Modern Rhodium-Catalyzed Organic Reactions

Edited by
P. Andrew Evans

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Editor:

Prof. P. Andrew Evans
Department of Chemistry
Indiana University
Bloomington, IN 47405
USA

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To Rebecca and Sarah

Foreword

The extensive application of transition metal-catalysts to organic synthesis over the last 40 years has dramatically changed the manner in which organic compounds are now prepared. Among the many transition metal-catalysts used in organic synthesis, the noble metal triad, namely palladium, ruthenium and rhodium, has played an increasingly important role in this regard. Hence, it is not an exaggeration to say that the present day is the golden age of these noble metals, which of course have their own characteristic features. Currently, palladium represents the most widely used and versatile metal, given its synthetic utility for carbon-carbon and carbon-heteroatom bond formation. More recently, ruthenium-catalysts have provided exquisite functional group tolerance and selectivity in olefin metathesis and the asymmetric hydrogenation of carbonyl compounds.

Organorhodium chemistry on the other hand has a long history, which dates back to its emergence as the metal of choice in carbonylation processes. Historically, commercial hydroformylation was carried out using a cobalt carbonyl complex as the catalyst. However, this catalyst was gradually replaced by a more active rhodium catalyst, which remains the one predominantly utilized today. A noteworthy example is the Monsanto process, which is a rhodium-catalyzed carbonylation reaction that was developed in early 1970's for the production of acetic acid from methyl iodide. The discovery of the Wilkinson complex by Wilkinson in the mid 1960's proved to be the harbinger of the development of modern organorhodium chemistry, since its discovery opened the new field of homogeneous hydrogenation. This development ultimately led to the remarkable progress in asymmetric hydrogenation, as exemplified by the commercial production of L-Dopa by a rhodium-catalyzed asymmetric hydrogenation developed in 1974 by Monsanto. Notwithstanding the early developments in hydroformylation and the discovery of the Wilkinson complex, progress in organorhodium chemistry seemed to be somewhat slower than that of organopalladium chemistry. Nonetheless, organorhodium chemistry is now rapidly emerging in organic synthesis as the number of useful synthetic methods increases. A number of new rhodium-catalyzed reactions, including several new types of cycloadditions have been discovered, offering unique synthetic methods that are often complimentary to those of palladium and ruthenium. More recent advances have come from the rhodium-catalyzed decomposition of diazo compounds to generate metal carbenoids, which in the presence of alkenes afford cyclopropanes and other derivatives. Indeed, these studies have paved the way for the recent advances in C–H activation, which facilitates the selective formation of carbon-carbon and carbon-nitrogen bonds.

Although numerous rhodium-catalyzed reactions have now been reported, frankly speaking it has been somewhat difficult to often categorize them in a systematic manner. From this standpoint, a book that summarizes the newer aspects of modern organorhodium chemistry is clearly overdue. The publication of this book, edited by Professor P. Andrew Evans, is both timely and worthwhile. The editor, in the first attempt to summarize the field of organorhodium chemistry, brings together nearly twenty topics, covering almost all known aspects of rhodium-catalyzed reactions. This book covers the following asymmetric rhodium-catalyzed organic reactions: hydrogenation (Zhang), hydroboration (Brown), conjugate addition (Hayashi), olefin isomerization and hydroacylation (Fu), hydroformylation, hydrosilylation and silylformylation (Leighton and Matsuda), cycloisomerization and cyclotrimerization (Ojima), Alder-ene (Brummond), allylic substitution (Evans and Fagnou), carbocyclizations (Jeong, Robinson and Wender), cyclopropanation and carbon-hydrogen insertion (Davies, Doyle and Taber), oxidative amination (Du Bois), ylide rearrangements (West), 1,3-dipolar cycloadditions (Austin), in which each of the chapters is clearly written by an expert in the field.

Overall, this book clearly illustrates "what we can do in organic synthesis using rhodium catalysis" and I have no doubt that it will serve as an excellent reference text for both graduate students and synthetic chemists at all levels in academia and industry. Moreover, I anticipate that this book will stimulate additional research in the area of organorhodium chemistry, and serve to inspire those involved in the development and application of new synthetic methodology.

November 2004

Jiro Tsuji
Professor Emeritus
Tokyo Institute of Technology

Preface

Although there are countless examples of rhodium-catalyzed organic reactions in the chemical literature, it is often very difficult to categorize and thereby appreciate the full impact of this transition metal within the context of target directed synthesis. *Modern Rhodium-Catalyzed Organic Reactions* provides the first comprehensive account of some of the most exciting and seminal advances in this rapidly developing field, and also serves as a historical guide to the origin of many of these impressive advances. I have tried to match internationally recognized scholars within each of the individual areas covered, while trying to be as inclusive as possible, to provide a fairly comprehensive overview of the field. However, as with any project of this nature, there are additional topics that could have been included. This book represents the contributions that utilize two of the most common oxidation states, namely rhodium(I) and (II), as catalysts and pre-catalysts for synthetic applications.

The chapters highlight the synthetic utility of the various transformations, covering each reaction from inception to its development as a synthetically useful process that is capable of achieving exquisite selectivity with excellent efficiency. Throughout each chapter the authors describe rhodium-catalyzed reactions in terms of the scope, selectivity, and mechanism, thereby providing important insight into each transformation. I think it is fair to say that many of these contributions are quite unique since they have not been previously reviewed. Moreover, the most striking feature of each contribution is the underlying difference in chemical reactivity of the rhodium-catalyzed version of a specific transformation to that involving an alternative metal-complex. Indeed, having read all the chapters the reader is left with the notion that rhodium-catalysis is unique, since it provides unparalleled levels of chemo-, regio- and stereoselectivity for many synthetic reactions. The chapters also provide a brief summary and outlook for the continued development of each of the transformations, which will be helpful to individuals already active in this area as well as those planning on breaking into the field. It is my hope that this book will provide an excellent resource for graduate students, and be a suitable reference text for a graduate level course. I also believe that this book will serve practicing synthetic chemists in academia and industry, by providing an up-to-date account of the field that given the current state-of-the-art will provide an indication of where the specific challenges remain.

I would like to dedicate this book to my loving daughters Rebecca and Sarah, in the hope that they will one day understand all the hard work required to provide a wonderful life full of opportunities. I also acknowledge my parents for their unwavering strength and encouragement to pursue my dreams irrespective of the outcome.

I would like to sincerely thank David K. Leahy, Erich W. Baum, and Santosh J. Gharpure for their assistance with the proofreading of the various chapters. I would especially like to thank and acknowledge the efforts of James R. Sawyer, who gave a significant amount of his time to painstakingly assist in the editing of the manuscript. I sincerely thank Katie for her love, support and understanding throughout what was often a very difficult time. Finally, this book would not have be possible without the participation of the authors; I am deeply indebted to each of them for taking the time out of their busy schedules, and their enduring patience throughout this project.

November 2004 *P. Andrew Evans*

Contents

List of Contributors

David J. Austin
Yale University
Department of Chemistry
225 Prospect Street
New Haven, CT 06520
USA

John M. Brown
University of Oxford
Chemical Research Center
Oxford OX1 3TA
United Kingdom

Kay M. Brummond
University of Pittsburgh
Department of Chemistry
Pittsburgh, PA 15260
USA

Yongxiang Chi
Pennsylvania State University
Department of Chemistry
104 Chemistry Building
University Park, PA 16802
USA

Huw M. L. Davies
State University of New York
University at Buffalo
Department of Chemistry
Buffalo, NY 14260-3000
USA

Michael P. Doyle
University of Maryland
Department of Chemistry
and Biochemistry
College Park, MD 20742
USA

Justin Du Bois
Stanford University
Department of Chemistry
Stanford, CA 94305-5080
USA

Christine G. Espino
Stanford University
Department of Chemistry
Stanford, CA 94305-5080
USA

P. Andrew Evans
Indiana University
Department of Chemistry
800 E. Kirkwood Avenue
Bloomington, IN 47405
USA

Keith Fagnou
University of Ottawa
Department of Chemistry
10 Marie Curie
Ottawa, Ontario K1N 6N5
Canada

Gregory C. Fu
Massachusetts Institute of Technology
Department of Chemistry
77 Massachusetts Avenue
Cambridge, MA 02139
USA

Masaki Fujiwara
Central Glass Co., Ltd.
Chemical Research Center
2805 Imafuku-Nakadai Kawagoe-shi
Saitama 350-1151
Japan

Gabriel G. Gamber
Stanford University
Department of Chemistry
121 S.G. Mudd
Stanford, CA 94305-5080
USA

Tamio Hayashi
Kyoto University
Graduate School of Science
Department of Chemistry
Sakyo, Kyoto 606-8502
Japan

Nakcheol Jeong
Korea University
Department of Chemistry
310 Asan Science Building
Seoul 136-701
Korea

Pramod V. Joshi
University of Delaware
Department of Chemistry
and Biochemistry
Newark, DE 19716
USA

David K. Leahy
Bristol-Myers Squibb
One Squibb Drive
New Brunswick, NJ 08903
USA

James L. Leighton
Columbia University
Department of Chemistry
3000 Broadway, Mail Code 3117
New York, NY 10027
USA

Isamu Matsuda
Nagoya University
Graduate School of Engineering
Chikusa, Nagoya 464-8603
Japan

Jamie M. McCabe
University of Pittsburgh
Department of Chemistry
Pittsburgh, PA 15260
USA

Iwao Ojima
State University of New York
Department of Chemistry
Stony Brook, NY 11794
USA

John E. Robinson
Array BioPharma
3200 Walnut Street
Boulder CO 80301
USA

Ruben M. Savizky
Yale University
Department of Chemistry
225 Prospect Street
New Haven, CT 06520
USA

Douglass F. Taber
University of Delaware
Department of Chemistry
and Biochemistry
Newark, DE 19716
USA

Wenjun Tang
Scripps Research Institute
Department of Chemistry
10550 North Torrey Pines Road
La Jolla, CA 92037
USA

Abbas M. Walji
State University of New York
University at Buffalo
Department of Chemistry
Buffalo, NY 14260-3000
USA

Paul A. Wender
Stanford University
Department of Chemistry
121 S.G. Mudd
Stanford, CA 94305-5080
USA

Frederick G. West
University of Alberta
Department of Chemistry
W5-67 Gunning-Lemieux Chemistry
Centre
Edmonton, Alberta T6G 1T7
Canada

Travis J. Williams
Stanford University
Department of Chemistry
121 S.G. Mudd
Stanford, CA 94305-5080
USA

Kazuhiro Yoshida
Chiba University
Faculty of Science
Department of Chemistry
Yayoi-cho, Ingae-ku, Chiba 263-8522
Japan

Xumu Zhang
Pennsylvania State University
Department of Chemistry
104 Chemistry Building
University Park, PA 16802
USA

1
Rhodium-Catalyzed Asymmetric Hydrogenation

Yongxiang Chi, Wenjun Tang, and Xumu Zhang

1.1
Introduction

Molecular chirality plays a very important role in science and technology. For example, the biological activity of many pharmaceuticals and agrochemicals is often associated with a single enantiomer. The increasing demand for enantiomerically pure pharmaceuticals, agrochemicals, and fine chemicals has therefore driven the development of asymmetric catalytic technologies [1, 2]. Asymmetric hydrogenation, using molecular hydrogen to reduce prochiral olefins, ketones, and imines, has become one of the most efficient, practical, and atom-economical methods for the construction of chiral compounds [3]. During the last few decades of the 20th century, significant attention was devoted to the discovery of new asymmetric catalysts, in which transition metals bound to chiral phosphorous ligands have emerged as preferential catalysts for asymmetric hydrogenation. Thousands of efficient chiral phosphorous ligands with diverse structures have been developed, and their application to asymmetric hydrogenation has been established. Indeed, many represent the key step in industrial processes for the preparation of enantiomerically pure compounds. The immense significance of asymmetric hydrogenation was recognized when the Nobel Prize in Chemistry was awarded to Knowles and Noyori.

In this chapter, we focus on the rhodium-catalyzed hydrogenation and the development of chiral phosphorous ligands for this process. Although there are other chiral phosphorous ligands, which are effective for ruthenium-, iridium-, platinum-, titanium-, zirconium-, and palladium-catalyzed hydrogenation, they are not discussed in this account. However, this does not preclude complexes of other transition metals as effective catalysts for asymmetric hydrogenation. Fortunately, there are numerous reviews and books that discuss this particular aspect of asymmetric hydrogenation [3].

1.2
Chiral Phosphorous Ligands

The invention of efficient chiral phosphorous ligands has played a critical role in the development of asymmetric hydrogenation. To a certain extent, the development of asymmetric hydrogenation parallels that of chiral phosphorous ligands.

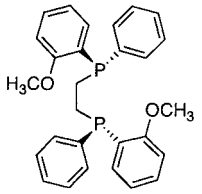
The introduction of Wilkinson's homogeneous hydrogenation catalyst, $[RhCl(PPh_3)_3]$ [4], prompted the development of the analogous asymmetric hydrogenation by Knowles [5] and Horner [6] using chiral monodentate phosphine ligands, albeit with poor enantioselectivity. Kagan and Knowles each demonstrated that improved enantioselectivities could be obtained using bidentate chiral phosphine ligands. For example, Kagan and Knowles independently reported the C_2-symmetric bisphosphine ligands, DIOP [7] and DIPAMP [8], for rhodium-catalyzed asymmetric hydrogenation. Due to its high catalytic efficiency in rhodium-catalyzed asymmetric hydrogenation of dehydroamino acids, DIPAMP was employed in the industrial production of L-DOPA [9]. Subsequently to this work, several other successful chiral phosphorous ligands were developed, as exemplified by Kumada's ferrocene ligand BPPFOH [10] and Achiwa's BPPM ligand [11].

The mechanism of the asymmetric hydrogenation is fairly well established, due to the seminal work of Halpern [12] and Brown [13]. Indeed, much of the early work in this area focused on the development of chiral rhodium catalysts, rather than expanding the reaction's substrate scope, which was limited to α-dehydroamino acids. In 1980, Noyori and Takaya reported an atropisomeric C_2-symmetric bisphosphine ligand, BINAP [14, 15]. This ligand was first used in rhodium-catalyzed asymmetric hydrogenation of α-(acylamino)acrylic acids, in which high selectivities were reported for certain substrates [16]. The discovery that the Ru–BINAP system could efficiently and selectively affect the asymmetric hydrogenation of various functionalized olefins [17], functionalized ketones [18], and unfunctionalized ketones [19] led to the development of other atropisomeric biaryl bisphosphine ligands, as exemplified by Miyashita's BICHEP ligand [20] and Schmid's BIPHEMP/MeO-BIPHEP [21, 22] ligands.

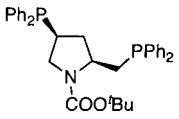
Achiwa has successfully developed the modified DIOP ligands, MOD-DIOP and Cy-DIOP, by varying their electronic and steric properties; MOD-DIOP was applied to the asymmetric hydrogenation of itaconic acid derivatives with up to 96% enantioselectivity [23]. A series of modified BPPM ligands such as BCPM and MCCPM were also developed by Achiwa [24], and some excellent chiral 1,2-bisphosphane ligands such as NORPHOS [25] and PYRPHOS (DEGUPHOS) [26] have been developed for the rhodium-catalyzed asymmetric hydrogenation. Several 1,3-bisphosphane ligands, such as BDPP (SKEWPHOS) [27], have been prepared and examined.

Hayashi and Ito developed the (aminoalkyl)ferrocenylphosphine ligand **L1**, which was successfully applied to the rhodium-catalyzed hydrogenation of trisubstituted acrylic acids [28]. In the early 1990s, significant progress was achieved with the application of the chiral bisphosphorous ligands, DuPhos and BPE developed by Burk *et al.* [29, 30], to the enantioselective hydrogenation of α-(acylamino)acrylic acids, enamides, enol acetates, β-keto esters, unsaturated carboxylic acids, and itaconic acids. Scheme 1.1 shows the several important chiral phosphine ligands studied before the early 1990s.

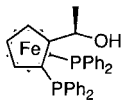
Inspired by the excellent results of chiral ligands such as BINAP and DuPhos, many research groups have devoted their efforts to designing and discovering new efficient and selective chiral phosphorous ligands. A major feature in the design of the new chiral phosphorus ligands is the ability to tune the steric and electronic properties of ligands within a given scaffold. These new ligands, which have proven efficient and selective for the asymmetric rhodium-catalyzed hydrogenation, can be divided into several different categories.



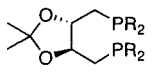
(*S*,*S*)-DIPAMP



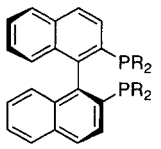
(*S*,*S*)-BPPM



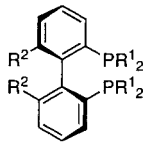
(*R*,*S*)-BPPFOH



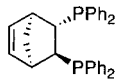
(*S*,*S*)-DIOP: R = Ph
(*S*,*S*)-Cy-DIOP: R = Cy
(*S*,*S*)-MOD-DIOP:
R = 3, 5-(Me)$_2$-4-(MeO)C$_6$H$_2$



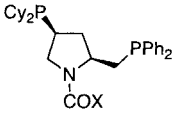
(*S*)-BINAP: R = Ph
(*S*)-TolBINAP: R = 4-MeC$_6$H$_4$
(*S*)-XylBINAP: R = 3,5-(Me)$_2$C$_6$H$_3$



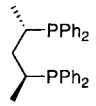
(*S*)-BICHEP: R^1 = Cy; R^2 = CH$_3$
(*S*)-BIPHEMP: R^1 = Ph; R^2 = CH$_3$
(*S*)-BIPHEP: R^1 = Ph; R^2 = OCH$_3$



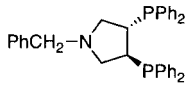
(*S*,*S*)-NORPHOS



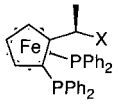
(*S*,*S*)-BCPM: X = O^{t}Bu
(*S*,*S*)-MCCPM: X = NHMe

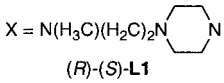


(*S*,*S*)-BDPP

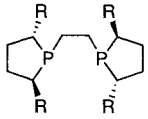


(*S*,*S*)-PYRPHOS

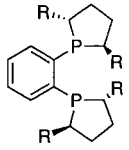




(*R*)-(*S*)-**L1**



(*S*,*S*)-Me-BPE: R = Me
(*S*,*S*)-Et-BPE: R = Et
(*S*,*S*)-^{i}Pr-BPE: R = ^{i}Pr

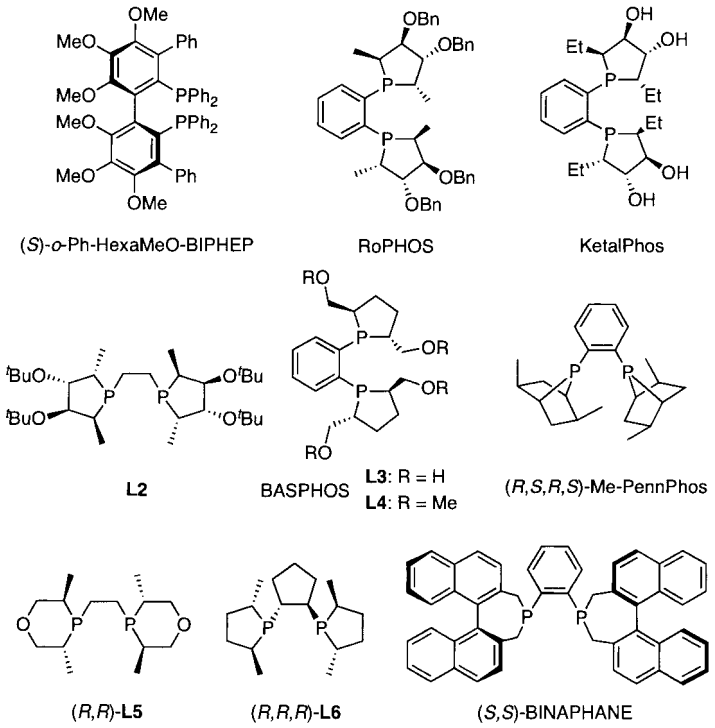


(S,*S*)-Me-DuPhos: R = Me
(*S*,*S*)-Et-DuPhos: R = Et
(*S*,*S*)-^{i}Pr-DuPhos: R = ^{i}Pr

Scheme 1.1

1.2.1
Atropisomeric Biaryl Bisphosphine Ligands

Modification of the electronic and steric properties of BINAP, BIPHEMP, and MeO-BIPHEP led to the development of new efficient atropisomeric ligands. Although most of them are efficient for ruthenium-catalyzed asymmetric hydrogenation [3], Zhang *et al.* have recently reported an *ortho*-substituted BIPHEP ligand, *o*-Ph-HexaMeO-BIPHEP, for the rhodium-catalyzed asymmetric hydrogenation of cyclic enamides (Scheme 1.2) [31].



Scheme 1.2

1.2.2

Chiral Bisphosphane Ligands Based on the Modification of DuPhos and BPE

An array of bisphosphanes has emerged based on modification of the DuPhos and BPE ligands, which have proven so successful for the asymmetric hydrogenation of functionalized olefins and ketones (Scheme 1.2). Börner [32], Zhang [33], and Rajan-Babu [34] have independently reported a series of modified DuPhos and BPE ligands – RoPhos, KetalPhos, and **L2** – derived from readily available D-mannitol. The ligand with four hydroxy groups, KetalPhos, enabled the hydrogenation to be carried out in aqueous solution with high enantioselectivity. Another water-soluble ligand, BASPHOS (**L3**), developed by Holz and Börner, also exhibits high efficiency for asymmetric hydrogenation in aqueous solution [35].

Zhang *et al.* reported a sterically bulky and conformationally rigid bisphosphane, PennPhos, which shows excellent enantioselectivity for rhodium-catalyzed hydrogenation of aryl/alkyl methyl ketones [36], cyclic enamides, and cyclic enol acetates [37]. Helmchen's bisoxaphosphinane ligand **L5** [38] and Zhang's bisdinaphthophosphepine ligand BINAPHANE [39] provide excellent enantioselectivity (up to 99% *ee*) for hydrogenation of *E*/*Z*-isomeric mixtures of *β*-substituted arylenamides. The BPE analog (*R*,*R*,*R*)-1,2-bis(phospholano)cyclopentane, **L6**, provides improved enantioselectivity for the hydrogenation of dehydroamino acids [40].