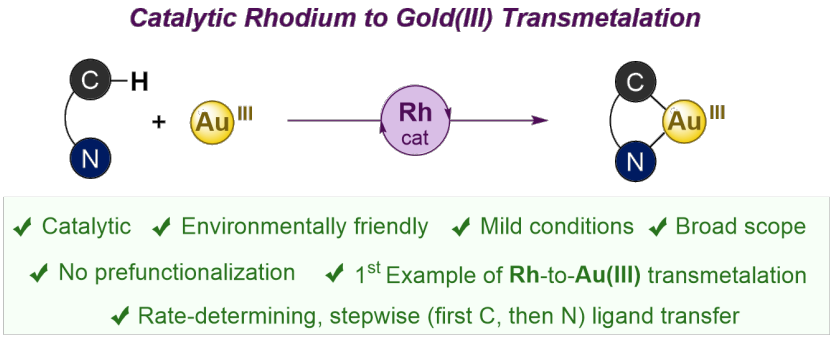
Unlocking Cyclometalation: Catalytic Transmetalation Towards Cyclometalated Gold(III) Complexes

J. Martín[1], E. Gómez-Bengoa[2], C. Nevado[1]*

[1]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, Zurich, CH 8057, Switzerland, [2]Department of Organic Chemistry I, University of the Basque Country UPV/EHU, Manuel Lardizabal 3, San Sebastián, Spain

Gold(III) complexes have a significant impact on several fields, including materials science, biomedical research, and catalysis.[1] Despite the strongly oxidizing nature of this metal, bidentate or tridentate ligands can stabilize gold(III) complexes against reduction, making them more durable and robust for translational applications. In this context, cyclometalated gold(III) species containing bidentate (C^N) ligands play a prominent role as tunable photochemical dopants in OLEDs and as antitumoral agents.[2] Unfortunately, only a few strategies tackling their synthesis are available to date. They rely on organomercury reagents, silver salts, or harsh conditions thus severely limiting the functional group compatibility, synthetic efficiency, and applicability of these systems in the abovementioned areas.

To overcome this challenge, we have successfully developed a catalytic, environmentally friendly and redox-neutral approach to synthesize a broad array of cyclometalated (C^N)gold(III) complexes. Our methodology relies on the catalytic Csp^2-H bond activation of 2-aryl-pyridine ligands using a commercially available and stable rhodium complex, followed by an unprecedented Rh-to-Au(III) transmetalation step. Detailed mechanistic investigations using kinetic measurements, control experiments, and DFT calculations revealed a rate-determining stepwise (C-then-N) transmetalation process underlying these transformations.[3]



[1] Luca Rocchigiani, Manfred Bochmann, *Chemical Reviews,* **2021**, 121, 8364-8451.

[2] Roopender Kumar, Cristina Nevado, *Angewandte Chemie International Edition,* **2017**, 56, 1994-2015.

[3] Jaime Martín, Enrique Gómez-Bengoa, Alexandre Genoux, Cristina Nevado, *Angewandte Chemie International Edition,* **2022**, 61, e202116755.