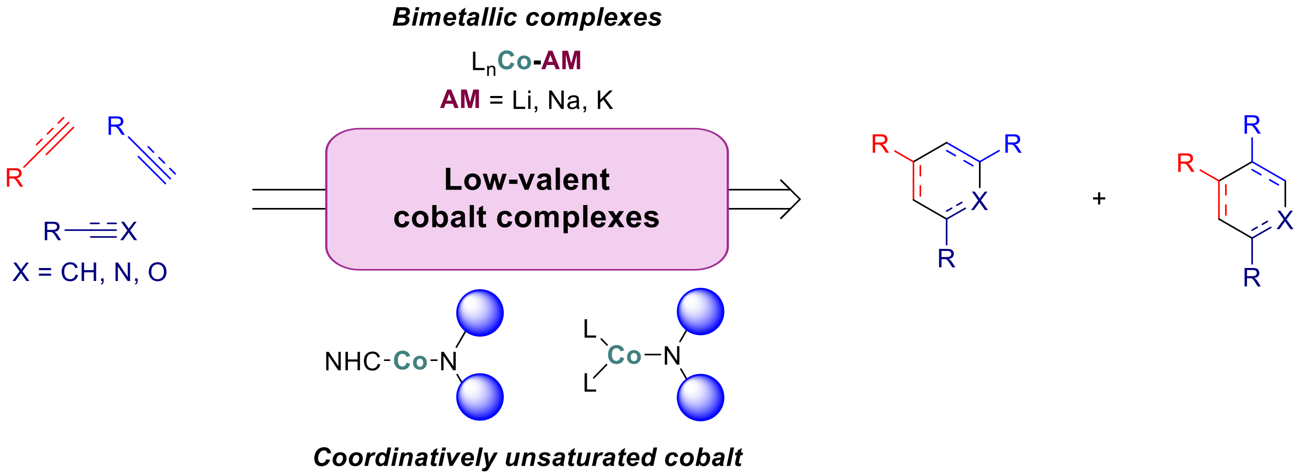
Designing Low-Valent Cobalt Complexes for Catalytic Applications

David Dejoz, Christian Bochet, Andreu Tortajada*

Chemistry Department, University of Fribourg, Chem. du Musée 9, Fribourg, Switzerland
david.dejozdiez@unifr.ch

Carbon-carbon (C–C) and carbon-heteroatom bond formation remains a central transformation in organic synthesis, with broad applications in the production of pharmaceuticals, agrochemicals, and advanced materials.[1] Traditionally, these transformations rely on precious second- and third-row transition metals such as rhodium and ruthenium.[2,3] However, in recent years low-valent first-row transition metals have gained attention as more sustainable and cost-effective alternatives, with cobalt standing out due to its versatility and earth abundance.[4] It has previously demonstrated catalytic activity in cycloaddition reactions, particularly with alkynes and activated olefins to form complex chemical structures.[5] Nevertheless, expanding its reactivity to less activated olefins and other small molecules remains a challenge due to the limited coordination of metal center to these π-motives.

Opening new avenues in cobalt catalysis, this project aims to develop a new class of more electron-rich cobalt complexes capable of promoting these catalytic reactions with non-activated olefins and other small molecules. Our strategy involves modulating the electron density at the cobalt center through two independent approaches: (1) formal reduction of cobalt center to form bimetallic cobalt-alkali metal species to access lower oxidation states, and (2) the introduction of both bulky and strong σ-donor ligands to stabilize coordinatively unsaturated complexes while also enhancing electron density over the metal. These systems are expected to promote olefin activation, improve catalytic efficiency, and broaden the substrate scope of cobalt-mediated C–C and C–X bond-forming reactions, ultimately, providing new tools for sustainable catalysis based on abundant 3d metals.



[1] J. Rayadurgam, S. Sana, M. Sasikumar, Q. Gu, *Org. Chem. Front.*, **2021**, *8*, 384–414.
[2] D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.*, **2010**, *110*, 624–655.
[3] R. S, Doerksen, T. Hodík, G. Hu, N. O. Huynh, W. G. Shuler, M. J. Krische, *Chem. Rev.*, **2021**, *121*, 4045–4083.
[4] C. C. Bories, A. Sodreau, M. Barbazanges, M. Petit, *Organometallics*, **2024**, *43*, 895–923.
[5] H. Rhyoo, B. Y. Lee, H. K. B. Yu, Y. K. Chung, *J. Mol. Catal.*, **1994**, *92*, 41–49.