

MAGICAL POWER OF D-BLOCK TRANSITION METALS AS DEMONSTRATED BY CATALYTIC ASYMMETRIC C–C BOND FORMATION

Negishi, E.

H. C. Brown Laboratories of Chemistry, West Lafayette, IN 47907-2084
Purdue University
USA
negishi@purdue.edu

Over the past several decades, d-block transition metals have been increasingly recognized and used as catalysts for various chemical reactions. In most cases, their superb catalytic properties may be attributed to one or both of the following two: (1) ability to provide simultaneously one or more each of the valence-shell empty orbitals that serve as LUMOs and filled nonbonding orbitals that serve as HOMOs; (2) ability to undergo simultaneously both reduction and oxidation under one set of reaction conditions in one reaction vessel. A combination of these two properties can be exploited in devising a wide variety of useful catalytic reactions for formation and cleavage of C–C, C–H, C–O and other bonds.

For critically important C–C bond formation, i) reductive elimination, ii) carbometalation, and iii) migratory insertion may be exploited. The representative examples of reductive elimination and carbometalation are the Pd-catalyzed cross-coupling proceeding via reductive elimination and **Zr**-catalyzed asymmetric carboalumination of alkenes (ZACA reaction) proceeding via carbometalation.

In this lecture, recent advances of ZACA reaction will be discussed with emphasis on several methodological developments including: (i) ZACA–lipase-catalyzed acetylation–transition metal-catalyzed cross-coupling processes for preparing various enantiopure chiral alcohols; (ii) one-step homologation for the synthesis of deoxypropionates; (iii) the ZACA reaction of dienes to generate chiral cyclic compounds including those with all-carbon quaternary stereocenters.

