Appel à Projets de Recherche Doctorale Partenariats internationaux 2025

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Synthesis of trinuclear clusters of gold and platinum in various oxidation states by modulation of the nature of the ligand and evaluation in homogeneous catalysis and photocatalysis

Project

The objective of this collaboration is to take advantage of the internationally recognized competences of both partners to obtain new catalytic species, namely trimetallic clusters of gold and platinum by playing on the degree of oxidation of the metal according to the nature of the ligand carried by it. We hope to find new reactivities in the field of gold and platinum catalysis.

Today, growing societal concerns about minimal waste production, use of less toxic and purer materials (drugs), cost and energy savings, require improved synthesis technologies, especially in terms of atom economy. The use of catalysts to efficiently and selectively promote various reactions is a powerful approach to achieve these goals, which nature does constantly by using enzymes. In this regard, the design of new catalysts is paramount to meet the criteria of chemoselectivity and stereoselectivity in catalytic processes.

This project aims at evaluating the catalytic properties of triangular trinuclear clusters of platinum and gold, aromatic metal complexes presenting an original cyclic structure involving only metal atoms. All the bonds are delocalized on the three atoms, in analogy with ordinary aromatic compounds. The effect of this electronic delocalization is that all M-M bond lengths are identical.

To date, three trinuclear aromatic gold clusters[1] and one platinum[2] have been described in the literature. Their catalytic properties have been evaluated in a limited number of reactions.[1,2] It is well known that the nature of the ligand carried by the metal has a strong influence on the catalytic properties of the corresponding mono or binuclear organometallic complexes. This is particularly true in gold catalysis.[3] In the case of trinuclear gold clusters, the nature of the ligand seems to have an influence on the oxidation states of the gold atoms, however no rationalization has been made between the nature of the ligand carried by the gold (Au) and the oxidation states of the three atoms. Their effect on the catalytic properties of the complexes is similarly underdeveloped.

First, Pt and Au clusters previously described in the literature will be synthesized to extend their catalytic properties. Then new trinuclear clusters of gold and platinum will be synthesized, following Maestri's conditions, from commercial mononuclear Au(I) complexes or synthesized by one of the partners with a large variety of ligands having various electronic properties (phosphines, NHC, indolizy carbenes).[4] These trinuclear clusters will be fully characterized by NMR (^{1}H, ^{13}C and ^{31}P if needed), mass spectroscopy, UV visible, Infrared and X-ray diffraction. The redox properties of the complexes will also be studied by cyclic voltammetry to determine the oxidation states of the metal atoms (Pt and Au) in order to better orient the choice of catalytic reactions. In parallel, DFT calculations will be performed by one of the partners to guide the choice of ligands (Figure 1).

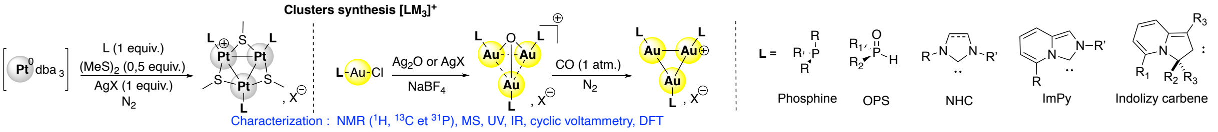
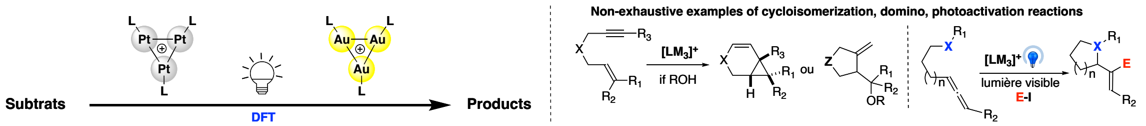


Figure 1: New clusters synthesis.

The catalytic properties of these new clusters will be evaluated in diagnostic cycloisomerization reactions of polyunsaturated compounds but also in multicomponent reactions widely studied by the Paris team on other catalytic systems.[5] Once their reactivities are proven, more complex or less reactive systems will be considered such as amination reactions, double bond activation but also C-H activation, which are very poorly developed to date with these types of metals. The photochemical properties of the complexes will be studied to evaluate their reactivities in dual redox catalysis or by energy transfer in cross coupling process, by analogy to palladium chemistry. This is highly challenging in present case due to the high Au(III)/Au(I) redox potential, but it can become an original linchpin in order to activate unreactive substrates.[6] Very recently, one example of photoactivation of trinuclear gold clusters by SET has been described for 1,2-aminoalkylation and 1,2-alkylarylation of alkenes using non-activated alkyl bromides with good selectivity, offering a proof of principle of the feasibility of the approach.[7]

Each elementary step of these processes will be studied to have a good understanding of the systems.



An important challenge will be to obtain Au(II) clusters, an oxidation state difficult to isolate in mononuclear complexes due to the instability of the species because they are easily oxidized or reduced to Au(III) or Au(I) complexes respectively. Indeed, Au(II) species[8] are postulated but not proven in photocatalysis processes. The reactivity of these Au(II) species will be therefore explored for the development of new reactivities in classical catalysis processes as well as in photocatalysis.

Finally, it is proposed to exploit the aromatic stabilization of the complexes to promote their recycling at the end of the reactions, in order to minimize the consumption of the rare elements present which compose them. This approach is particularly original compared to the literature concerning homogeneous catalysis with mononuclear Au and Pt complexes, and thus aims to become a new reference to increase the durability of the associated synthetic methods.

Methodology, work program and dissemination of results

The thesis work will be shared between the laboratory in Parma, Italy, for the synthesis of the clusters and the laboratory in Paris, France, for their evaluation in catalysis. The person who will be recruited to carry out this research project will share his/her time between the two teams over periods of 4 to 6 months depending on the progress of the work in the team concerned. During this research work between these two laboratories, the PhD student will exploit the knowledge of both research groups and will be able to familiarize himself/herself with the synthesis and characterization of trinuclear metallo-aromatic complexes characterized by the presence of delocalized chemical bonds, while developing, in parallel, competences in the field of computational chemistry, with particular attention to methods capable of efficiently rationalizing the metal-metal chemical bonds typical of these structures. Skills in organic synthesis and catalysis will be obtained during the evaluation of the complexes with a part dedicated to the understanding of the reaction mechanisms involved.

Weekly progress reports will be shared with both teams' supervisors, forming the basis for monthly videoconferences to discuss the research. At least one in-person meeting will be held annually to guide future developments and strengthen collaboration.

As a result, the doctoral student will develop a complex set of skills that will favor his or her future professional career. Moreover, the attention of the host research groups to sustainability issues, expressed in this project with the aim of minimizing the consumption of scarce elements, represents a fundamental area for the training of new generations of researchers. Indeed, the stakes of the ecological transition require a growing awareness of the importance of minimizing waste formation in chemical processes, making this approach particularly crucial in this context. The project's results will be disseminated through publications in high-impact international journals and presented at national and international conferences, ensuring wide visibility in the scientific community, particularly for the PhD student.

This project was funded in 2023, but after one year the PhD student resigned to change career direction. In between, the Italian partner agreed to fund 1 year of PhD. Therefore, this project should be funded as follows: 2 years by the Sorbonne University and 1 year by the Italian partner

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