

Perez-Temprano Group



Group Leader: Mónica H. Pérez Temprano

Administrative support: María José Gutiérrez

Postdoctoral researchers: Sara Martínez / Juan M. Sarria / Daniel Gallego (until Jan.)

PhD students: Jesús San José/ Angel Luis Mudarra

Master students: Alèria Garcia (until Aug.) / Raül Lleberia (until Oct.)

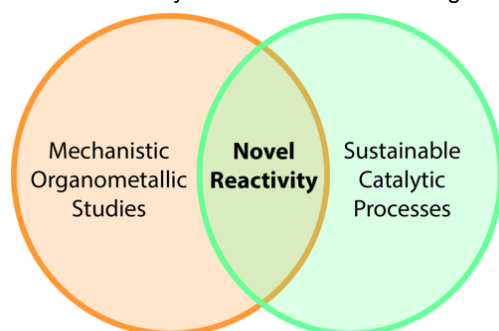
Summer Fellow: Raül Lleberia

Visiting students: Raül Lleberia (Feb.- June)

Abstract

The Pérez-Temprano group is focused on understanding organometallic processes relevant to catalytic transformations. Our goal is

not only to provide critical mechanistic information on well-known reactivity, but also to discover, design and develop novel transition metal-catalyzed reactions.



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Over the past decades, mechanistic investigations have been often envisioned as a posteriori tool focused on understanding successful transformations. However, our group understands fundamental mechanistic knowledge as an extremely powerful resource to overcome limitations and design innovative and more efficient reactivities, especially in emerging fields, such as cobalt catalysis.

In the last 5 years, Cp*Co^{III} catalysts have emerged as a potential alternative to precious metals in directed C–H functionalization reactions. When compared to noble metals, cobalt catalysts offer obvious advantages, including being earth-abundant and cheaper. Despite the significant growth of the field, these cobalt systems are still at their infancy when compared to analogous Rh-based ones, especially due to the limited fundamental organometallic understanding of these systems. The investigation of the underlying reaction mechanisms of Cp*Co^{III}-catalyzed C–H functionalization reactions has been hampered by the difficulty of trapping high reactive transient cobalt intermediates and the proposed reversible nature of the C–H metalation step.

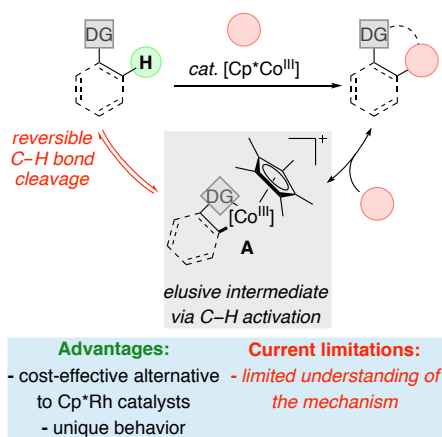


Figure 1. Cp*Co^{III}-catalyzed C–H functionalization reactions

In this regard, our group reported a pioneering mechanistic picture on this type of transformations, in particular on the C–H oxidative alkyne annulation processes. We developed a novel synthetic approach for accessing/trapping a direct analogue one of the most widely invoked intermediates in Cp*Co^{III}-catalyzed C–H functionalization reactions, via a ligand-assisted oxidative addition. We used this cobaltacycle (**1**) in stoichiometric and catalytic experiments with diphenylacetylene as model coupling partner to reveal previously inaccessible mechanistic intricacies of this transformations, including:

(i) the intermediacy and structure of two long-sought cyclometalated Cp*Co^{III}

intermediates, **1** and **2**, in the reaction mechanisms due to the unique ability of acetonitrile to trap otherwise highly reactive cobalt intermediates;

(ii) the first observation and full characterization of a cobalt resting state (**2**) under catalytic conditions;

(iii) strong experimental evidence for previously suggested Co^{III} catalytic cycle.

Moreover, based on these mechanistic features, we were able to optimize significantly the previously reported catalytic conditions, providing the lowest cobalt catalyst loading (1 mol%) reported to date for this type of reactions in a short reaction time of 2 hours.

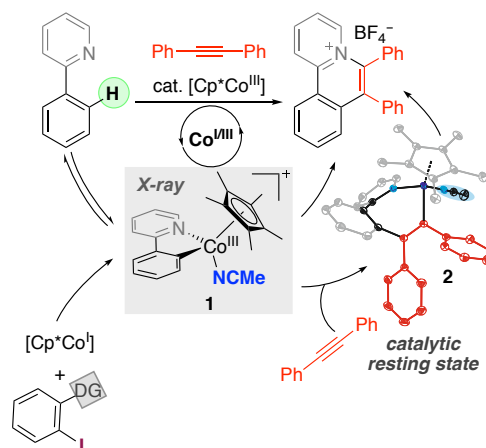


Figure 2. Mechanistic study on Cp*Co-catalyzed C–H oxidative alkyne annulation.

This comprehensive mechanistic study was published as a communication in *Angewandte Chemie International Edition* and selected as Inside Cover (Figure 3).

2017 Annual Scientific Report

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Over the past few years ...

... Cp*Co^{III} complexes have demonstrated their potential to catalyze C–H functionalization. However, these systems remain in their infancy, especially concerning the lack of information on the mechanisms of these processes. In their Communication on page 12137 R. M. H. Pérez-Temprano et al. describe the use of MeCN to capture highly reactive cobalt species and uncover previously inaccessible mechanistic features of Cp*Co^{III}-catalyzed C–H oxidative alkyne annulation.



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Figure 3. Inside Cover in Angewandte Chemie.

Articles

“Capturing elusive cobaltacycle intermediates: a real-time snapshot of the Cp*Co^{III}-catalyzed oxidative alkyne annulation”

Angew. Chem. Int. Ed. (2017), 56, 12137-12141.
 Jesús Sanjosé-Orduna, Daniel Gallego, Alèria Garcia-Roca, Eddy Martin, Jordi Benet-Buchholz, Mónica H. Pérez-Temprano