

MECHANISTIC STUDY OF COPPER-CATALYZED REVERSIBLE DECARBOXYLATION PROCESS

TITRE (Arial, 14 pts, gras; 2 lignes maximum; interligne simple)

K. Phung,^a J.-C. Berthet,^a et T. Cantat,^a

^a LCMCE, IRAMIS, NIMBE, CEA, CNRS, Université Paris-Saclay, 91191 Gif-sur-Yvette, France
kieu.phung@cea.fr, <https://iramis.cea.fr/Pisp/thibault.cantat/>

Keywords : Coordination chemistry; Copper complexes; Decarboxylation/carboxylation catalysis.

Copper-catalyzed decarboxylation process of aromatic carboxylic acids has been intensively studied thanks to its efficiency in the formation of C-C or C-heteroatom bonds.¹ However, limited substrate scopes and forcing reaction conditions remains as drawbacks.^{2,3} Therefore, a mechanistic understanding of these processes is of interest to facilitate these complex systems.

One proposition to exploit these systems is to track the process by dynamic isotope exchange. This reversible decarboxylation reaction has been successfully proved, in which ¹⁴CO₂ (or ¹³CO₂) was transferred to a series of aryl carboxylic salts using copper as catalyst.⁴

To carried on from this work, and because nitrogen ligand are helpful for this transformation, the aim is to isolate potential copper(I) intermediates with the choice of phenanthroline (phen) as ligand. Once different copper(I) species are isolated and characterized, the goal is to investigate their reactivity toward decarboxylation/carboxylation processes via multiple analysis methods, for instance, NMR spectroscopy, cyclic voltammetry and DFT calculation.

In order to enhance copper(I) aryl complexes stability and to avoid common redistribution of the ligand,^{5,6} we focus on the bulky 2,9-ditertbutyl-1,10-phenanthroline ligand (dtbp),⁷ which was applied for the synthesis of aryl carboxylated and aryl copper(I) complexes.

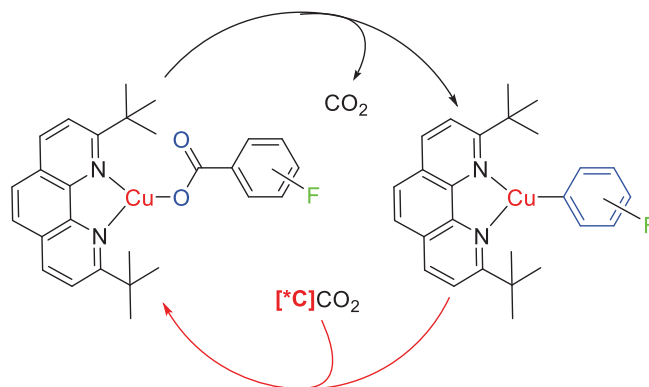


Fig. 1 Copper-catalyzed dynamic isotope exchange of CO₂

1. Goossen, L.J.; Rodriguez, N. *Chem. Soc. Rev.* **2011**, *40*, 5030.
2. Ye, W; Peng, H; Min, Z; Weiping, S. *Chem. Rev.* **2017**, *117*, 8864.
3. Goossen, J.L; Rodriguez, N; Goossen, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 3100.
4. Cantat, T; Audisio, D. *JACS.* **2019**, *141*, 780.
5. Do, H.Q; Khan, R.M.K; Daugulis, O. *JACS.* **2008**, *130*, 15185.
6. Baur, A; Bustin, K.A; Aguilera, E; Petersen, J.L; Hoover, J.M. *Org. Chem. Front.* **2017**, *4*, 519.
7. Pallenberg, A.J; Koenig, K.S; Barnhart, D.M. *Inorg. Chem.* **1995**, *34*, 2833.