D202-3pm-08

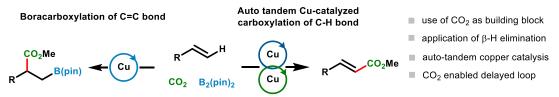
Auto-tandem copper-catalysed carboxylation of undirected alkenyl C–H bonds with CO₂

(¹Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science, ²Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research)

 \bigcirc Harekrishna Sahoo,¹ Liang Zhang,^{1,2} and Zhaomin Hou^{1,2}

Keywords: Auto-tandem catalysis, β -hydride elimination, CO₂ delay loop, Copper, Carboxylation

Development of new catalytic reactions enabling control of the selectivities of chemical processes for the divergent synthesis of value-added compounds lies at the heart of modern organometallic chemistry and catalysis. β -Hydride elimination is one of the most fundamental reactions in organometallic chemistry. However, the incorporation of a β -hydride elimination process into productive *auto-tandem catalysis* is highly challenging because of the instability of the in-situ generated metal hydride species, which often results in catalyst deactivation. The development of a straightforward approach to overcome this problem is of utmost importance because it will greatly extend the potential of β -hydride elimination in organometallic catalysis and synthetic applications. Carbon dioxide (CO_2) is an attractive one-carbon (C1) building block for the assembly of important chemicals because it is abundant, readily available, cheap, and renewable. Our group has been working on CO₂ fixation with a wide range of organic substrates using copper catalysts.¹ In this presentation, we would like to present an auto-tandem copper-catalyzed carboxylation of undirected alkenyl C-H bonds with CO₂. This unprecedented transformation has been achieved through the β -hydride elimination of an alkyl copper species to give a copper hydride, which then undergoes a delayed loop with insertion of CO₂ to form an active catalyst to promote two mechanistically distinct catalytic cycles. On the other hand, by suppressing the β -hydride elimination process, the boracarboxylation of the alkene C=C unit has been exclusively achieved.



a) Zhang, L.; Hou, Z. Chem. Sci. 2013, 4, 3395. b) Li, Z.; Zhang, L. Nishiura, M.; Luo, G.; Luo,
Y.; Hou, Z. J. Am. Chem. Soc. 2020, 142, 1966. c) Carry, B.; Zhang, L.; Nishiura, M.; Hou, Z. Angew.
Chem. Int. Ed. 2016, 55, 6257. d) Zhang, L.; Cheng, J.; Carry, B.; Hou, Z. J. Am. Chem. Soc. 2012, 134, 14314. e) Ohishi, T.; Zhang, L.; Nishiura, M.; Hou, Z. Angew. Chem. Int. Ed. 2011, 50, 8114. f)
Zhang, L.; Cheng, J.; Ohishi, T.; Hou, Z. Angew. Chem. Int. Ed. 2010, 49, 8670. g) Ohishi, T.;
Nishiura, M.; Hou, Z. Angew. Chem. Int. Ed. 2008, 47, 5792.