## Metal-catalyzed Cross-Coupling Reactions

F. Diederich and P. J. Stang (eds)
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The key step in a multistage organic synthesis often involves the formation of a carbon–carbon bond, R–R′, and if this is carried out at a late stage in the synthesis, the reaction must be tolerant of a variety of functional groups. There is family of related reactions which can meet this demand, which involves transition-metal catalysts that can vary their valence by ±2, and which derive the groups R and R′ from a halide RX and a main-group organometallic R′M. Typically, the transition metal may be palladium. A $Pd^0$ complex, $Pd^0L_2$, reacts with the halide by oxidative addition to give the $Pd^{II}$ complex $RPd^{II}XL_2$. This undergoes transmetallation with the organometallic R′M to give MX and $RPd^{II}R'L_2$, then reductive elimination gives R–R′ and regenerates the catalyst $Pd^0L_2$. The transmetallation step is often rate-determining, and with the less reactive organometallics (B, Si) may require the addition of an activating ligand to the metal.

There are many variants on this theme, and the most popular are labelled with the names of their developers: the metal M may be tin (Stille, to whom the book is dedicated), boron (Suzuki), lithium, magnesium (Kumada), zinc (Negishi), aluminium, silicon, copper or zirconium, and the transition-metal catalyst may be nickel or palladium. In one variant, CO may be incorporated to give the carbonyl compound RCOR′. In another, the Heck reaction, an olefin, $R'CH{=}CH_2$, takes the place of the organometallic compound R′M and inserts into the R–Pd bond to give $RCH_2CHR'Pd^{II}XL_2$, which then gives $Pd^{II}HXL_2$ (and thence $Pd^0L_2$ and HX) and the olefin RCH=CHR′ by $\beta$-elimination.

This field has developed rapidly in the past 20 years, and until recently it has been rather poorly served with suitable texts. This book, written by experts in the field, goes a long way to make good that deficiency.

The first chapter, by Negishi and Liu, deals with the reactions where the metal M is zinc, magnesium, aluminium or zirconium. An obvious problem here is the high reactivity of these organometallics, which require careful handling, and may react with functional groups in the organic substrates.

Chapter 2, by Suzuki, covers reactions involving organoboron compounds. These are commonly boronic acids, $R'B(OH)_2$, or their derivatives, which are less sensitive to air and much more tolerant towards functional groups, and need a fourth ligand, often $HO^-$, to activate them.

The third chapter, by Bräse and de Meijere, covers the Heck reaction, and Chapter 4, by Mitchell, deals with coupling reagents involving organotin compounds. The organotins are readily available, easy to handle, and usually inert towards functional groups, and these (Stille) reactions are probably currently the most popular in this family of reactions. Mitchell's analytical review supplements nicely the recent 50th volume of *Organic Reactions* on the Stille reaction by Farina, Krishnamurthy, and Scott, which gives comprehensive tabulations of all the known examples (and was reviewed in *Applied Organometallic Chemistry* **12,** 299 (1998)).

Chapter 5, by Sonogashira, covers cross-coupling reactions to *sp* (alkynyl) carbon, and Chapter 6 by Link and Overman deals with intramolecular Heck reactions in natural-product chemistry.

Chapter 7, by Marek and Normant, covers carbometallation reactions in which organometallic compounds RM are added to the multiple bonds of olefins or acetylenes, and Chapter 8, by Bäckvall, discusses palladium-catalysed 1,4-additions to conjugated dienes. Chapter 9, by Knockel, covers reactions involving organozinc reagents.

Organosilicon compounds have a rather low intrinsic reactivity in this kind of chemistry, but it can be enhanced by further ligation, particularly by fluorine, and this chemistry is covered in Chapter 10 by Hiyama. The final chapter, by Tsuji and Mandai, deals with palladium-catalysed coupling of propargylic compounds.

Each chapter gives an excellent account of the present standing of the subject, and is concluded with experimental details for typical reactions. I would have appreciated a general introductory, integrating, chapter by the editors describing the common factors between these various reactions, and their relative merits, and the conditions which govern which variant to choose.

The integration of the chapters into the book is less good, and the formatting of the formulae, equations, and schemes is not consistent. I used to work with a great man, Joseph Kenyon, who had reduced the reading of a Ph.D. thesis to a fine art. He would find the word *asymmetric*, and then the word *desiccator*, and the spelling of these would determine the course of the viva. I was reminded of this because the present book fails Kenyon's *asymmetric* test in the Contents list on page xi. On the whole, the number of errors is not great, and they are largely confined to inconsistencies in the formulae and in the author index. The subject index is excellent, but the author index shows signs of being composed by computer and then never checked. It includes only those people who are mentioned by name in the text, so that it covers only two and a half pages, and the vast majority of the authors in the references are not mentioned. It includes names such as Migita-Kosugi, Suzuki-Miyaura, and Kumada-Tamao, who in fact are each two people, and Heck-Aldol which represents a man and a reaction. In these two and half pages, I found 35 errors before I gave up counting.

Don't be put off by these minor quibbles. This is an excellent account of an important and fascinating area of organometallic chemistry which bridges organic and inorganic interests, and will be a valuable source of reference to anyone engaged in organic synthesis.

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