Understanding Organometallic Reaction Mechanisms and Catalysis: Computational and Experimental Tools

Computational methods are rapidly becoming "just one of the tools" in the study of organometallic reaction mechanisms. In that context, a book on this topic is timely.

More than half of the chapters in this volume focus on the traditional "energy profile" approach to understanding and distinguishing between mechanisms. Of these, I particularly enjoyed Chapters 3 (by Slattery, Lynam, and Fey) and 4 (by Schoenebeck) because they explained how choices were made between experimental and computational approaches, depending on the problem being considered. These authors also emphasize that theory alone will rarely provide a comprehensive picture of a reaction.

Chapter 5 (by Gutierrez and Kozlowski) describes numerous complex rearrangements catalyzed by Pd and Au, where computational methods have certainly been useful in elucidating mechanisms. However, no unifying picture seems to emerge from these studies. Similarly, Chapter 6 (by Fan and Lin) on CO_2 functionalization mainly presents rationalizations of experimental results, aided by calculations. These authors make the important point that many such reactions are thermodynamically unfavorable.

Chapter 8 (by Lup, Christensen, and Fristup) is more methodological, and focuses on "Hammett plot" and "kinetic isotope effect" approaches to determining mechanisms. The selected examples are elegant, but unlike the rest of the book this chapter is marred by annoying errors.

Chapter 9 (by Kozuch) should be required reading for anyone who contemplates publishing an energy profile and using it to understand kinetics. It starts out in a somewhat heavy mathematical style, but is very readable and a bit tongue-in-cheek. In reviewing manuscripts, I have frequently seen even experienced researchers fall into some of the "traps" mentioned in this chapter, and I wish that I could have referred such authors to this text.

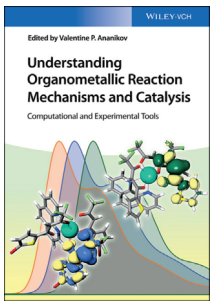
A few chapters cover topics of a somewhat more exotic nature. Chapter 1 (by Kretschmer, Schlangen, and Schwarz) discusses gas-phase reactivity of ions, where the connection between theory and experiment is clearer but the relation to everyday chemistry is weaker. Chapter 7 (by Zhivonitko and co-authors) on para-hydrogen induced polarization first explains the principles of this elegant technique well, but then focuses on studies of heterogeneous catalysis, where interpretation of the results is difficult, if at all possible.

Chapter 10 (by Barone, Biczysko, and Carmineo), the longest in the book, is rather formula-heavy but does a good job in illustrating the impressive accuracy one can achieve with modern tools in predicting vibrational and electronic spectra. Unfortunately, the connection with "organometallic reaction mechanisms" is somewhat tenuous.

The final chapter (Chapter 11, by Polynski and Ananikov) reviews computational studies of metals interacting with graphene. It starts with a rather extensive discussion of methods and benchmarks, but then summarizes about 60 case studies. This is certainly a "hot" area, but I have the impression that many of the models studied computationally have only a modest basis in experiment. A clear conclusion is that this type of chemistry is dominated by defects and edge functionalities of graphene sheets, and consequently the task of modeling these systems is far from trivial.

As can be seen above, the book covers a wide area of chemistry, from gas-phase atomic reactivity via traditional solution-phase organometallics to nanoclusters on graphene, and the volume is roughly organized along this "from smallest to largest" progression. The approach is not very balanced or comprehensive. For example, on the computational side, dynamic methods are not covered at all (although Chapter 11 refers to several dynamics studies) while on the experimental side surface-specific techniques receive little attention. The authors approach their topics in different ways, some mostly highlighting an interesting selection of their own work, while others aim to give a comprehensive review of an area. Therefore, despite the real quality of many chapters, the book feels somewhat like a collection of monographs without a strong unifying theme.

Who should buy this book? It is probably too heterogeneous in nature to be used for a graduate course in mechanistic studies, although some individual chapters (3, 4, 8, and certainly 9) would be useful in such a context. For experimentalists, this work will probably increase the appreciation of what computational chemistry can and cannot do. For researchers already working in the area, using computational methods in conjunction with experimental approaches, this volume provides some valuable insights and gives a good impression of what would nowadays be considered "middle-of-the-road" and "state-of-the-art" computational work. Your university library should probably have a copy.



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