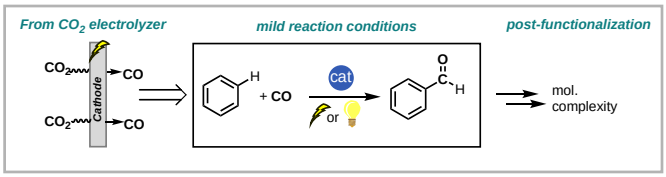
Dr. Julien Bonin, Dr. Niklas von Wolff
Laboratoire d'Électrochimie Moléculaire (LEM, UMR 7591)
Université de Paris
75013 Paris
France
Email : julien.bonin@u-paris.fr or niklas.von-wolff@u-paris.fr
@n_vonwolff or @GroupReacte

Towards Efficient Catalytic Photo- and Electro-chemical Benzene Carbonylation

The chemical industry is responsible for around 25% of global industrial energy consumptions. For a circular and sustainable economy of the future, the development of new energy and resource efficient chemical transformations is thus crucial. With the recent development of performing electrolyzes,[1,2] CO_2 could become a valuable and renewable C1-synthon for the generation of bulk and value-added chemicals in the near future. While a plethora of carbonylation reactions are available today, some particularly challenging examples offer opportunities for the design of new energy and atom efficient reaction pathways for the creation of new C–C bonds ultimately derived from CO_2. The UV-photo-carbonylation of benzene represents a highly interesting and challenging example for the generation of molecular complexity from unactivated and unfunctionalized starting material.[3]



Today's bottle-necks of this reaction are the high energy irradiation needed (UVC), the use of catalysts based on scarce transition metals (mainly Rh), as well as low turnover numbers. Using a combination of spectro-/electrochemical techniques (CV, Laser spectroscopy, spectro-electrochemistry), it will be probed how existing metal-ligand cooperative (MLC) complexes can facilitate this challenging reaction. DFT will assist these mechanistic studies. New cobalt based MLC complexes will be synthesized and their possibility to undergo electrochemical activation will be analyzed.[4,5] Furthermore, the combination of photo and electrochemical activation in custom-made flow reactors will be used to push the boundaries of this reaction.[6]

The PhD project thus offers an excellent opportunity to learn key aspects of modern molecular catalysis, ranging from electrochemistry, photochemistry to organometallic synthesis and DFT calculation. In particular the program also includes a roughly 6 months stay at the Weizmann Institute of Science in the group of Prof. David Milstein, a globally recognized leader in the domain of green organometallic catalysis.

Literature:

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