

Iridium Complexes in Organic Synthesis

Catalysis of organic reactions by the platinum group metals is a cornerstone of modern chemistry, in terms of both fundamental research and industrial applications. Of these transition metals, those from the 4d series (Ru, Rh, Pd) are generally perceived to be the more active catalysts for organic transformations, while those from the 5d series (Os, Ir, Pt) are often viewed as more inert, while providing useful models for reactive complexes from the second row. In reality, there are many exceptions to this general perception, and many useful catalysts based on the heavier metals are known. This book is the first to provide comprehensive coverage of the application of one of these metals, iridium, in organic synthesis. An impressive list of authors has contributed 15 chapters that review progress across the full range of current research in this area.

In the opening chapter, Blaser gives a concise and authoritative overview of the application of iridium catalysts in the fine-chemicals industry. This includes an iridium–diphosphine-catalyzed imine hydrogenation process (developed by Ciba-Geigy, now Solvias) for production of the herbicide (*S*)-metolachlor, which is currently the largest commercial application of enantioselective catalysis. Potential opportunities for the development of new iridium-based fine-chemicals processes are also considered by Blaser.

Chapters 2 and 3 deal with the organometallic chemistry of particular classes of iridium complex and their catalytic applications. Oro discusses triisopropylphosphine complexes and their behavior in hydrogenation reactions, while Peris and Crabtree review the recent growth in the use of N-heterocyclic carbene ligands in iridium chemistry and catalysis. In both chapters there is an emphasis on the fundamental organometallic chemistry and mechanistic aspects. The following two chapters focus on hydrogenation and hydrogen-transfer processes, an area of substantial research interest.

Bianchini and co-authors provide detailed coverage of C=O hydrogenation reactions, with particular emphasis on the wide variety of ligands that have found use in these processes. Fujita and Yamaguchi then review the use of pentamethylcyclopentadienyl iridium complexes in hydrogen-transfer reactions. A chapter by Dorta on hydroamination of alkenes and alkynes gives extensive coverage to both the catalytic behavior and reaction mechanisms. This is followed by an informative review of boron addition reactions by Fernández and Segarra.

A chapter by Kalck and Serp, dealing with the carbonylation of methanol, illustrates how an

iridium catalyst can compete effectively with an established and successful rhodium-based process.

Asymmetric allylic substitutions catalyzed by iridium complexes are addressed by Helmchen, with reactions of C, N, and O nucleophiles being considered in turn. Carbon–carbon (and carbon–heteroatom) bond-forming reactions are covered in chapters by Ishii and co-authors (coupling reactions) and Shibata (cycloadditions). Albrecht and Morales-Morales then review the application of iridium pincer complexes in a range of bond-activation processes.

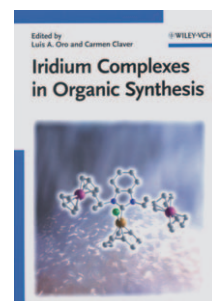
Iridium has played a significant role in the development of C–H activation chemistry, and this is further exemplified in the subsequent chapter by Morales-Morales on alkane dehydrogenation. The recent combination of iridium pinners with molybdenum alkylidene complexes to give a “tandem” catalyst for alkane metathesis provides a notable topical example in these sections. Marciniec and Kownacki describe iridium catalysts for transformations of organosilicon compounds and, in the final chapter, Scholten and Dupont review the catalytic properties of soluble iridium nanoparticles, another topic of growing importance.

It is apparent, from the large number of catalytic reactions covered, that iridium complexes are active for a very wide range of organic processes and that informed choice of appropriate supporting ligands and reaction conditions is key to the development of efficient catalysts. For any researcher working in the field of homogeneous catalysis, this book will certainly prove useful for making such selections and designing new catalysts. It also gives considerable insight into the fundamental organometallic chemistry and underlying reaction mechanisms. As well as providing historical context, the book also includes many illuminating examples from the recent literature, representing the current state of the art. It is expertly edited by Oro and Claver who are widely recognized for their expertise in organometallics and catalysis. The index enables cross-referencing to link themes from different chapters.

In summary, both academic and industrial practitioners of transition-metal catalysis and organometallic chemistry will find this volume to be a very useful addition to their bookshelves. I would also recommend it for university library collections, where it will prove to be a valuable reference source for graduate students.

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