

“Iridium Catalysis”

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“Iridium Catalysis”, edited by Professor Pher Andersson of Uppsala University, Sweden, is another excellent contribution in the outstanding series, Topics in Organometallic Chemistry. Here for the first time in this series is a collection of modern applications of iridium organometallic complexes for the catalysis of organic reactions. The eight chapters cover a range of types of reactions (described below) that are of strong interest in organic synthesis, and provide extensive up-to-date coverage of both the scope and limitations of the catalysts. This work will be a valuable resource for those who are just entering into the field and want to obtain a thorough overview of how iridium can be used in catalysis.

History of Iridium in Catalysis

The book opens with a chapter by Robert Crabtree (Yale University, USA), in which he presents a personal historical perspective of the development of iridium in catalysis. It is astonishing to realise that early on, iridium found little use in organometallic catalysis, as the more successful rhodium-based Wilkinson’s catalyst (1) was dominating interest in the field. Crabtree takes the reader through the series of step-by-step developments in iridium chemistry, focusing on the contributions that individual researchers have made to propel the field forward, for example, Richard Schrock (Massachusetts Institute of Technology, USA), John Osborn (Laboratoire de Chimie des Métaux de Transition et de Catalyse associé au CNRS, Université Louis Pasteur, Institut Le Bel, Strasbourg, France), Hugh Felkin (CNRS Natural Products Institute, Gif-sur-Yvette, France) and Gilbert Stork (Columbia University, USA). He presents the development of important breakthroughs leading to the widespread use that iridium catalysts enjoy today, including the use of alcohol functionality to selectively direct hydrogenations to only one face of an olefin and the importance of *t*-butylethylene as a hydrogen acceptor. This chapter was fun to read and is one that I will share with my students to show them how a field develops over time by the successive contributions of individuals.

Iridium-Catalysed Hydrogenation

Chapter 2 by Carmen Claver *et al.* (Universitat Rovira i Virgili, Tarragona, Spain) describes the broad range of phosphines, both bidentate and monodentate, which have been employed in iridium-based hydrogenations of C–N double bonds. One nice feature of the report is that comparative data are provided with different phosphines. For example, enantioselective imine hydrogenations with BINAP, DIOP (**Figure 1**), and bis(diphenylphosphino)pentane are presented in tabular form so that one can quickly determine which ligand is best for which type of substrate. About a dozen different chelates are presented and compared, as are several chiral monodentate phosphites and phosphoramidites. Substrates include imines, enamines, quinolines and quinoxalines.

Chapter 3 by David Woodmansee and Andreas Pfaltz (University of Basel, Switzerland) focuses on enantioselective olefin hydrogenations, in which iridium is ligated by P–N or C–N chelates. In an immediate recognition of the importance of mechanism, the authors highlight the effect of the anionic counter ion on the rate of the cationic iridium catalysts. A large non-coordinating anion such as 'BAR^F₄[−]' ([B{3,5-(CF₃)₂C₆H₃}₄][−]) is the counter ion of choice in most examples presented. Preferred choices between diastereotopic hydrogenation intermediates are revealed using the PHOX chiral ligand (**Figure 2**). Many combinations of ligand and substrate are then presented to provide a broad view of the capabilities of these catalysts. Stereocontrol is outlined in the hydrogenation of substrates including trisubstituted olefins, fluorinated olefins, vinylboronates, allylic alcohols, conjugate double bonds, *gem*-disubstituted olefins and enol ethers.

Hydrogen Transfer Reactions

Chapter 4 by Ourida Saidi and Jonathan Williams (University of Bath, UK) presents iridium-catalysed hydrogen

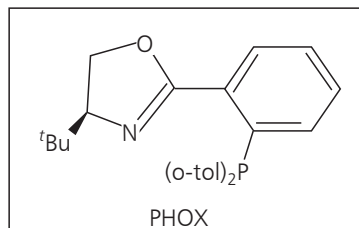


Fig. 2. The structure of the PHOX ligand

transfer reactions, focusing mainly on ketone/aldehyde exchanges but also including other substrates. First, three distinct mechanisms for metal-based hydrogen transfer are presented and the case is made that each is potentially feasible for the reversible hydrogenation of ketones or aldehydes depending on the nature of the ligands present. Next, extension to other substrates such as α,β -unsaturated ketones, styrenes and imines is given. Examples of asymmetric hydrogen transfer to these same substrates are presented using ligands that react *via* the concerted hydrogen transfer mechanism (see **Figure 3**). Several iridium complexes are shown to be effective for the reverse reaction, alcohol oxidation, and as a result, dynamic kinetic resolution processes have been developed by coupling the reversible step with a second enantioselective enzymatic step. Reversible imine/amine hydrogenation is also shown to permit manipulations of the groups attached to nitrogen.

Chapter 5 by John Bower and Michael Krische (University of Oxford, UK, and University of Texas at Austin, USA) addresses C–C bond formation *via* iridium-catalysed hydrogenation and transfer hydrogenation. The first part shows how alkynes and allenes can be used to serve as vinyliridium surrogates to allow C–C additions to electrophilic substrates, or to alcohols following dehydrogenation. Examples of iridium-catalysed

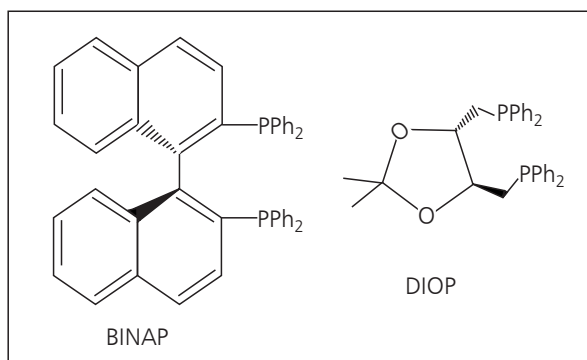


Fig. 1. The structures of the BINAP and DIOP ligands

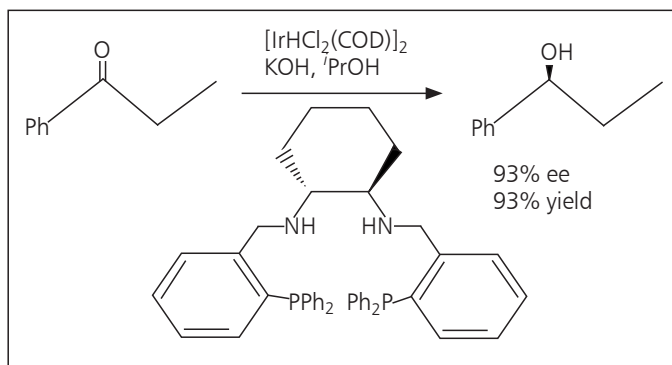


Fig. 3. Iridium-catalysed concerted hydrogen transfer reaction

reactions in which dienes, alkynes and allylic acetates provide allyliridium intermediates that couple with aldehydes to give homoallylic alcohols, in some cases enantioselectively, are given.

Functionalisation of C–H Bonds

Chapter 6 by Jongwook Choi and Alan Goldman (Rutgers, The State University of New Jersey, USA) summarises iridium-catalysed C–H bond functionalisation. The authors quickly move from the earliest reports of iridium-based alkane transfer dehydrogenation for the production of olefins to the important development of ‘acceptorless’ dehydrogenation. As an example of a tandem reaction involving alkane dehydrogenation by iridium, a second metathesis catalyst takes the olefin formed, scrambles the chain length *via* olefin metathesis, and the iridium complex then re-hydrogenates the metathesised olefin. The net result is ‘alkane metathesis’. Other types of dehydrogenations using iridium catalysts are also described, allowing formation of enamines from alkylamines. Iridium catalysts have found a broad use in arene borylation, producing the highly valued arylboron reagents for use in Suzuki coupling. These iridium catalysts have found applications in arene silylation using disilane reagents for direct C–H arylation. Iridium catalysts are also reported that have limited use in C–C bond formation, such as alkylation of arenes and biaryl formation.

Allylic Substitution

Chapter 7 by John Hartwig and Mark Pouy (University of Illinois, USA) covers iridium-based allylic substitution. As with other chapters, Hartwig and Pouy present a historical overview of nucleophilic attack on iridium-allyl complexes. This proceeds through a survey of ligands used for enantioselective C–C forming reac-

tions using PHOX, PYBOX, DIAPHOX, phosphoramidite, and chiral phosphite ligands. The authors then proceed to discuss recent advances in catalyst design resulting from identification of the catalytic intermediate in the phosphoramidite reaction, in which a C–H activation of the ligand had occurred. Fine tuning of the ligand led to excellent yields and enantiomeric excesses (ees) for enantioselective coupling of amines and soft carbon nucleophiles with allyl carbonate substrates (see **Figure 4**). The chapter concludes with detailed mechanistic discussion of the intermediates involved in these coupling reactions and the challenges that remain in allylic substitution.

1,3-Dipolar Cycloadditions

Chapter 8 by Daniel Carmona and Luis Oro (University of Zaragoza-CSIC, Spain) finishes off the collection by presenting a summary of 1,3-dipolar additions to alkenes and alkynes using iridium catalysis. For comparison, related reactions with other transition metal complexes (for example, iron or ruthenium), are included. With iridium, the enantioselective dipolar addition of a nitron to methacrolein is discussed as one of the more studied reactions with iridium. Both the catalytic cycle and the origin of the enantioselectivity are discussed.

Conclusion

Overall, “Iridium Catalysis” will serve as a useful up-to-date resource for both those entering the field and those experienced chemists who may not be aware of the advances that have been made. In one location, one has access to a range of organometallic catalysis using the latest ligands and reaction conditions. The only topic that I did not see covered is the industrial uses of iridium catalysis (for example, in the Cativa™

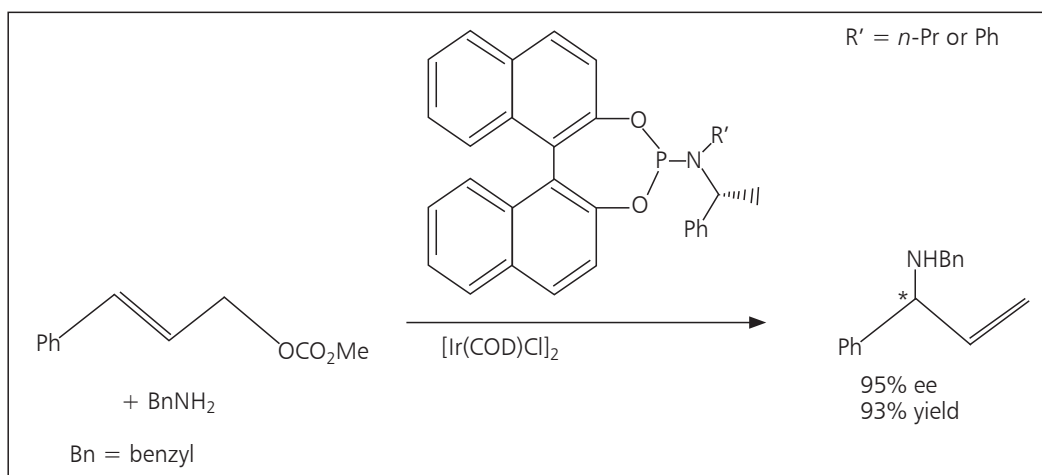


Fig. 4. An example of an enantioselective coupling of an amine and a soft carbon nucleophile with allyl carbonate substrate, with an iridium catalyst

process (2)), but otherwise the book is complete. Many examples of iridium catalysis in enantioselective chemistry are included. The book includes a historical perspective on some of the problems that shows chemistry as a living subject. Readers will be stimulated to find new applications for iridium in catalysis after they examine this book.

References

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The Reviewer



William D. Jones received his BS in Chemistry at Massachusetts Institute of Technology, USA, in 1975. He obtained a PhD degree in Chemistry at California Institute of Technology in 1979 with Robert G. Bergman, and moved to the University of Wisconsin as a National Science Foundation (NSF) postdoctoral fellow with Professor Chuck Casey. He began at the University of Rochester in 1980, where he is now the Charles F. Houghton Professor of Chemistry. Jones' research interests include organometallic research in strong C–X bond cleavage, catalysis, model studies, mechanisms, kinetics, thermodynamics and synthetic applications.