

## China Scholarship Council

Appel à projets

Campagne 2022

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Title of the research project: **New Allene bis-Phosphine Ligands. Applications in catalysis and materials sciences**

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PhD student currently supervised by the thesis supervisor (number, year of the first inscription): 2, 2019. 1, 2020.

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**AVIS et VALIDATION de l'ÉCOLE DOCTORALE :**

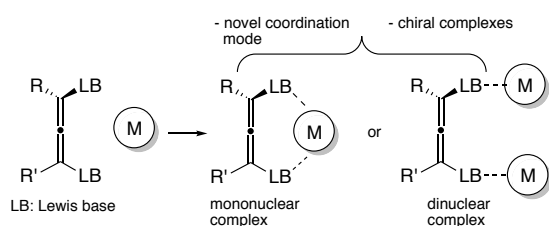
*Avis favorable*

**D<sup>r</sup> Cyril OLLIVIER**  
Directeur de l'École Doctorale  
de Chimie Moléculaire

**Subject description:**

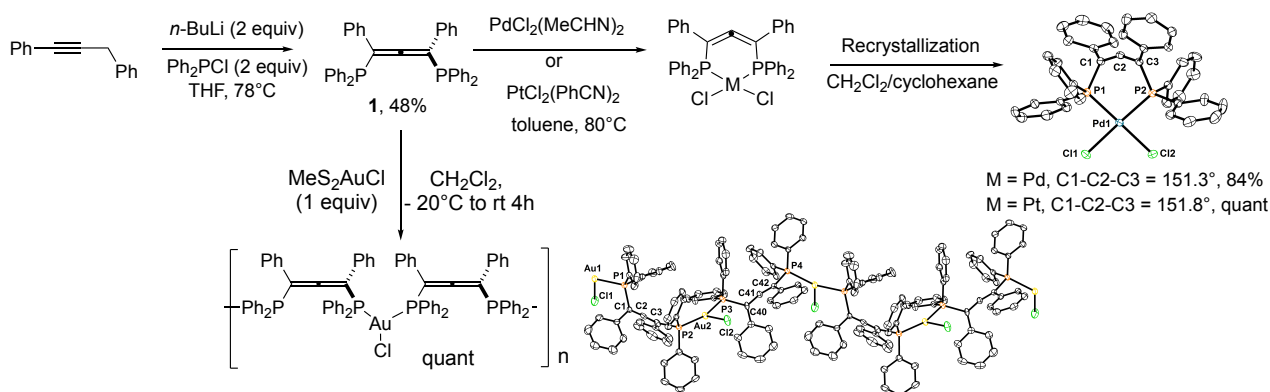
**1. SCIENTIFIC AND TECHNOLOGICAL OBJECTIVES**

Coordination chemistry has been at the center of chemists' preoccupations since the pioneering works of venerable scientists such as Christian Wilhem Blomstrand, Sophus Mads Jorgensen and Alfred Werner in the 19<sup>th</sup> century. This fundamental and intense domain of investigation has continuously irrigated several fields of applications such as catalysis, material sciences, supramolecular and medicinal chemistry.<sup>[1]</sup> Based on the interaction between a ligand and a metal center, the combinations of both components appear unlimited and the number of existing coordination adducts is still limited, leaving a vast unexplored chemical space. Nevertheless, a rationale design is desirable to guarantee the preparation of objects with optimized properties. This approach generally requires to start from elementary building blocks (ligand or metal) with specific attributes. Thus, thanks to its unique stereoelectronic features, allene scaffolds bearing Lewis base moieties and possibly conveying some chiral information sites appeared to us as a valuable targets (Scheme 1).<sup>[2]</sup> One can imagine dual modes of coordination featuring mononuclear or dinuclear complexes. Moreover, there has been a very limited number of allene-derive ligands involved in metallic coordination complexes. Krause reported the formation of silver and copper complexes from allene-containing bipyridine ligands, but no catalytic activity was reported.<sup>[3]</sup> Chiral diphosphine oxide allenes were first used as organocatalysts by Ready who described the highly enantioselective formation of epichlorhydrines from *meso*-epoxides with SiCl<sub>4</sub>.<sup>[4]</sup> Later, the same group devised chiral allene-containing bisphosphines, that when coordinated to Rh(I), were able to promote the asymmetric addition of arylboronic acids to  $\alpha$ -keto esters with high enantioselectivity.<sup>[5]</sup>



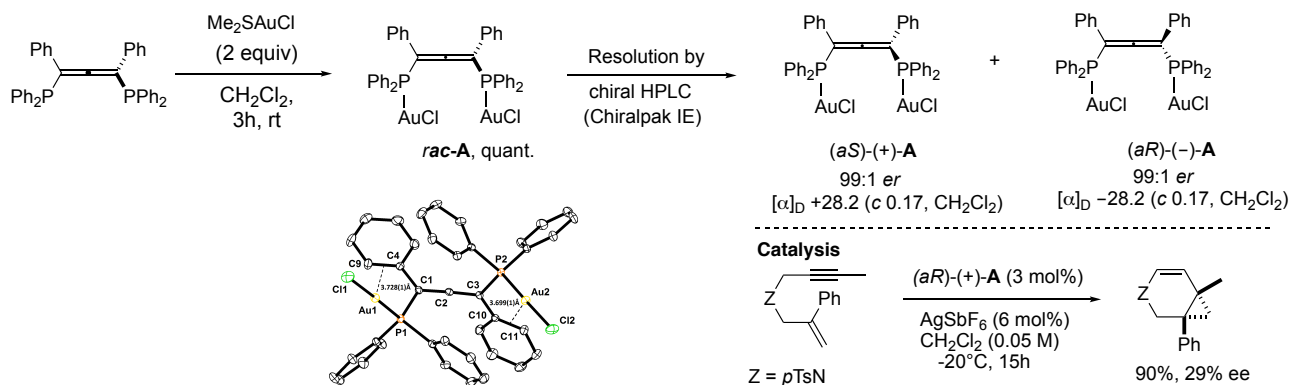
**Scheme 1.** New coordination complexes based on allene ligands

In line with this strategy, our attention was drawn to bis-phosphine 1,3-bis(diphenylphosphino)-1,3-diphenylallene **1** featuring direct attachment of the phosphorus moieties on the allene backbone, which has been so far very rarely encountered.<sup>[6]</sup> The Schmidbaur group previously described the synthesis of **1**.<sup>[7]</sup> Following their procedure, we obtained **1** in a consistent yield of 48 %. We synthesized from **1** Pd(II), Pt(II) and Au(I) complexes. The Pd(II) and Pt(II) complexes show a highly bent allene (Scheme 2).<sup>[8]</sup>



**Scheme 2.** Coordination complexes obtained from allene **1**

With one equivalent of Au(I), a coordination polymer is obtained but with two equivalents of Au(I), a dinuclear Au(I) complex is obtained. The latter could be resolved in the two corresponding enantiomers and preliminary results in asymmetric catalysis were provided (Scheme 3).



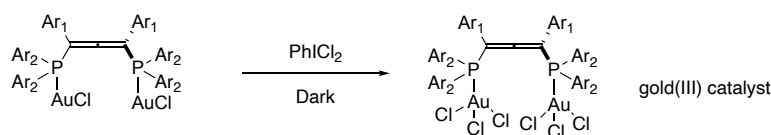
**Scheme 3.** Applications in catalysis of the dinuclear gold catalyst **A**

## 2. RESEARCH DESIGN AND METHODS

This project aims at examining new coordination complexes from **1** and also exploiting the full potential of the complex **A** (*rac*- or enantiopure) for other applications.

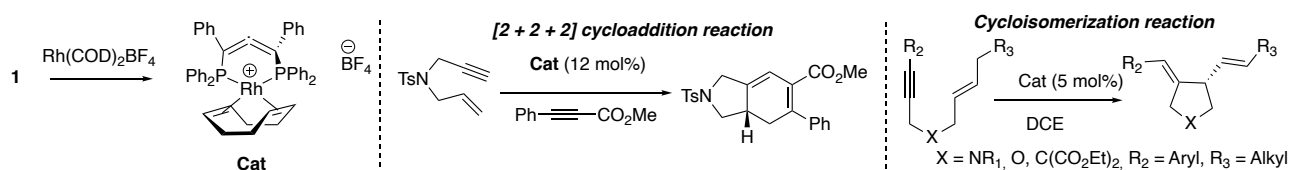
### **Task 1: Synthesis and characterization of new derivatives of complex A and applications of the new complexes in asymmetric catalysis**

We will embark into the preparation of new bis-phosphine allene ligands bearing aryl groups  $Ar_1$  and  $Ar_2$  with different substitution patterns. The synthesis of the Au dinuclear complexes analogue to **A** should be easy and we wish to characterize them to assess the influence of the aryl groups  $Ar_1$  and  $Ar_2$  with different substitution patterns on the structures of the complexes. The synthesis of Au(III) complexes will be considered, indeed few chiral Au(III) are known, especially with bis-phosphine ligands. Moreover, for the moment, chiral Au(III) complexes involved in asymmetric catalysis are even scarcer (Scheme 4).<sup>[9]</sup>



**Scheme 4.** Design of new di-gold(I) complexes analogue to **A**. Synthesis of chiral gold(III) complexes

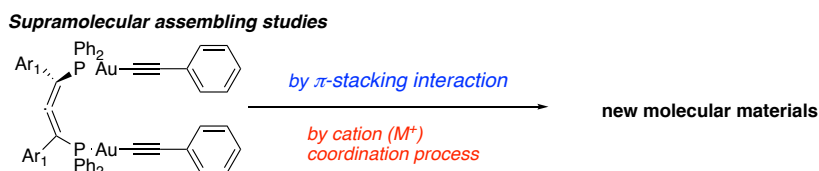
We also want to study the ability of these new bis-phosphine allene to coordinate other transition metals. This, new rhodium complexes are very attractive in order to study the reactivity of the new chiral complexes in enantioselective [2+2+2]<sup>[10]</sup> and cycloisomerization reactions (Scheme 5).<sup>[11]</sup>



**Scheme 5.** An example of a new rhodium(I) complex. Catalytic studies

## Task 2: Applications of the new complexes in materials

We also plan to substitute the chloride atom on the gold(I) with alkyne, alkene, arene moieties and study the properties of these new complexes. Coordination chemistry with other metals of these organometallic platforms will be examined. Notably, we will consider the synthesis of supramolecular assembly by  $\pi$ -stacking interactions or based on cation coordination processes (Scheme 6).



**Scheme 6.** Supramolecular assembling studies

One of the goals will be to study the luminescence properties of the alkynyl gold derivatives. Notably, we wish to examine the influence of the Au(I)...Au(I) interactions on the potential emissive properties.

## 3. CONCLUDING REMARKS

All these approaches are of fundamental importance but can also generate rapidly very practical solutions. The proposed work will also rely on combined DFT calculations and dedicated spectroscopic methods (NMR, EPR, electrochemistry and also luminescence) as well as mass spectrometry from established collaborations that are present mainly in our institute and which have already proven their efficiency. For the PhD candidate, it will be as well a very educating experience. We have moved four years ago into brand new laboratories with all facilities. This should also ensure a smooth development of the project. Teamwork is also an important marker of this doctoral project. Finally, the PhD student will be exposed to a very international environment.

## 4. References and notes

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