

Metalloradical Catalysis for Homolytic Radical Chemistry

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Abstract

Organic synthesis has been dominated by chemical reactions that are based on two-electron ionic processes, either stoichiometrically or in catalytic fashion. While one-electron radical chemistry is equally rich, its application in organic synthesis has been hampered by several enduring challenges. Over the past decade, we have been in the process of formulating “Metalloradical Catalysis” (MRC) as a general concept to develop fundamentally new approaches for controlling both reactivity and stereoselectivity of radical reactions as well as for catalytic generation of carbon-, and nitrogen-based radicals from common organic precursors. For achieving enantioselective radical reactions via MRC, we have developed a family of unique chiral metalloradical catalysts based on structurally well-defined Co(II) complexes of D_2 -symmetric chiral porphyrins with tunable electronic, steric, and chiral environments. These Co(II)-based metalloradical catalysts have been shown to be highly effective for a wide range of stereoselective organic reactions, including olefin cyclopropanation, olefin aziridination, C–H alkylation and C–H amination. Due to their distinctive radical mechanisms that involve unprecedented α -metalloalkyl and α -metalloaminy radical intermediates, the Co(II)-based metalloradical systems enable addressing some long-standing problems in these important organic transformations.