

24

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Preface

The most essential step in the catalytic cycle in a variety of transition metal catalyzed reactions is the formation of carbon-metal bonds. Among possible isomers, the generation of a single isomer of the organometallic compound, in which the metal is stereo- and regioselectively attached to the carbon of interest, necessarily leads to the selective formation of organic products. In many cases, the stereo- and regioselectivities are controlled mainly by steric and/or electronic factors. Chelation is also a reliable method for controlling stereo- and regiochemistry. Cyclometalation using Li, Mg, Mn, and Pd has traditionally been relied upon in ortho C–H bond functionalization. Directed hydrometalation and carbometalation, using Li, Al, Mg, and Zn, have also been utilized for the regio- and stereoselective generation of organometallic species. Despite the obvious strength of these approaches in stoichiometric systems, they are rarely applied to catalytic reactions. Recently, a chelation-assisted catalytic transformation has been recognized as one of the most useful methodologies, not only for controlling regio- and stereoselectivity of reactions, but also for accelerating reactions. In particular, the chelation methodology has been used as a new activation method, in which a carbon-metal bond is generated directly from a C–H bond, a reaction rarely achieved using conventional methods.

Although this monograph cannot possibly provide a comprehensive review of all transition metal catalyzed reactions involving directed metalation, a critical summary is given, which illustrates the power of this methodology in a rapidly developing field. For example, C–H bond activation reactions are some of the most extensively studied reactions that rely heavily on the development of chelation methodology. A wide variety of C–H bond functionalization reactions have been developed recently and are highlighted in this monograph. This methodology is now being applied to the activation of other unreactive bonds, such as C–C, C–F, C–O, and C–N. Other metalation reactions such as the hydroformylation of alkenes are described. Although this reaction is one of the largest volume industrial applications of homogeneous catalysis, it has not been widely used as a synthetic transformation on a laboratory scale. However, a unique stereo- and regioselective process has been developed through the utilization of directed hydrometalation. The regioselective Mizoroki–Heck reaction is another example in which directed carbometalation can be used to achieve a high regioselectivity.

This book will be a useful resource for researchers, teachers, and students, both expert and novice, who are interested in learning more about how this innovative methodology can contribute to different fields of chemistry. Finally, as editor I would like to thank all contributors for their participation in this project and for their patience throughout the entire process.

Osaka, Japan, August 2007

Naoto Chatani

Contents

Catalytic Addition of C–H Bonds to C–C Multiple Bonds F. Kakiuchi	1
Chelation-Assisted Arylation via C–H Bond Cleavage L. Ackermann	35
Catalytic Arylation and Vinylation Reactions Directed by Anionic Oxygen Functions via Cleavage of C–H and C–C Bonds T. Satoh · M. Miura	61
Chelate-Directed Oxidative Functionalization of Carbon–Hydrogen Bonds: Synthetic Applications and Mechanistic Insights D. Kalyani · M. S. Sanford	85
Directed C–C Bond Activation by Transition Metal Complexes C.-H. Jun · J.-W. Park	117
Directed Rhodium-Catalyzed Hydroformylation of Alkenes B. Breit	145
Directed Mizoroki–Heck Reactions M. Oestreich	169
Author Index Volumes 1–24	193
Subject Index	203