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Modern Palladium Catalysis

PALLADIUM REAGENTS AND CATALYSTS: NEW PERSPECTIVES FOR THE 21ST CENTURY

BY J. TSUJI, John Wiley & Sons, Ltd., Chichester, 2004, 670 pages
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This book is intended as an update to the original title "Palladium Reagents and Catalysts – Innovations in Organic Synthesis" written by the same author and published by Wiley in 1995 (1). It is to be used in conjunction with the original review to "cover the whole of organopalladium chemistry, from the past to the present" (mid-2003). The book gives a detailed overview of the main recent advances in organopalladium chemistry from a synthetic organic chemist's view point.

The book is organised by types of organic reactions that are catalysed or effected by organopalladium reagents. The first chapter comprises a very concise and useful summary of the basic chemistry of organopalladium catalysis. This is followed by separate chapters on each type of synthetic reaction.

The first types of reaction to be considered are oxidative reactions with Pd(II) compounds. As the author states in his introduction, 'oxidative' normally refers to a reaction of Pd where the oxidation state of the metal is increased. This chapter, however, refers to oxidation in the classical organic sense, for example, the conversion of an alkene to an aldehyde catalysed by a Pd(II) compound. The narrative begins with the first major example of this reaction, the Wacker process, and proceeds to more specific and recent examples. This chapter is detailed and includes some important chemistry contributed by the author himself. This is obviously an area close to his heart!

Pd(0)-Catalysed Reactions of Halides and Pseudohalides

The third chapter considers Pd(0)-catalysed reactions of sp^2 organic halides and pseudohalides. This is the main body of the book, comprising roughly half of the content (325 pages). It is a good reflection of both the weight of academic research into this area of chemistry, and the increasing level of industrial interest and application.

This field is often referred to as 'cross-coupling' reactions. The introduction to the chapter tries to make some sense of the many variations in this type of reaction, and each subsection describes a different type of coupling reaction. The chapter is organised in a systematic chemical manner based on the type of substrate reacted with the 'aryl halide'. A useful addition, however, is the inclusion of the generic 'names' for each type of reaction in the titles and contents. This makes it easy for a synthetic chemist to find details on each 'named reaction', for example, Heck, Sonogashira, Suzuki, Stille, Negishi and Hiyama, which is often the way coupling reactions are referred to in practice. One important area that is included, but not named as such in this chapter, is the area often referred to as Hartwig-Buchwald amination. This reaction is listed as 'arylation of nitrogen nucleophiles' and included in the general group of C, N, O, S and P nucleophiles.

This chapter reviews each type of coupling reaction well, with some mention of the historical development of the methodology and good details of the most recent, important contributions and methodologies. While it does not aim to provide details on the synthetic methods, the subject coverage is very thorough and the references provide ample leads for practical application of the chemistry. I believe I am reasonably well informed in some areas of coupling chemistry, and I was pleased to see all of the major recent contributions in the specific areas in the text. Based on this observation, it is clear that the author has provided a well-researched and comprehensive overview of this vast chosen field of palladium chemistry.

Pd(0)-Catalysed Reactions of Allylic Compounds

The next major area reviewed is that of the reactions of allylic compounds. This is a well-established area of chemistry and has both achiral and chiral synthetic utility. There is a useful general introduction to the various types of this reaction. This chapter covers chemistry from 1965 to the present, so there is a much to cover. It is well ordered in a logical, chemistry/reagent based system. Almost every reaction possible with an allylic substrate catalysed by Pd is mentioned, and the references provide a useful follow-up.

Other Pd-Catalysed Reactions

The next three chapters cover reactions of 1,2- and 1,3-dienes and methylenecyclopropanes; propargyl compounds; and alkynes and benzynes. These short chapters (of 20 to 30 pages) provide a good flavour of these less common areas of Pd chemistry and again most of the main issues and recent advances are covered.

The final three chapters deal with alkenes, and miscellaneous reactions, and mention palladium-catalysed reactions that the author sees as important but which do not fit in with the systematic subject order of the main chapters. This is useful and interesting to see glimpses of possible future areas of important chemistry. There is also a useful set of tables detailing a long list of the ligands mentioned in the book. On perusal it appears that all of the major advances in ligand technology are there.

In conclusion, this monograph is well written and a very well researched review of recent years in palladium chemistry. It provides the reader with a reliable starting point for learning about and even performing palladium-catalysed reactions. It is definitely worth the investment.

The author has succeeded in completing his aim to cover the whole of organopalladium chemistry, in a systematic and logical manner. The book can act as a valuable learning tool and reference point to release the potential of the wealth of palladium chemistry that is now available.

The only criticism, from my point of view, could be that the book does not try to compare various contributions to the fields of chemistry in terms of their actual usefulness to the practical or industrial chemist. However, the author is to be congratulated on taking on such a massive task and in his success in making some sense of the vast explosion in palladium-catalysed chemistry over recent years.

Reference

1 M. V. Twigg, *Platinum Metals Rev.*, 1996, **40**, (3), 126

The Reviewer

Mark Hooper is a Senior Development Chemist in the Catalyst Development Department, at Johnson Matthey in Royston, U.K. He holds a B.A. (Hons), chemistry, and a D.Phil., in organometallic chemistry from Oxford University. From 2000–2002 he held a post-doctoral position with Professor John Hartwig at Yale University, working on palladium catalysed amination. He joined Johnson Matthey in 2002. He is interested in novel homogeneous catalysts, especially Pd catalysts for coupling chemistry and anchored homogeneous catalysts and has worked with Smopex for the recovery/ separation of precious metals.