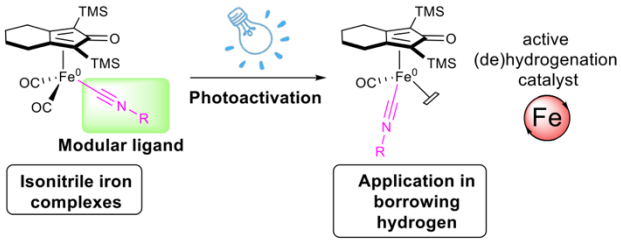
NOVEL IRON-BASED CATALYSTS FOR PHOTOINDUCED REVERSIBLE HYDROGEN TRANSFER REACTIONS

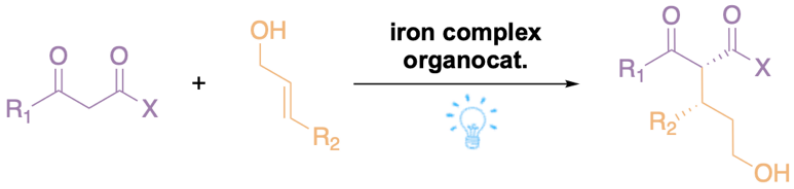
Gaëtan Quintil,[a,b] Léa Diebold,[b] Adrien Quintard[a]*, Amélie Kochem[b]*

[a] Univ. Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France.
[b] Université Grenoble Alpes, CNRS, CEA, LCBM (UMR 5249), 38000 Grenoble, France.
Gaetan.Quintil@univ-grenoble-alpes.fr

The quest for sustainable and cost-efficient synthetic processes has led to the development of iron cyclopentadienone catalysts, replacing costly noble metal complexes notably for hydrogen transfer reactions. These catalysts, featuring cooperativity between iron and the cyclopentadienone ligand, provided unique reactivities, particularly in borrowing hydrogen reactions.[1],[2] Modification of these catalysts has mainly focused on changing the cyclopentadienone core, but little has been done with the iron tricarbonyl structure. In order to potentially enhance the activity of these complexes and obtain different reactivities, the CO ligands were replaced by different isonitrile ligands, creating a library of modular complexes.[3]



These catalysts demonstrated notable activity, surpassing classical catalysts, in a photoinduced multicatalytic borrowing hydrogen process. This enabled easy enantioselective functionalization of allylic alcohols under mild conditions.



To gain a comprehensive understanding of these complexes' reactivity and establish a structure-activity relationship, their behavior was carefully investigated by spectroscopy and computational chemistry. This approach offers profound insights into the catalyst's activity origin and properties.

References:

[1] Quintard, A.; Constantieux, T.; Rodriguez, J. An Iron/Amine-Catalyzed Cascade Process for the Enantioselective Functionalization of Allylic Alcohols. *Angew. Chem. Int. Ed.* **2013**, *52*, 12883–12887.

[2] Quintard, A.; Rodriguez, J. Iron Cyclopentadienone Complexes: Discovery, Properties, and Catalytic Reactivity. *Angew. Chem. Int. Ed.* **2014**, *53*, 4044–4055.

[3] Quintil, G.; Diebold, L.; Fadel, G.; Pécaut, J.; Philouze, C.; Clémancey, M.; Blondin, G.; Bjornsson, R.; Quintard, A.; Kochem, A. CO to Isonitrile Substitution in Iron Cyclopentadienone Complexes: A Class of Active Iron Catalysts for Borrowing Hydrogen Strategies. *ACS Catal.* **2024**, *14*, 7795–7805.