



New Trends in Cross-Coupling – Theory and Applications

Of all the many contributions of homogeneous catalysis by organometallic complexes to synthesis, palladium-catalyzed cross-coupling stands out.

The ability to make new C-C or C-X bonds direct above careful links of the standard of the st

by direct chemospecific linkage of reaction partners has very broad consequences. Cross-coupling has a reach across chemistry from materials to molecular biology, it is well liked by industry and widely utilized there at all scale levels, and rarely requires forcing conditions. Since the award of the 2010 Nobel Prize to Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki for their pioneering contributions to the field, the level of activity in both innovation and application has remained high.

Countless reviews and several full books have been dedicated to the general field of crosscoupling, or to more specific aspects. The standard edited reference work by Diederich and Stang was published in 1998, updated by de Meijere and Diederich in 2004 and then again by de Meijere, Bräse, and Oestreich in 2013, roughly doubling in size each time.^[1] The series "Science of Synthesis" has given full attention to the basic synthetic reactions of Cross-coupling, most recently in a dedicated three-volume Workbench Edition.[2] Molnár's book, revised in 2013,[3] has strong technical coverage of methodologies and reaction media for cross-coupling. The new multi-author volume edited by Thomas Colacot needs to be assessed against this background of recent activity; is it generally useful, and does it also possess unique features?

To this reviewer, the main strengths of the book lie in its ability to provide access to structured information that informs the choice of reaction type and conditions. Colacot himself provides a brief succinct summary and historical development in the first chapter. We learn that almost 50% of all publications in the field involve Suzuki–Miyaura reactions and that the dominance is currently sustained. This introductory material is followed by five separate chapters that respectively discuss ligand types, phosphine-based precatalysts, Pdcarbene complexes in catalysis and ligand design for a variety of arylation reactions including

heteroatom couplings. Late chapters with comparably specific focus address catalysis involving flow rather than batch processes, a perspective on how palladium catalysis may qualify as "green chemistry", the problems associated with scale-up, and the analytical detection of residual Pd, highly relevant in pharmaceutical applications. The organization of the remainder is less clearly defined, containing useful chapters on individual topics that include stereochemical aspects of Suzuki-Miyaura coupling, the mechanism of catalytic activation of the boron nucleophile in this same reaction, Pd-catalyzed carbonylation, and the formal additions of aryl iodide than can occur by capture of the intermediate in intramolecular Heck reactions. It is nearly fifteen years ago that a comprehensive review of the Heck reaction was published; updated here by the original authors. Catalysts based on metals other than palladium appear where relevant. All in all there is broad coverage with pleasingly low levels of overlap and relatively few areas of omission; C-H activation is largely limited to arylation and the current popularity of Sonogashira coupling (> 2000 references in the last four years, we learn from Chapter 1) might have merited independent coverage.

This is a weighty book (or e-book if desired) that will be a useful source for any group that regularly uses palladium catalysis, or indeed for anyone who needs rapid and continuing access to the topics therein.

John M. Brown Oxford (UK)

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- Metal-catalyzed Cross-coupling Reactions (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, 1998; Metal-Catalyzed Cross-Coupling Reactions, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, 2004; Metal-Catalyzed Cross-Coupling Reactions and More (Eds.: A. de Meijere, S. Bräse, M. Oestreich), Wiley-VCH, 2014.
- [2] Science of Synthesis: Cross Coupling and Heck-Type Reactions, Workbench Edition (Eds.: G. Molander, J. P. Wolfe, M. Larhed), Thieme, 2013.
- [3] Palladium-Catalyzed Coupling Reactions: Practical Aspects and Future Developments (Ed.: Á. Molnár), Wiley-VCH, 2013



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