

CATALYTIC RADICAL-TYPE TRANSFORMATIONS; Catalytic Reactivity of Co^{II} & 'Carbene and Nitrene Radicals'

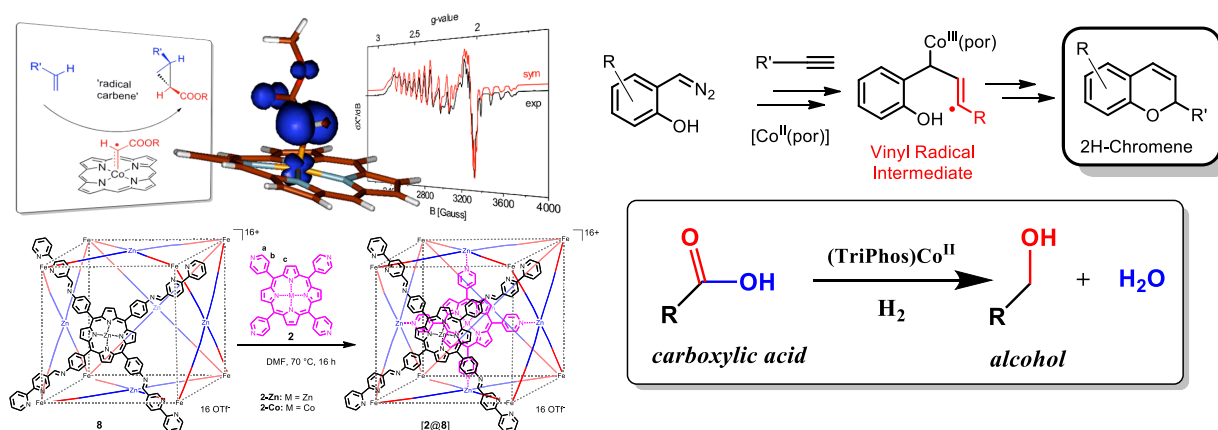
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Radicals are intrinsically reactive, and were long believed to be *too reactive to be selective*. However, in the coordination sphere of transition metals highly selective radical-type processes are certainly possible. In fact, radical-type reactions are tremendously important in several bio-synthetic pathways mediated by metallo-enzymes..

Inspired by such intriguing catalytic radical-type transformations mediated by metallo-enzymes, we are currently investigating new catalytic transformations mediated by synthetic (open-shell) organometallic catalysts. Special interest in such open-shell organometallic species comes from their expected higher and different reactivity compared to their closed-shell counterparts, and these 'metallo-radical complexes' may well allow us to steer and control radical-type reactions.^[1]



In this contribution we will discuss the available bio-inspired tools to steer and control the reactivity of cobalt(II). We will show that in several cases this metal triggers the formation of 'substrate radicals' in the coordination sphere of the metal, and we disclose their application in several catalytic reactions involving 'nitrene radicals' and 'carbene radicals'.^[2-4] In addition we will show that cobalt(II) is a suitable metal for catalytic hydrogenation of carboxylic acids.^[5] Reactivity studies, EPR spectroscopy and complementary DFT calculations are used to unravel the open-shell pathways of the paramagnetic Co^{II} species.

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