

Rhodium and Palladium Compounds

Transition Metal Organometallics for Organic Synthesis

BY F. J. MCQUILLIN, D. G. PARKER AND G. R. STEPHENSON, Cambridge University Press, Cambridge, 1992, 594 pages, ISBN 0-521-33353-9, £100, U.S. \$200.00

Interest in the application of transition metal organometallics towards organic synthesis has been growing steadily over the past twenty-five years, and this book is directed at newcomers to the field. It highlights the major synthetic methods which employ organometallic reactions and covers the literature up to the end of 1988.

The first chapter provides an introduction with an emphasis on the reactivity of ligands co-ordinated to metals. The next eleven chapters deal with application by reaction or complex type, and form the bulk of the text.

A chapter on isomerisation includes the application of rhodium to carbon-carbon double bond isomerisation, which is used industrially in 1-menthol synthesis. The relevance of palladium and rhodium in other rearrangements, such as the ring opening of cyclopropanes and epoxide rearrangements, is also discussed.

The oxidation of alkenes is dominated by the palladium catalysed Wacker process, and this, the extension of the chemistry to natural product synthesis and the introduction of masked ketones into molecules, is examined in Chapter 4. This is followed by a section on co-ordinated alkenes and alkynes as synthetic intermediates where the addition of nucleophiles to alkenes may be facilitated by palladium reagents or catalysts. The next chapter describes palladium π -allyl complexes. After dealing with their stoichiometric formation and alkylation, their catalytic applications, including reaction stereochemistry, asymmetric synthesis and types of nucleophile for use in allylic alkylation, are discussed.

Carbonyl insertion is discussed in Chapter 9. The industrial importance of the hydroformylation reaction is illustrated by cobalt and rhodium catalysts and the development of the low pressure rhodium oxo process to produce butanal. The application of this chemistry to form: perfumery chemicals, such as homocitronello, ketones, lactones and asymmetric carbonyls with

related rhodium catalysts is described. Carbonylation using palladium reagents is exemplified by the synthesis of β -substituted carboxylic acid derivatives, dicarboxylates and the application of intramolecular variants of carbonylations to the synthesis of lactones. However, the preferred industrial route to acetic acid, by rhodium catalysed carbonylation of alcohols, occupies only as much space as discussion of the rhodium catalysed reaction of carbon monoxide with hydrogen to form ethylene glycol, which received much attention in the early 1980s.

Further insertion and coupling reactions are examined in Chapter 10. The use of complexes of rhodium and ruthenium, containing phosphine ligands for hydrogenation reactions, especially carbon-carbon multiple bonds, is described as are platinum and rhodium complexes for hydrosilation. Palladium reagents and catalysts are useful for a myriad of coupling reactions involving unsaturated hydrocarbon fragments.

Chapters on organometallic cycloaddition reactions and carbene complexes provide more examples of the versatile palladium and rhodium reagents, such as palladium compounds to effect annulation reactions, and rhodium carboxylates to close the β -lactam ring in the synthesis of methylcarbapenems.

The final three chapters cover special topics, and subjects dealt with elsewhere in the book are pulled together. The synthetic strategies to be achieved using the unusual reactivity profiles of organotransition metals are emphasised. These different strategies are exemplified by the Wilkinson rhodium catalyst in achieving deprotection via isomerisation of alkenes, in natural product syntheses where palladium reagents can aid the synthesis of pheromones via oxidation.

Cross-referencing deals adequately with topics covered in more than one chapter, and the book is illustrated by clear diagrams with over 1700 references.

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