



HAL
open science

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

Karinne Miqueu, D. Bourissou

► **To cite this version:**

Karinne Miqueu, D. Bourissou. Gold chemistry under ligand control. Computational chemistry and experiments: an ideal partnership to explore new reactivities and bonding situation. Les XVIIIèmes rencontres ThéMoSiA-RCTF, Université de Rouen; INSA Rouen, Jun 2024, Rouen, France. hal-04793224

HAL Id: hal-04793224

<https://univ-pau.hal.science/hal-04793224v1>

Submitted on 20 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Gold chemistry under ligand control.

Computational chemistry and experiments : an ideal partnership to explore new reactivities and bonding situation.

MIQUEU Karinne,^A BOURISSOU Didier^B

A) CNRS/Univ. Pau et des Pays de l'Adour, IPREM UMR 5254, 64053 Pau Cedex 09, France.

B) CNRS/Univ. Paul-Sabatier, LHFA UMR 5069, 31062 Toulouse, France.

karinne.miqueu@univ-pau.fr

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 spectacularly¹ 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 examples³ are : i) the oxy-arylation of alkenes *via* Au(I)/Au(III) catalysis using (P,N) ligand; ii) the authentication 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.

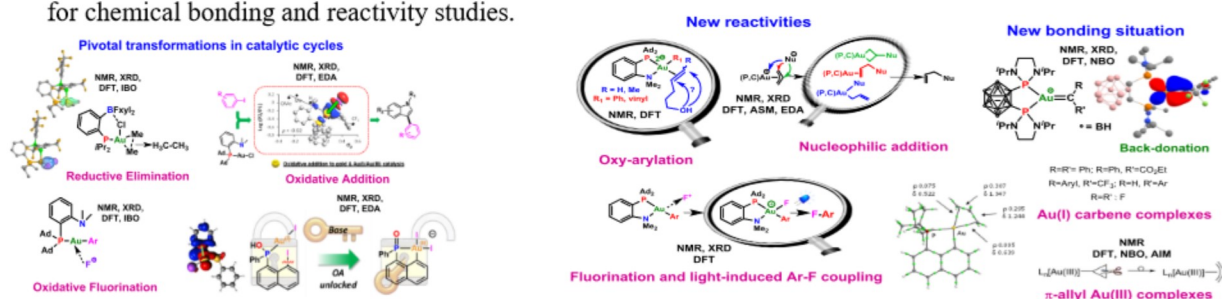


Figure 1. New reactivities and bonding situation at gold

¹ F. D. Toste and V. Michelet in *Gold Catalysis: An Homogeneous Approach*, Imperial College Press (2014).

² a) A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune and D. Bourissou, *Nature Com* 8. (2017) 565. b) J. Rodriguez, A. Zeineddine, E. D. Sosa Carrizo, K. Miqueu, N. Saffon Merceron, A. Amgoune and D. Bourissou, *Chem. Sciences* 10 (2019) 7183-7192. c) E. Marelli, J. Monot, B. Martin-Vaca, S. Ladeira-Mallet, Y. Garcia-Navarro, K. Miqueu and D. Bourissou, *Chem. Eur. J.* (2023) e202301091. d) C. A. Theulier, Y. Garcia-Rodeja, K. Miqueu, G. Bouhadir and D. Bourissou, *JACS* 145 (2023) 10800-10808. d) D. Vesseur, S. Liu, S. Mallet-Ladeira, K. Miqueu and D. Bourissou, *JACS* (2024) just accepted, doi.org/10.1021/jacs.4c00913.

³ a) M. Rigoulet, K. Miqueu and D. Bourissou, *Chem. A Eur. J.* (2022) e202202110. b) J. Rodriguez, M. S. Martinsen Holmsen, Y. Garcia-Rodeja, E. D. Sosa-Carrizo, P. Lavedan, S. Mallet-Ladeira, K. Miqueu and D. Bourissou, *JACS* 143 (2021) 11568-11581. c) M. S. Martinsen Holmsen, D. Vesseur, Y. Garcia-Rodeja, K. Miqueu and D. Bourissou, *Ang. Chem. Int. Ed. Engl.* 62 (2023) e202305280.

⁴ a) M. Joost, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune and D. Bourissou, *Ang. Chem. Int. Ed. Engl.* 53 (2014) 14512-14516. b) M. Rigoulet, D. Vesseur, K. Miqueu and D. Bourissou, *Angew. Chem. Int. Ed. Engl.* 61 (2022), e20220478. c) J. Rodriguez, G. Szalóki, E. D. Sosa Carrizo, N. Saffon-Merceron, K. Miqueu and D. Bourissou, *Ang. Chem. Int. Ed. Engl.* 59 (2020) 1511-1515.

Keywords: Gold Catalysis - DFT calculations - Mechanisms - Electronic properties - Bonding situation