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"Understanding Organometallic Reaction Mechanisms and Catalysis: Computational and Experimental Tools"

Edited by Valentine P. Ananikov (Russian Academy of Sciences, Russia), Wiley-VCH Verlag GmbH & Co KGaA, Germany, 383 pages, ISBN: 978-3-527-33562-6, £115.00, €138.00, US$190.00

Reviewed by Balaji Sukumar
Johnson Matthey Inc
900 Forge Avenue, Suite 100, Audubon,
Pennsylvania 19403, USA

Email: Balaji.Sukumar@jmusa.com

This review is about the book "Understanding Organometallic Reaction Mechanisms and Catalysis: Computational and Experimental Tools" edited by Valentine P. Ananikov, a professor at the Russian Academy of Sciences who has contributed much to the field of catalysis in the past decade. His work has received international attention along with many awards and research grants. He has been working on developing new concepts in transition metal and nanoparticle catalysis, sustainable organic synthesis and mechanistic studies of complex chemical transformations, which gives him the required background and expertise to edit a book that consolidates various experimental and computational tools used by various research groups around the world.

This book is a collection of chapters written by renowned professors and researchers in this field from Russia, Italy, Denmark, Germany, the United Kingdom, Hong Kong and the United States of America. Although there are many other books on organometallic reactions focusing separately on fundamentals, experiments and computational studies, the uniqueness of this book is to highlight new horizons in studying reaction mechanisms by drawing from the first-hand experience of experts who have worked both on computational and experimental tools. The book succeeds in convincing the reader about the importance of translating the knowledge obtained from state-of-the-art theoretical methods to experimental studies and *vice versa* to facilitate mechanistic studies leading to better understanding and innovation in the field of catalysis.

The book consolidates studies from different groups that emphasise the benefits of integrating experimental techniques along with computational tools (mainly density functional theory (DFT)) to understand organometallic reaction mechanisms and catalysis. The book is aimed at people looking for ways to use the recent advances in experimental and computational chemistry in their research. It assumes readers have prior background in kinetics and the fundamentals of DFT.

There are some chapters in this book that deal only with case studies, presenting their results and discussion without much introduction or discussion of fundamentals. Such chapters are useful for those who are familiar with that particular area of research but will be more difficult to follow for a reader who is looking for generic information on what and why certain techniques are used. Out of the 11 chapters, this review covers Chapters 1 to 4, 8 and 9.

Chapter 1 is written by Robert Kretschmer, Maria Schlangen and Helmut Schwarz (Institut für Chemie, Germany). This chapter focuses on two gas-phase carbon-nitrogen coupling processes with metal complexes bearing carbon- and nitrogen-based ligands (**Figure 1**). The studies look at thermal reactions of these ligands with ammonia and hydrocarbons, elucidating the mechanisms of metal-mediated coupling reactions. This chapter launches immediately into the case study at hand without introducing the reader to any background connecting to the title of the book. This was rather disappointing as the chapter would have benefited from additional background to introduce the topic given its position within the book.

Adrian Varela-Alvarez and Djamaladdin G. Musaev (Emory University, USA) have written the second chapter on transition-metal-catalysed C–H bond alkylation by diazocarbene precursors. The chapter is well written with a nice flow of thought, starting from the electronic structure of free carbenes and discussing the nature and factors affecting the stability of the metal-carbene bond. Theoretical models and methods used (such as the polarisable continuum model) are introduced first, followed by an example to show how to use these theoretical methods to design a catalyst with a non-redox-active metal and a non-innocent ligand. Based on the theoretical predictions (there is no experimental proof), the chapter concludes that the inclusion of donor substituents to the carbene fragment makes diazocarbene decomposition more exergonic and a benzylic C–H bond alkylation catalysed by a complex containing a non-redox calcium(II)-centre and a non-innocent pyridine diimine (PDI) ligand is practically possible.

Chapter 3 is written by John M. Slattery, Jason M. Lynam (University of York, UK) and Natalie Fey (University of Bristol, UK). This is a very well written chapter keeping in mind the scope of the book. Initially the authors talk about the importance of experimental and computational techniques and how both should go hand in hand – backed by nice examples – using metal vinylidene complexes. This chapter gives an excellent overview of experimental and computational methodologies, different options in DFT calculations and pitfalls in using the functionals – a good source of information for a beginner. After discussing extensively the methodologies, the chapter proceeds to a selection of case studies. Four case studies looking at the mechanisms of: (a) Rh-mediated alkyne to vinylidene transformation, (b) ruthenium-vinylidene complex formation, (c) vinylidenes in gold catalysis, and (d) the effects of metal on alkyne/vinylidene tautomers are discussed in detail.

Chapter 4 is written by Franziska Schoenebeck (RWTH Aachen University, Germany). This is again a nice chapter that concentrates on selected mechanistic studies using both experimental and computational approaches to study reactivities derived from palladium

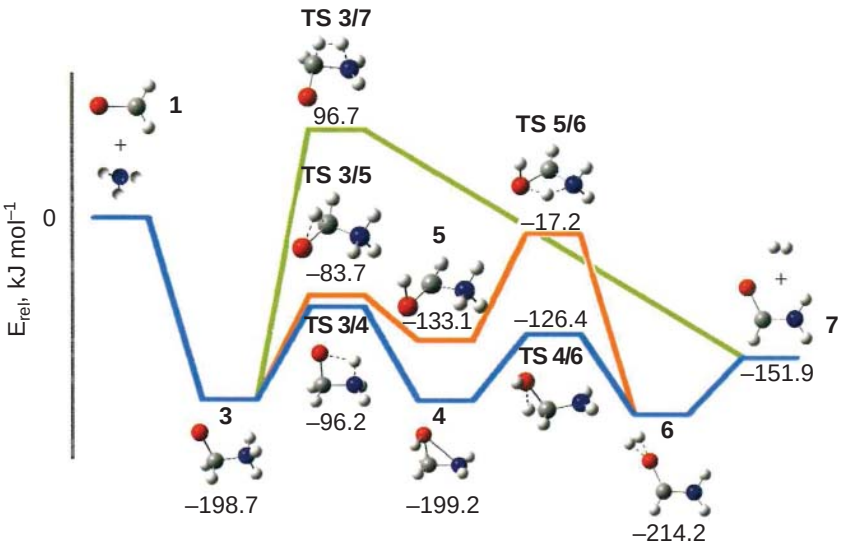


Fig. 1. Simplified potential energy surface (PES) of the reaction $[Pt(CH_2)]^+/NH_3$ > $[Pt(CHNH_2)]^+/H_2$ calculated for the doublet spin surface at the B3LYP/TZP//B3LYP/DZP level. Red = Pt, grey = C, blue = N, white = H (Adapted with permission from (1). Copyright 1999 American Chemical Society)

in oxidation states (0) to (III). This led to mechanistic insights and reactivity discoveries relating to additive, ligand and solvent effects. The computational studies focus on selectivities and relative reactivities rather than the full catalytic cycle. In selectivity studies, the nature of the crucial points of the energy surface is generally quite similar and hence error cancellation will be beneficial. This chapter gives the reader a better understanding of how rational development of desired reactivities can be carried out.

Experimental and Computational Techniques

Daniel Lupp, Niels Johan Christensen and Peter Fristrup (Technical University of Denmark) contribute Chapter 8 of this book, exploring reaction mechanisms in catalysis by transition metals (**Figure 2**). This chapter explains kinetic isotopic effects and Hammett substituent effects which can benefit by the advancements in computational chemistry. There is a detailed section on recent developments in DFT relevant to transition metal catalysis, divided into four areas: computational efficiency, dispersion treatment, solvation treatment and effective core potentials. A very useful section for many readers searching for a direction on connecting theory to experiment (through Gibbs free energy, Boltzmann population, relative reactivity) is given in this chapter. In addition there are four case studies each targeting a specific catalyst type based on rhodium, iridium, palladium and ruthenium.

Chapter 9 is written by Sebastian Kozuch (University of North Texas, USA). This chapter is a highlight of the book. The author knows how to keep the reader engaged and presents an excellent chapter on myths and facts in the analysis of catalytic cycles. It will be a good starting point for many budding researchers in catalysis and chemistry. The author touches upon various basics in kinetics like rate constants, activation energies, kinetic graphs, turnover frequencies, Sabatier volcano and power law.

Conclusion

The book in itself is a collection of case studies on different organometallic catalyst studies. I consider this more as a collection of journal papers with slight modifications to add the flavour of a book. Based on the title, one would expect to learn in depth about the experimental and computational tools that can be used in catalysis, followed by case studies that use or implement the introduced tools. In contrast, each chapter is written by separate groups talking about the

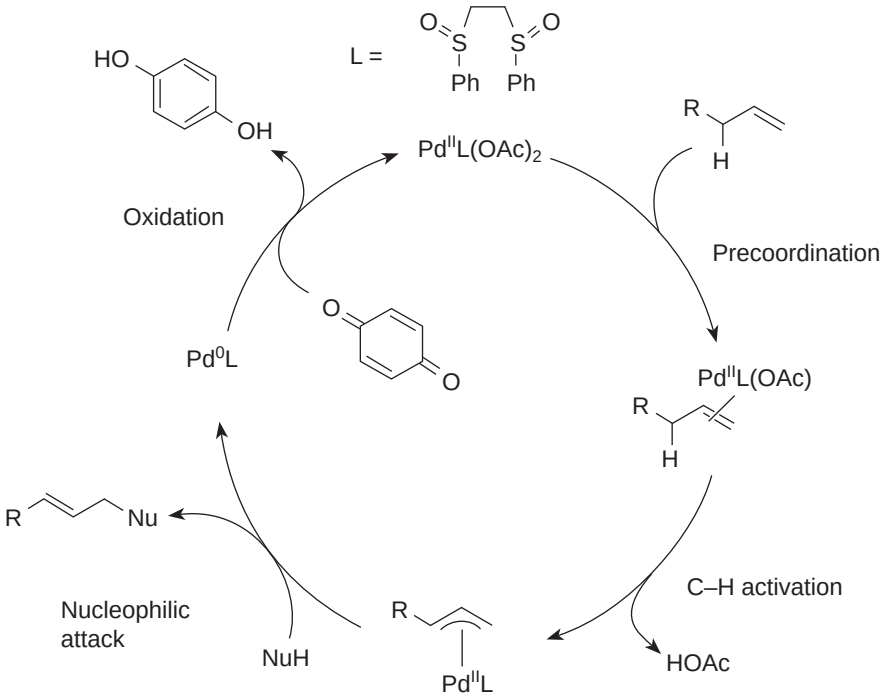
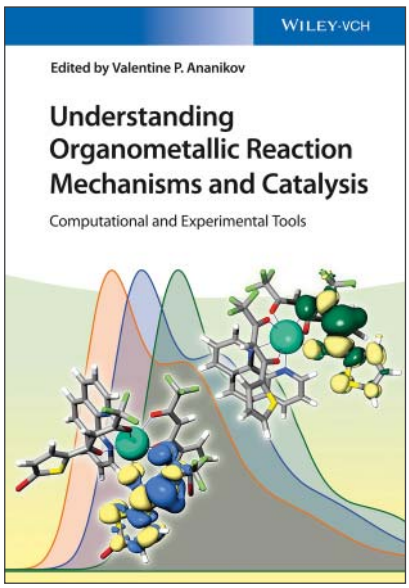


Fig. 2. Proposed catalytic cycle for the palladium-catalysed allylic C–H allylation (reproduced with permission of Wiley-VCH Verlag GmbH & Co KGaA)

research conducted in their laboratories. In my opinion, the continuity between each chapter is missing and this has a negative effect on the smooth flow of information through the book. It could have been structured in a better way by, for example, arranging Chapters 3, 4, 8 and 9 as initial chapters. Some chapters feel more like reading a research report rather than a book.

The book does however give the reader an insight as to how systematic theoretical studies can build better understanding and innovative directions when combined with targeted experiments. Some chapters are very well written with a neat introduction, describing the analytical aspects and successfully taking the reader on a journey to connect theory and experiment. The evidence presented by the various authors to tie theory with experiment to enhance the understanding of kinetics is good and convincing. If you are looking for basics of computational and experimental tools used in organometallic catalysis, this book will give you a general overview, but it is not a one-stop place and you might have to dig into the enormous references in each chapter to find more complete answers to your questions.



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Reference

1 M. Diefenbach, M. Brönstrup, M. Aschi, D. Schröder and H. Schwarz, *J. Am. Chem. Soc.*, 1999, **121**, (45), 10614

The Reviewer

Balaji Sukumar obtained his PhD in Chemical Engineering from the National University of Singapore in 2007 and completed his post-doctoral studies at Carnegie Mellon University, USA, from 2007–2009. Later, he worked at Industrial Learning Systems, USA, where he designed a novel high-temperature casting process for continuous production of single crystalline silicon wafers. He currently manages the computational modelling group in the Emission Control Technologies division at Johnson Matthey Inc, USA. Dr Sukumar specialises in computational modelling, data analysis and control of process systems. His expertise includes design and advanced control of processes in exhaust aftertreatment, solar grade silicon production, silicon wafering, gasification and chemical looping combustion.