

Book Review

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Transition metal reagents and catalysts: innovations in organic synthesis

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Tsui quite rightly states in the preface of this book that transition metal reagents and catalysts have revolutionized the field of organic synthesis and that they continue to open up new opportunities for creativity in design. This statement is easily justified when one sees the diversity of reactions that are described in this book, and realizes how many of these bond-forming processes would be all but inaccessible in the absence of transition metal assistance. This book is aimed at – and indeed should be very attractive to – the synthetic organic chemist wishing to expand his/her repertoire of reactions for carrying out synthesis.

The book is divided into 11 chapters. Chapters 1 and 2 serve as an introduction to transition metal organometallic chemistry. The first provides an interesting historical perspective on the area by describing how a relatively few industrial processes, developed in the early part of the 20th century, were the harbingers for most of the more recent developments and applications in fine synthesis. The second chapter then summarizes the key steps in the mechanisms of reactions involving transition metals, in addition to discussing the importance of coordination number and the crucial role of ligands. Whilst the book is not aimed at the reader desiring an in-depth understanding of how transition-metal-mediated reactions proceed, Chapter 2 is nevertheless sufficiently detailed for the reactions discussed in the following chapters to be broadly rationalized. Furthermore, since each subsequent chapter/major section begins with a short summary of the mechanistic processes involved in the reactions discussed in the ensuing pages, the reader is continually reminded of the more salient mechanistic details.

Chapters 3 to 7 are organized according to organic substrate, with each chapter describing how a particular class of organic molecules can be used in transition-metal-mediated reactions. All the key reactions already in widespread use, and many more besides, are covered in these sections; furthermore, by organizing the chapters by organic substrate, they are also easy to locate. Chapter 3 discusses the use of organic halides and pseudohalides, Chapter 4 allylic compounds, Chapter 5 conjugated dienes,

Chapter 6 propargylic compounds, and Chapter 7 alkenes and alkynes.

The remaining four chapters concentrate on specific properties of transition metal complexes, each describing how they have been applied to organic synthesis.

Chapter 8 describes the synthetic applications of transition metal carbenes. It quite rightly concentrates on their use in alkene and alkyne metathesis, as this reaction has, more than most, had a profound impact on synthetic planning and design over the last decade. Other important applications of transition metal carbenes, however, are not ignored: carbonyl alkenylation, cyclopropanation and ring annulation, for example, are all well covered.

Transition metal complexation frequently modifies the reactivity of an organic substrate so profoundly that it causes a reversal in inherent reactivity of the substrate. For example, whilst benzene is susceptible to electrophilic attack, complexation by $\text{Cr}(\text{CO})_3$ renders the aromatic ring much more prone to nucleophilic attack. Chapter 9 describes the ways in which transition metals have been used as stoichiometric reagents for protecting unsaturated organic functional groups and for modifying their reactivity.

Hydrogenation of unsaturated groups is undoubtedly one of the most important transition-metal-catalysed reactions for industrial processes, and with the development of asymmetric versions this continues to have a profound impact on the enantioselective synthesis of chiral compounds on the large scale as well as in the laboratory. Chapter 10, therefore, is devoted entirely to catalytic hydrogenation, transfer hydrogenation and hydrosilylation. More chiral ligands have probably been developed for these reactions than for any others, and some of the most important referred to in this chapter (as well as elsewhere in the book) are conveniently printed on the inside cover at the back of the book.

The final chapter of the book describes the use of $\text{Pd}(\text{II})$ as an electrophile in promoting a range of reactions with electron-rich substrates. Throughout the book Tsui concentrates on catalytic processes; these do, after all, provide the most atom economical use of often expensive transition metal reagents. Rendering reactions mediated by $\text{Pd}(\text{II})$ catalytic can be particularly difficult; however, the author clearly describes a number of approaches that can be used successfully for making reactions catalytic in palladium, and therefore synthetically more attractive to the end user.

Chapters 3 to 11 comprehensively cover all of the most important and widely used reactions mediated or catalysed by transition metals. A very large

number of examples are provided in each case, many of which come from the very recent literature, outlining the state of the art as well as providing important advances in more established reactions. Since the book is aimed at the synthetic organic chemist, it is also good to see how the author has carefully selected examples from syntheses of complex natural products from many of the world's finest exponents in organic synthesis to illustrate the synthetic utility of transition-metal-mediated reactions and demonstrate their power and elegance when applied to total synthesis.

As already stated, this book is not suited to the reader seeking a detailed mechanistic rationale of reaction outcomes, although, of course, the comprehensive referencing directs the reader to the primary sources where this can be found. However, it would have been beneficial had a little more attention been paid to the various selectivity issues that arise in many of the examples cited. Unfortunately, all too frequently, reaction schemes are also poorly drawn, omitting key aspects of, for example, relative stereochemistry, which then detracts from the example. One is often left asking whether the reaction is stereoselective or not?

On the whole, the book has been well written and the author is to be commended for bringing together so many reactions in such a clear and logical fashion. There are a few recurring grammatical errors (e.g. the frequent omission of articles) and too many typographical errors that should have been found in the editing process. Likewise in the reference sections, whilst admirably comprehensive, there are also too many small errors. These are generally author omissions, incorrectly spelled names and non-standard journal abbreviations; fortunately, they generally do not prevent the reader from locating the desired reference. It is hoped that these will be amended for future reprints with improved editing.

In summary, apart from a few minor quibbles, this book will be of much use to the synthetic chemist. The breadth of subject material described, combined with comprehensive sets of references, has generated a book that should prove an invaluable source from which to explore further the fascinating field of transition-metal-mediated reactions and to encourage chemists to apply transition metal complexes in new and imaginative ways in future syntheses.

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