Copper-Mediated Cross-Coupling Reactions

Starting with the seminal work of Ullmann and Goldberg in 1901 on copper-mediated cross-coupling reactions, copper was widely applied in C–C and C–heteroatom bond-forming reactions half a century before the advent of palladium catalysis in the 1970s. In the subsequent decades, the field of Pd catalysis developed at a tremendous pace, and at the time seemed set to supersede Cu catalysis. However, after a sharp increase in the price of palladium, substantial research activity has shifted to Cu as a widely available alternative, thus reviving its legacy in cross-coupling chemistry. The sophisticated tools for the development of new reactions and ligands, in parallel with the reaction screening and instrumental analysis that had enabled such an explosive progress in Pd chemistry, were now implemented also for the advancement of Cu catalysis. Copper has since become a fully viable metal catalyst in many chemical transformations, and organic chemists are eager for a guideline on how Cu catalysis can be applied to their particular synthetic tasks.

Thus, Evano and Blanchard could not have found a better time to compile a book on copper-mediated cross-coupling reactions. They have done an excellent job of structuring the wealth of material in this rapidly expanding field into a coherent book, with strictly delineated topics and minimal redundancy. They have teamed up with competent co-authors, among them such reputed experts as I. P. Beletskaya, M. Beller, L. S. Liebeskind, M. Taillefer, and Y. Yamamoto, to produce a very welcome comprehensive guide to modern copper catalysis.

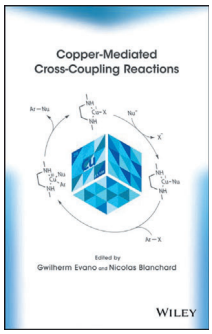
The main facets of Cu-mediated transformations are extensively and thoroughly reviewed within about 800 pages and 20 chapters. In an elegantly written foreword, S. L. Buchwald, an expert in both Pd and Cu catalysis, emphasizes the complementarity of the two fields. His balanced assessment prevents the reader from reducing the role of copper to that of a cheap substitute for palladium, even if the conclusions of some chapters might suggest so. Another true highlight of this book is the preface, in which Gwilherm Evano and Nicolas Blanchard provide a chronology of pioneering discoveries that paved the way for the modern developments that are discussed later.

The body of the book is divided into three major parts. Part I deals with the use of copper catalysts for the formation of C–heteroatom bonds. It consists of seven individual chapters arranged according to the types of bonds and products formed. Chapter 1 covers the arylation of N-nucleophiles by aryl halides, Chapter 2 the arylation of alcohols and thiols, and Chapter 3 the formation of C–P bonds. Chapter 4 deviates from this product-based classification by describing emerging reagents for the arylation of heteronucleophiles. Chapter 5 covers the vinylation, alkynylation, and allenylation of heteronucleophiles, and Chapter 6 deals with the aromatic/vinylic Finkelstein reaction. Chapter 7 concludes this first part of the book by discussing mechanistic work on modern Ullmann–Goldberg coupling reactions.

Part II, which is also divided into seven chapters, centers on Cu-catalyzed C–C bond formation. Chapter 8 presents the state of the art in Cu-catalyzed arylations of C–H acidic derivatives, Chapter 9 covers the cyanation of aryl halides, and Chapter 10 focuses on aryl–aryl bond formation. Chapter 11 continues this logical structure by discussing alkynylation, alkenylation, and allylation reactions of aryl derivatives, and Chapter 12 covers the analogous reactions of alkynyl derivatives, leading to diynes and enynes. It would have been beyond the scope of any single book to comprehensively cover Cu as a co-catalyst in bimetallic systems. It was therefore a wise decision to focus on monometallic Cu catalysts. Chapter 13 alone deviates from this concept by reviewing Pd/Cu co-catalyzed 1,3-diene syntheses. Chapter 14 concludes this second part by covering the "hot topic" of Cu-mediated trifluoromethylations of aryl derivatives.

These first two parts of the book competently guide synthetic chemists towards identifying the most promising catalyst systems for their own planned applications. The great practical value of these parts derives also from the comprehensive list of the best ligands currently available for every kind of reactivity. In these chapters, the discussion of the synthetic utility of Cu catalysts is mainly based on simple model systems. The reader learns about the importance of choosing the right ligands and carefully optimizing the reaction conditions. In Chapter 2, Marc Taillefer's key message to method developers is that the decisive factor in achieving lower catalyst loadings and discovering new reaction modes will be the design of new ligand systems. Another message to be extracted from these chapters is that Cu makes possible various novel cross-couplings based on C–H activation, which will likely be at the heart of highly important developments in the future.

Part III excellently complements the other two by providing a comprehensive overview of successful applications of Cu catalysts in the synthesis of complex molecules, such as heterocycles, natural products, and industrially important structures. This part, which consists of six chapters, is a treasure trove for chemists seeking guidance on how to make optimal use of Cu catalysis in their



Copper-Mediated Cross-Coupling Reactions
Edited by Gwilherm Evano and Nicolas Blanchard. John Wiley & Sons, Hoboken, 2013. 840 pp., hardcover, € 156.00.—ISBN 978-1118060452

synthetic applications. In Chapter 15, Cu-mediated cyclization reactions are presented as elegant entries to heterocyclic structures. The following chapters review applications of Cu-catalyzed bond formation in the synthesis of complex molecules. Thus, Chapters 16, 17, and 18 describe syntheses with formation of C–N, C–O/C–S, and C–C bonds respectively. In Chapter 19, the use of Cu catalysis in industrially important processes is summarized, and in Chapter 20 the current state of the art in immobilization and re-use of copper catalysts is discussed. Overall, the third part of the book gives a realistic impression of the great impact that Cu-based methods have in academic and industrial applications.

As well as thoroughly covering all essential mechanistic aspects of Cu catalysis, the material in the book is also accessible to anyone active within the area of organic chemistry. As a result, it is an excellent textbook for anyone wishing to quickly gain a detailed overview of the field, or to identify the best ligands for a specific synthetic problem. Synthetic organic chemists, in particular, will benefit from the product-class orientated structure, because it quickly directs them towards the most relevant material for their intended applications. Method developers looking for reactivity concepts rather than product classes are provided with a detailed 14-page keyword index. The book is a key resource for copper chemistry and a must-have, for experts and students alike.

Frederic W. Patureau, Lukas J. Gooßen
Fachbereich Chemie
Technische Universität Kaiserslautern (Germany)

DOI: 10.1002/anie.201403795