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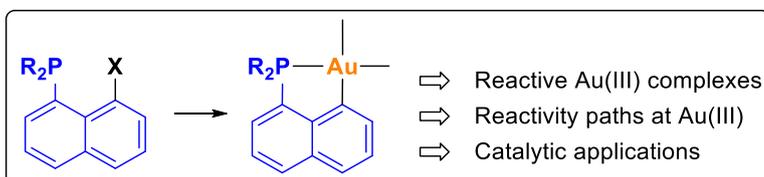


FONDATION
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(P,C)-Cyclometallated Au(III) Complexes

The research in our group is focused on the development and understanding of new classes of main-group compounds (P, B...) and transition metal complexes (Au, Pd...), as well as their application in small molecule activation and catalysis. In one of our research lines, we take advantage of ligand design to stabilize highly reactive gold complexes (carbenes...) to emulate unprecedented reactivity at gold (such as oxidative addition...) and to develop new gold-catalyzed transformations. This post-doctoral project aims at exploring and advancing these three facets of gold chemistry on (P,C)-cyclometallated Au(III) complexes.



1. New reactive (P,C)-cyclometallated Au(III) complexes

We have shown that P-chelation assisted oxidative addition provides efficient access to (P,C)-cyclometallated Au(III) complexes from *peri*-halogenated naphthyl phosphines (*J. Am. Chem. Soc.* **2014**, *136*, 1778). This rigid backbone imparts high stability while maintaining two reactive sites at gold. It was leveraged to prepare and fully characterize unusual Au(III) species, in particular C–H agostic, π -arene and π -allyl complexes (*Angew. Chem. Int. Ed.* **2016**, *55*, 3414; *Chem. Sci.* **2017**, *8*, 4539; *Angew. Chem. Int. Ed.* **2020**, *59*, 1511). This is the first aim of the project to generalize this approach, varying the structure of the cyclometallated ligand and targeting new reactive Au(III) complexes.

2. New reactivity paths at Au(III)

The (P,C)-cyclometallated Au(III) complexes have also proved highly reactive, and elementary transformations unprecedented for gold such as migratory insertion of alkenes and β -H elimination were substantiated (*Angew. Chem. Int. Ed.* **2015**, *54*, 1266; *J. Am. Chem. Soc.* **2016**, *138*, 11920). With the new cyclometallated Au(III) complexes in hands, thorough reactivity studies will be carried out to identify systems and conditions in which Au(III) engages in new reaction paths. Particular interest will be devoted to σ -metathesis and metal-ligand cooperativity as this may offer new possibilities for activation of strong bonds and inert molecules at gold.

3. Catalytic applications of Au(III) complexes

The third objective is to take advantage of the new reactive Au(III) complexes and reactivity paths at Au(III) in catalysis. Here, Au(III) catalysis will be first targeted, as it is still underdeveloped (For application of (P,C)-cyclometallated Au(III) complexes in the hydroarylation of alkynes, see: *Angew. Chem. Int. Ed.* **2018**, *57*, 11732). Dual approaches combining Au(III) complexes and other activation modes (metal-ligand cooperativity, photo and/or redox catalysis) will also be investigated.

Keywords: gold, ligand design and coordination, structure & reactivity, catalysis, mechanistic studies

Sous la co-tutelle de

