LABORATOIRE HETEROCHIMIE FONDAMENTALE ET APPLIQUEE
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TEAM: Bifunctional Ligands and Biodegradable Polymers (LBPB)
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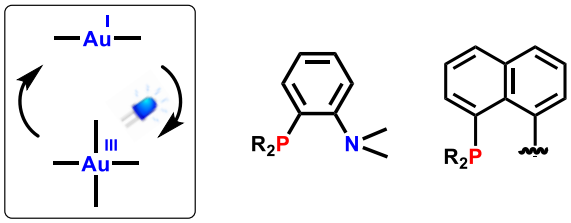
Shining Light on Au(III) Complexes

Keywords: gold complexes, light, coupling reactions, catalysis

Context: The organometallic chemistry of gold has progressed spectacularly over the past 10 years, opening entirely new perspectives in homogeneous gold catalysis such as Au(I)/Au(III) 2-electron (photo)redox cycles.[1] Notably, careful ligand design turned to emulate unprecedented reactivity at gold such as oxidative addition (OA), migratory insertion…[2] In particular, our group has demonstrated that the hemilabile P^N ligand MeDalphos is most efficient to cycle between the Au(I) and Au(III) redox states,[3] and that P,C-cyclometalated Au(III) complexes are robust and very active catalysts for the hydroarylation of alkynes.[4]



Objectives: Given the spectacular progress achieved recently in photocatalysis, we are very interested in combining light activation and gold chemistry. In particular, generating Au(III) complexes in excited states is very attractive to promote synthetically useful but very challenging transformations such as C(sp^3)–C(sp^3) and C–F reductive elimination. We have discovered during preliminary studies that such key coupling reactions might indeed be achieved upon irradiation of well-defined Au(III) complexes by visible light. It is the point of this Master project to start to address the questions opened by these exciting results and to explore thereby new facets in Au(III) chemistry. What about the excited states of Au(III) complexes? How to access them? What about their fate with respect to both ionic and radical paths? What are the controlling factors and how to take advantage of these photo-induced processes in catalysis?

Research plan: Taking advantage of our experience in ligand design and Au(I)/Au(III) chemistry, well-defined photoactive Au(III) complexes will be prepared. Their photophysical properties and reactivity (under both thermal and photochemical conditions) will be explored in detail. The work will combine synthesis, characterization and reactivity studies. Special attention will be given to the electronic structure of the prepared complexes, in their ground and excited states, by experimental and computational means. Reactivity studies will be carried out, towards challenging reductive elimination in particular. Catalytic applications will be investigated, with major interest for fluorination (C–F coupling) reactions.

This project will give the master student the opportunity to work under inert atmosphere, to use a number of advanced analytical methods (multi-nuclear NMR, X-ray diffraction, UV-vis absorption/emission, electrochemistry…) and to discover the interplay between calculations and experiments (thanks to our collaboration with expert theoreticians). The candidate should be very enthusiastic and enjoy working closely with a team.

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Selected relevant references (with hyperlinks)

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