Gold chemistry under ligand control. Computational chemistry and experiments : an ideal partnership to explore new reactivities and bonding situation.

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Long considered as a noble element, too inert and therefore useless in catalysis, the status of gold changed in the 1990s when interesting reactivities were discovered and applied in several reactions of industrial importance. During the past two decades, this homogeneous gold catalysis has grown spectacularly[1] and broadly applied. Besides the unique ability of gold complexes to activate $\pi_{C=C}$ bonds of unsaturated substrates towards nucleophilic addition, entirely new perspectives have been opened recently in gold Au(I)/Au(III) (photo)redox catalysis and careful ligand design played a crucial role to emulate unprecedented reactivity at gold.

In close collaboration with the team of D. Bourissou, we explore in depth the reactivity of new gold(I) and gold(III) complexes involving P-based chelate, hemilabile or ambiphilic ligands by combining experimental and computational studies. Thanks to rationale ligand design, pivotal transformations in many processes were made possible, intra or intermolecular oxidative addition of C-X bonds, challenging Csp^3-Csp^3 reductive elimination...[2] Recently, ligand-enabled oxidative fluorination of Au(I) with (P,N) ligand has also been investigated and light-induced Ar-F coupling at Au(III).[2]

These ligands opened up novel reactivities and new possibilities for catalysis. Recent and representative examples[3] are : i) the oxy-arylation of alkenes *via* Au(I)/Au(III) catalysis using (P,N) ligand; ii) the authentification of π-allyl Au(III)-complexes and the study of their reactivity toward β-diketo enolates. Special interest has also been devoted to the in-depth description of unusual bonding situation such as Au(I) carbene complexes and Au(III) π-allyl complexes.[4] In this oral presentation, the fruitful interplay between computational chemistry and experiments will be illustrated, with a focus on the contribution of DFT and computational tools for chemical bonding and reactivity studies.

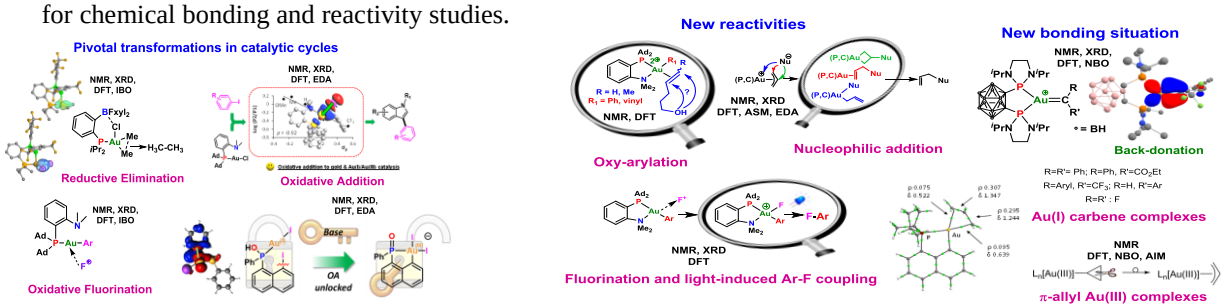

Figure 1. New reactivities and bonding situation at gold

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