Gold Catalysis Under Ligand Control

The research in our group is focused on the development and understanding of new classes of main-group compounds and transition metal complexes, as well as their application in small molecule activation and catalysis. Our work intimately mix experimental and theoretical investigations. Particular attention is dedicated to structure-reactivity relationships, mechanistic understanding and rational design.

In one of our research lines, we take advantage of ligand design to emulate unprecedented reactivity at gold (such as oxidative addition, migratory insertion, β-H elimination…) and to stabilize highly reactive gold complexes (C–H agostic, π-arene, carbonyl, carbene…). (Angew. Chem. Int. Ed. 2015, 54, 15022 & Act. Chim. 2018, 432, 63). The two following projects are representative of current research in the group:

1. **Au(I)/Au(III) catalyzed cross-coupling**

   We have discovered that chelating (P,P) and hemilabile (P,N) ligands promote the oxidative addition of Ar–X compounds to gold, a transformation considered so far inaccessible for this transition metal. This reactivity opens a new facet in gold catalysis, enabling to achieve Au(I)/Au(III) catalytic cycles without the need for strong external oxidant. Following our preliminary results on the direct arylation of electron-rich arenes and heteroarenes with Ar–I and Ar–Br derivatives, we aim at (i) extending the variety of catalytic transformations to C–N coupling (arylation of amines, amides…) and (ii) extrapolating the approach to the activation of allyl–X substrates and to catalytic allylation reactions. (J. Am. Chem. Soc. 2014, 136, 14654 & Nature Commun. 2017, 8, 565)

2. **Au(III) catalyzed hydroarylation**

   Here, we seek to take advantage of (P,C) cyclometallated gold(III) complexes which are readily accessible by phosphine-assisted oxidative addition to gold. Our first results suggest that these are very efficient catalysts for the hydroarylation reaction, which consists formally in the addition of a C–H bond of electron-rich arenes to alkynes. This is a very important but challenging transformation. The (P,C) chelate enables to generate a highly electron-deficient and reactive Au(III) center. It offers a unique balance between stability and reactivity. We now aim to exploit the structural diversity of the (P,C) complexes and to extend the catalytic scope to heteroarenes and alkenes. (J. Am. Chem. Soc. 2014, 136, 1778 & Angew. Chem. Int. Ed. 2018, 57, 11732)

Keywords: gold, ligands, oxidative addition, catalysis, reactivity, mechanistic studies, DFT calculations

Licence and Master students willing to join our group for an internship and to participate to one of this research project are encouraged to contact us. For more information on our research activities, see http://lhfa.cnrs.fr/index.php/thematiques-lpbp