. Ndiaye, Q. Gaignard Gaillard, L. Bettoni, N. Joly, M. D. Mbaye, A. Poater, S. Gaillard, J.-L. Renaud *Tetrahedron* **2021**, *90*, 132187.
- 11) *Knölker Iron Catalysts for Hydrogenation revisited: Non Spectator Solvent and fine-tuning.*
M. Gimferrer, N. Joly, S. Escayola, E. Viñas, S. Gaillard, M. Solà, J.-L. Renaud, P. Salvador, A. Poater, *Organometallics* **2022**, *41*, 1204-1215.
- 12) *Blue-light Induced Iron-Catalyzed α -Alkylation of Ketones.*
M.-S. Abdallah, N. Joly, S. Gaillard, A. Poater, J.-L. Renaud, *Org. Lett.* **2022**, *24*, 5584-5589.

13) *Enhancement of Knölker Iron Catalysts for Imine Hydrogenation by Predictive Catalysis: From Calculations to Selective Experiments.*

N. Joly, M. Gimferrer, S. Escayola, M. Cendra, S. Coufourier, J.-F. Lohier, Q. Gaignard Gaillard, S. Gaillard, M. Solà, J.-L. Renaud, A. Poater, *Organometallics* **2023**, *42*, 1784-1792.

14) *Blue-light Induced Iron-Catalyzed Synthesis of γ,δ -Unsaturated Ketones.*

N. Joly, A. Colella, M.-E. Mendy, M. D. Mbaye, S. Gaillard, A. Poater, J.-L. Renaud *ChemSusChem* **2024** *in press*. (doi:10.1002/cssc.202301472)



Girona, March 11th, 2024

Expression of interest

Universitat de Girona is interested in co-supervising a PhD student with Sorbonne Université.

The PhD student will enroll in the PhD program in Chemistry from which he/she will receive a PhD diploma. Work for the thesis will be performed at Universitat de Girona and Sorbonne Université according to the research plan agreed by both institutions. Both universities will sign a cooperation agreement for the co-supervision of the thesis.

Sorbonne Université will provide a “Appel à projets international” grant, entitled “*Enabling Sustainable Synthesis Through the Merge of Catalysis and Light.*”, that furnishes the salary of the PhD student for the three years PhD contract. Consumables and travel expenses necessary to carry out the research program will be provided by the Universitat de Girona for the period spent by the student for his research time in Universitat de Girona at Girona. In particular, Dr. Albert Poater research group from Universitat de Girona will be responsible, and will cover all these costs.

Universitat de Girona will help the student to find accommodation for the stays in Girona and will also give him the opportunity to take courses to learn Catalan and/or Spanish.

Yours sincerely,

Dr. Albert Poater

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