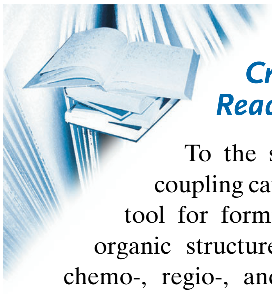


Metal-Catalyzed Cross-Coupling Reactions and More

To the synthetic chemist, cross-coupling catalysis is an indispensable tool for forming an eclectic array of organic structures, often with exquisite chemo-, regio-, and/or stereocontrol. It is the one synthetic tool which can be compared to a monkey wrench for the car mechanic or stethoscope for a doctor. But, the cross-coupling catalysis tool is much more than that, it is a catch-all tool containing hundreds of tools within it—arguably, cross-coupling catalysis is the ultimate Swiss Army Knife in chemical synthesis.

The field of cross-coupling catalysis by metals is vast. It is the one area which attracts a significant number of researchers from across many disciplines within chemistry. To write a book set in this area must have required the editors and internationally leading authors to have taken a very deep breath when considering reviewing this topical and popular area of research.

This three volume book set represents, as described by the editors, a follow-up handbook to *Metal-Catalyzed Cross-Coupling Reactions*—it is not a new edition—it is a new book with ca. 50% more content. With so many recent developments being made, particularly in the area of C−H bond activation / functionalization (either by C−H bond arylation, alkenylation, or alkylation, or oxidative functionalization), it was imperative that this area was reviewed.

All of the key cross-coupling reactions (Buchwald–Hartwig, Hiyama/Hiyama–Denmark, Kumada, Mizoroki–Heck, Negishi, Sonogashira, Suzuki–Miyaura, Stille–Migita, etc.) are covered in this book set. The topic of cross-coupling catalysis is now a mature one, but one which continues to expand at a staggering rate. The authors have endeavored to present each topic from an historical perspective, whilst also showcasing recent cutting-edge developments (up to about mid-2012).

In terms of the book review it is impossible to go through every section in detail. However, selected below are those sections which stood out as being particularly attractive and interesting.

Chapter 1 begins with a thorough discussion of the mechanistic aspects of metal-catalyzed C−C and C−X bond-forming reactions (by Echavarren and Homs). This is a good entry point to the area. Many of the other Chapters include some mechanistic discussion, which for me was a real treat. More detailed mechanistic aspects are adequately cited in the form of key reviews, which are numerous in this book set.

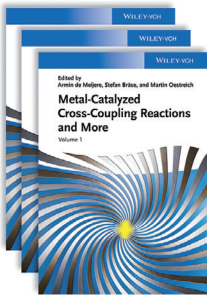
It is quite apparent from the book set that other transition metals are beginning to complement the reactivity demonstrated by Pd in various transformations. For example, the use of iron has come to the fore, due to its low cost and bountiful Fe-catalyzed reactions that have recently been developed. Examples include Fe-catalyzed Suzuki–Miyaura cross-coupling reactions of alkyl halides with organoborate species (Section 2.3.2, vol. 1) and the cross-coupling of arylmagnesium reagents with alkyl halides (section 5.3.1.3).

Good examples of asymmetric synthesis were presented in this book set. I particularly enjoyed reading about the: 1) stereoselective Suzuki–Miyaura cross-couplings of stereodefined alkyl halides (section 2.3.2.1.2, vol. 1); 2) synthesis of enantiomerically enriched atropisomers (section 2.2.4, vol. 1); 3) Zr-catalyzed asymmetric carboalumination of alkenes and sequential Pd- and Cu-catalyzed cross-coupling processes (section 3.4, vol. 1); 4) enantioselective Heck couplings (section 8.5, vol. 2).

In Chapter 7 (vol. 2), Denmark and Sweis introduce the reader to organosilicon cross-coupling chemistry. The authors describe “strain-release Lewis acidity”, which is supported by leading transformations that are laid out in an attractive manner. We then see covered substituent effects, convergence in mechanistic pathways and a detailed section on kinetic analysis and mechanistic implications (starting section 7.3, vol. 2). This is one of the definitive Chapters in this book set, in that it covers concepts, synthetic transformations and applications in target-orientated synthesis (with links to other transformations such as ring-closing metathesis and C−H bond activation), mechanistic aspects and provides useful experimental procedures. Each facet within this theme was balanced well, and this is seen in other chapters within the book set too.

By way of another example, although in a different style, the chapter by Yamaguchi and Itami on C−H arylation affording biaryls (Chapter 17, vol. 3) collates the synthetic examples/transformations in a useful manner, the details of which can be assessed easily—a good example is given in Scheme 17.9 (section 17.2.3, vol. 3), which shows the chemical transformation, catalyst, reagents, lead author and reference in each case.

Higher oxidative state Pd catalysis is covered to a certain extent (e.g. Pd^{IV}), particularly in the latter chapters within the book set (Chapters 17 and 19, vol. 3, particularly). The chapter by Baudoin et al. (Chapter 19, vol. 3) on C−H bond alkylation (including hydroarylation of alkenes) was particularly interesting, covering Ni, Pd, Fe, Rh and Ru catalyzed processes. To aid the flow of the synthetic transformations, Baudoin et al. included well-placed catalytic cycles, so that the reader was



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Edited by Armin de Meijere, Stefan Bräse, and Martin Oestreich

Metal-Catalyzed Cross-Coupling Reactions and More

Volume 1

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aware of the mechanistic implications. One aspect of Chapters 17 and 19 was the use of "bolded" bonds to highlight the new bond being formed and the C–H bond being broken/functionalized. This presentation style was not uniformly adopted in the book series, but it was particularly helpful in the context of C–H bond functionalization processes.

Hydroamination is an area that has continued to grow over the last 20 years (Chapter 15, vol. 3). In this chapter, Shafer et al. cover a plethora of early to late metals which effectively mediate this synthetically useful transformation. Asymmetric hydroamination is mentioned at Ni, Pd, and Au (section 15.3.7, vol. 3), which shows some promise.

One area that could have been covered more extensively is the involvement of higher order Pd species. I say this having a specific interest in the role of such species, especially Pd nanoparticles/colloids. There is a body of evidence available on Pd nanoparticles, which are formed from common Pd precatalysts such as $Pd(OAc)_2$, palladacycles, and $PdCl_2$ under working reaction conditions. I was pleased to see that Bräse and de Meijere covered aspects of this subject in Chapter 8, focussed on Heck couplings (specifically on page 539). Also, Schaub and Kivala make reference to heterogeneous-catalyzed Stille cross-couplings in Chapter 9 (section 9.3.3, vol. 2), catalyst developments (section 9.2.2.2.2). In my opinion, the issue of Pd aggregation and role of higher order Pd species in cross-coupling requires more attention. In this context it is worth mentioning two other books edited by Ribas (*C–H and C–X Bond Functionalization. Transition Metal Mediation*, RSC Catalysis, No. 11, 2013) and Molnar (*Palladium-Catalyzed Coupling Reactions: Practical Aspects and Future Developments*, Wiley-VCH, 2013). Both books cover aspects relating to the involvement of Pd nanoparticles in cross-coupling processes, and are therefore highly complementary to this book set.

A particular aspect of the book set that I appreciated was the collation of complex data. A good example is Table 3.3 (Chapter 3), written by Negishi, showing the scope and limitations of the Pd-catalyzed cross-coupling of various organometallic coupling partners with a variety of organohalides, which also directs you to the requisite section within the chapter. This incredibly useful table also informs the reader of where the recent developments have been made and where relatively few examples are known.

The book set is particularly useful as each chapter gives examples of experimental procedures for the reader to peruse without having to go to the primary literature in the first instance. There is a consistency to these procedures, particularly in the way that they are laid out, which shows that the editorial process has been rigorous. One needs to accept that it is not obvious why certain procedures have been selected. The point of this section within each chapter is to allow the reader to get a feel of the types of procedure being used within a given topic. A good example is in Chapter 5 (vol. 1) on C–C bond formation involving organomagnesium reagents (page 411). Chapter 12 (vol. 2) on the cross-coupling reactions of π-allylmetal intermediates gives general experimental procedures for selected Pd-, Ir-, Ru-, and Rh-catalyzed allylic alkylation processes (page 983), which is helpful for any new starter wishing to try out this type of chemistry. Finally, each chapter has a specific abbreviations list, which is much simpler to navigate through than having one global abbreviations list for the complete book set.

In the main I thought that the review was well laid out and presented, and free of obvious mistakes. I have a few personal minor criticisms—I would prefer to see the orbital directionality (x,y,z coordinates) in orbital diagrams. An example on page 135 (vol. 1) makes it difficult to visualize the interacting orbitals, although it can be worked out. It was not clear to me what "feeble chirality" or "feebly chiral" meant (Scheme 3.100, page 257). Given the broader context of this book set, I did not feel that it was necessary to arbitrarily name specific chemical compounds in the index section, e.g. (*E*)-3-methoxystilbene, which was otherwise organized very efficiently.

In summary, this is an excellent book set.[*] It offers something for the novice and expert alike. A car mechanic will usually have 30 or so manuals available for repairing the most common vehicles on the road. For the synthetic chemist, this is one of those must have manuals, complementing and strengthening any library.

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[*] Quirky fact: A common criticism of book sets is that they are too heavy, difficult to transport and carry around. Over the last few months I have been able to carry the complete book set in my rucksack on a bicycle, travelling a distance of 10 km (ca. 6.5 miles) at a time.