Olefin Metathesis: Theory and Practice

During the last few decades, olefin metathesis has gained considerable importance in modern synthetic chemistry as a preferred methodology for the manipulation of carbon–carbon double bonds, offering an attractive and simplified alternative to traditional methods for synthesizing complex organic molecules and polymers. Historically, the late Yves Chauvin[*] will be remembered as the elder scientific father of this reaction, because he was the first to understand its mechanism, as published in 1971. More recently, major advances in the field were shaped by the introduction of the first generations of well-defined olefin metathesis catalysts, namely, Schrock's Mo-based catalyst in the 1980s, and Grubbs's Ru-based catalysts in the 1990s. The worldwide importance of these findings was recognized by the award of the 2005 Nobel Prize to Y. Chauvin, R. R. Schrock, and R. H. Grubbs. These major achievements and relevant developments were collected in the comprehensive three-volume Handbook of Metathesis edited by R. H. Grubbs in 2003. Since then, the continuing growth of the field has justified the timely publication of this single-volume book, a perfect companion for every chemist who wishes to enter the "change partners dance" of double bonds.

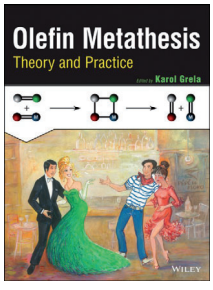
According to its title, this book covers all aspects of olefin metathesis, whereas the parent domains of alkyne and alkane metathesis reactions, whose parallel but more recent spectacular developments might deserve a separate coverage, are just mentioned in the introductory chapter. As the field of olefin metathesis is especially prolific (the numbers of new scientific publications have regularly reached 600 per year during the past decade), the editor's task must have been tremendous. Thanks to his well-known commitment and persuasive enthusiasm, he enrolled in the adventure a panel of 55 authors representative of world-class academic and industrial researchers from across various disciplines in chemistry in which metathesis is involved. The book of 25 chapters is structured in two main parts: "Applications of olefin metathesis reactions" and "Development of the tools". Each of these is sub-divided into two sections of a more specific nature. Although a classification can never be perfect, the present one has the merit of clarity. In this book review there is not enough space to go through each section in detail, but the following paragraphs give a rapid overview, highlighting specific chapters or points that seem particularly valuable.

The introductory chapter (Chapter 1, by Astruc) begins with a thorough discussion of the historical developments of olefin metathesis. We particularly appreciate the author's care to place the reported historical findings in the context of the contemporary scientific knowledge. It continues with an overview of the general trends in modern olefin metathesis. Actually, this chapter may be regarded as a summary reflecting the general content of the book, and as such it will be of great benefit to readers looking for a quick and concise entry into the field.

Section 2 describes in detail the different types of olefin metathesis reactions, and consists of six very well written and detailed chapters. The one on cross-metathesis, by Zukowska and Grela, stands out by introducing a new classification of cross-metathesis partners, based on the nature of the functional groups attached to the olefin and the length of the link. This nicely complements the earlier classification introduced by Grubbs in 2003. In the second chapter of the section, devoted to ring-closing metathesis, Fogg and co-workers have made an impressive job of reviewing, in a concise and understandable way, the myriad of (sometimes widely scattered) results. This deliberatively selective review (based, however, on 350 references) is well organized and will long remain an extremely useful guide for users. The chapter on domino reactions implying one or more metathesis steps will help the reader to appreciate the huge potential of this strategy in synthetic organic chemistry.

The same feeling prevails in the next section, on the applications of metathesis. The topics include the total synthesis of natural and pharmaceutical compounds, the synthesis of organometallic compounds, and the transformation of renewable feedstocks. Naturally, there are two chapters on metathesis in industrial processes. Particularly instructive and relevant are the authors' choices in Chapters 8 (total synthesis) and 12 (scaling the ring-closing metathesis reaction in the pharmaceutical industry), where they focus on three representative examples to discuss the requirements and challenges.

After Chapter 13, which deals with metathesis catalysts based on early transition metals, five chapters (14–18) are devoted to the broad palette of Ru-alkylidene metathesis catalysts. Here the unavoidable overlaps between these chapters might invite some minor criticism. However, as organometallic chemists we really appreciated Chapter 15 by Nolan, Cazin, and co-workers on the Ru-indenylidene, -vinylidene, and -allenylidene complexes, which is full of detailed information on organometallic synthesis and reactivity. In a different style, Chapter 16 by Ginzburg and Lemcoff,



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[*] Yves Chauvin passed away on January 28, 2015. This book review is dedicated to his memory.

devoted to Hoveyda-type complexes, is very helpful in showing the degree of sophistication now reached by these tunable pre-catalysts, and explaining how structural modifications of their modular components allow a precise control of the balance between stability, activity, and relevant catalytic performance. In addition, Chapter 19 on the theoretical aspects of Ru-based metathesis provides an indispensable contribution to give a rationalization and theoretical treatment of the observed trends. For simplicity, Cavallo and co-authors only present here the results of the theoretical calculations (reaction and deactivation pathways, etc.) conveniently sparing us too many computational details. Finally, Chapters 20–25 summarize the methods to develop recyclable and/or greener catalytic systems, which ideally can also lead to products free from traces of Ru.

Illustrative of the guiding intention of the book is Section 6, which lists the commercially available metathesis catalysts (62 entries!). The volume is also particularly useful in that almost every chapter includes inserts that give representative examples of experimental procedures, helping readers to figure out how metathesis reactions are typically carried out. The literature citations are very complete, and many of them date from after the publication of Grubbs's handbook (2003). Moreover, as the chapters are independent of each other, they can be read in any order. Inevitably, most of them start with almost the same list of metathesis catalysts, and as there is no unified labeling scheme the same compounds appear repeatedly from chapter to chapter with different label numbers, which is confusing for the reader.

In summary, this excellent book, whose artistic eye-catching cover is very elegant, will serve as a perfect companion to chemistry students for gaining a solid basic knowledge of modern metathesis, and also for researchers seeking an in-depth treatment of a specific metathesis topic. It will undoubtedly find its place on our bookshelves and in university and industrial libraries.

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