

Perez-Temprano Research Group

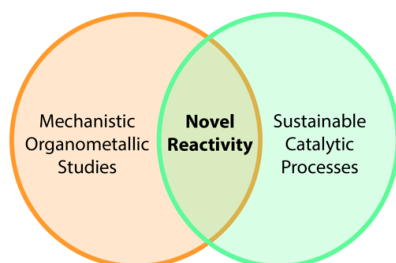


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Postdoctoral researchers: Sara Martínez / Dani Gallego
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Visiting students: Andreu Moral (June-July)
Administrative support: Beatriz Martín

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, develop and understand novel transition metal-catalyzed reactions.



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Our group interests are varied, but they are connected by the common theme of developing more sustainable approaches for the synthesis of organic molecules using fundamental organometallic chemistry. We want to contribute to address some of the major challenges that our world faces, such as global warming or minimizing the impact of chemical synthesis. To develop our research projects, we apply different approaches, ranging from synthetic organic chemistry to mechanistic studies including the preparation of key catalytic intermediates and a full complement of physical organic tools such as kinetic studies

The following projects are currently under development in our research group:

Investigation of Bimetallic Systems to Promote C–C Bond Forming Reactions

Formation of C–C bonds is one of the most remarkable transformations in organic chemistry and it has received special attention since the second half of the 20th century. By the late 1970s, Pd-catalyzed cross-coupling reactions emerged as a powerful tool for the construction of C–C bonds, providing new approaches for the construction of complex organic molecules. Indeed, in 2010, Suzuki and Negishi, along with Richard Heck, received the Nobel Prize in Chemistry for their contribution to enhancing the efficiency of organic synthesis. Although these methodologies supposed a significant breakthrough in organic chemistry, they have some limitations such as the instability of some organometallic nucleophiles, the formation of undesired waste due to the use of stoichiometric amounts of organometallic nucleophiles, or the requirement of pre-functionalized starting materials. Because of that, during the last decade, novel catalytic C–C bond-forming reactions have been explored in an attempt to overcome these limitations. Among them, the development of new methodologies based on the synergistic cooperation between two metal centers has received special attention.

Enzymes involving multiple metal centers represent an exceptional example of how the cooperativity of different metals can perform challenging transformations. However, it was not until the last decade when bimetallic catalysis emerged as an attractive tool for the synthesis of C–C bonds. The mechanism proposed for these bimetallic systems involves two different catalytic cycles (each with one transition-metal (TM) catalyst) connected by a transmetalation step. Despite the inherent utility and benefits exhibited by the reported bimetallic systems, the nature of the cooperation between the transition-metal couples in catalytic systems remains unclear. The group's goal is to investigate the synergy between different bimetallic couples, such as Pd/Ni or Pd/Ag, in relevant organometallic processes to obtain fundamental knowledge of

these systems that enables the rational design of new catalytic transformations.

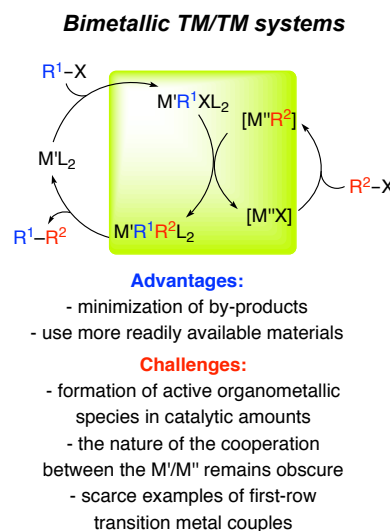
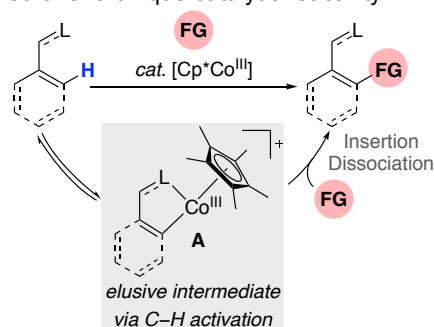


Fig. 1 – Bimetallic systems as an alternative to traditional cross-coupling reactions.

Cobalt catalysis: a cost-effective alternative to noble transition metals

Directed C–H functionalization has become one of the most powerful synthetic tools for the construction of organic scaffolds. For decades, this field has been dominated by the use of noble metals, such Pd or Rh. Earth abundant first-row transition-metal catalysts, in particular Cp*Co^{III} complexes, have recently shown their potential to construct C–C and C–X bonds. They not only represent a low-cost replacement to Cp*Rh^{III} catalysts, but also offer a unique catalytic reactivity.



- Advantages:**
- cost-effective alternative to Cp*Rh catalysts
 - unique behavior
- Current limitations:**
- limited understanding of the mechanism

Despite this significant progress, these Co systems are still at their infancy compared with the analogous rhodium and palladium ones. Ongoing work in our lab concerns understanding the mechanisms of these transformations, investigating the exact nature of the reactive cobalt intermediates and the discovery of new reactivity involving these cobaltacycle intermediates.