

Book Reviews

Palladium Reagents and Catalysts: Innovations in Organic Synthesis. By J. Tsuji. Wiley: New York, 1995, 560 pp, hardback. £125. ISBN 0-471-95483-7, paperback. £40. ISBN 0-471-97202-9.

There can be little doubt about the importance of palladium chemistry to organic synthesis. A modern book which discusses the reactions of palladium with respect to organic synthesis is therefore invaluable. Tsuji has taken on a formidable task in preparing "Palladium Reagents and Catalysts: Innovations in Organic Synthesis" but the result is a success, and will certainly be of benefit to readers.

The first two chapters are effective in laying the foundations for the rest of the book. Basic palladium catalysts are described as well as an explanation of the fundamental reactions which are involved in the heart of palladium catalysed transformations. The reactions which are catalysed by Pd(II) and Pd(0) are summarised, with cross references to the rest of the book. This information could have been somewhat more detailed, but was nevertheless useful.

The first major chapter describes various oxidative reactions involving Pd(II) reagents. Logically starting with a review of the Wacker reaction and the principles of recycling the palladium catalyst, the chapter progresses through over 500 references. Included in this discussion are an analysis of the stereochemistry of the oxidation of dienes, oxidative reactions involving C-C bond formation and carbonylation.

The next chapter, chapter 4 is 400 pages long and forms the bulk of the book. However, this chapter is fairly well subdivided, with references provided at the end of each major sub-section. The Heck reaction is discussed early on, although it was not obvious from the index that this was where the most detailed discussion of the Heck reaction would be found. Inter- and intramolecular examples, as well as related reactions involving alkynes were all well documented, making a valuable account of this reaction. Cross-coupling reactions between halides (and pseudo-halides) and organometal reagents are described including Stille and Suzuki reactions as well as the coupling of other organometal reagents. There are many synthetic examples given, including Stille macrocyclisation reactions, and the Nicolaou rapamycin synthesis. The organisation of this

section was more by reaction type than by the substrate involved, which enabled a comparison between related reactions (e.g. organozinc reagent versus organoboron).

Allylic compounds were treated separately from other substrates, and the next major section gave a good account of palladium catalysed allylic substitution reactions, especially from a synthetic perspective. Other reactions involving allyl substrates were also given fair coverage, including rearrangement reactions and carbonylation reactions. The remaining sections within this enormous chapter involved discussions of reactions involving more specialised substrates including dienes, propargylic compounds, alkynes and alkenes. Other reactions including hydrosilylation, reduction and the use of methylenecyclopropanes are also discussed at the end of this chapter.

The final chapter is, in comparison, only 20 pages long, and picks up a few reactions which were not otherwise discussed, and were generally more specialised.

Overall, I was impressed by this book, and I am sure that those people involved with palladium chemistry who have not already bought the book, should do. Any library which serves an organic chemistry group will need a copy, as will non-palladium chemists with an interest in the area.

The book is easy to read, and the diagrams are clear and well-constructed. Palladium chemistry is a difficult subject to arrange in a clear order, and although this book contains a great deal of useful information, I found that it was not always easy to look up a particular reaction or area quickly, and further cross-referencing would have been useful in a work of this size.

J. Williams, University of Bath, UK.

Metals and Ligand Reactivity. By E. C. Constable. VCH: Weinheim, 1995, XIV, 312 pp, paperback. DM 68. ISBN 3-527-29277-2.

This book provides an unusual and interesting perspective on the chemistry of ligands coordinated to transition metal centers. Whereas there are many texts that deal with the chemistry of organometallic compounds and, in particular, reactions involving coordinated organic groups, in the present instance the focus is on complexes containing more traditional two-electron donor ligands. There are also a number of coordination chemistry texts in

which the focus is on the properties and reactivity associated with the metal center, and the reactivity of the ligands themselves is largely ignored. In this case, the author provides insight into the often subtle changes in the reactivity of a ligand which are observed when it is attached to a transition metal center.

The book begins with brief overviews of crystal field and ligand field theories, and thermodynamic and kinetic effects on the reactivity of coordination compounds, followed by a discussion of the nature of the metal-ligand bond. Although fairly elementary, these provide an excellent background for the topics discussed in the remainder of the book.

The next three chapters deal with nucleophilic attack on coordinated carbonyl compounds, such as esters and amides, reactions of other coordinated ligands with nucleophiles, and electrophilic attack on coordinated ligands. The first of these includes the hydrolyses of amino acid esters and amides. Nucleophilic attack on other ligands is separated into those involving sp , sp^2 and sp^3 hybridized carbon centers, and hydrolyses of thioethers and phosphate esters. The chapter on electrophilic attack focuses primarily on the reactions of coordinated enolates and amines, but covers a range of related reactions.

Following these more general chapters, the author goes on to show how many of the principles may be applied to macrocycles and the use of metal templates in their construction, and to supramolecular chemistry. Chapter 6 begins with a definition and rationale for the use of template

reactions, and goes on to describe strategies employed in the synthesis of macrocycles. Many examples are provided which illustrate the advantages and potential difficulties associated with the method. The next chapter takes the discussion into three dimensions, and includes such topics as molecular topology, supramolecular chemistry, molecular recognition and self assembly.

The last two major chapters deal with electrophilic and nucleophilic attack on coordinated aromatic and heterocyclic ligands, and oxidation of coordinated ligands, and both chapters concentrate on the use of very traditional reagents. The brief concluding section relates many of the preceding compounds and reactions to those found in biological systems.

The author has chosen to focus on a well-defined area of coordination chemistry, and he develops the subject logically and carefully, and provides many examples. His enthusiasm and humor are evident throughout the book. The illustrations are of excellent quality, and they add much to the appearance of the text. Lists of suggestions for further reading are provided at the end of each chapter, although they contain few references to the primary literature. This should not detract, however, from what is a very readable book, and one which provides an excellent introduction to an aspect of coordination chemistry that has been largely ignored.

G. K. Anderson, University of Missouri-St. Louis, USA

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