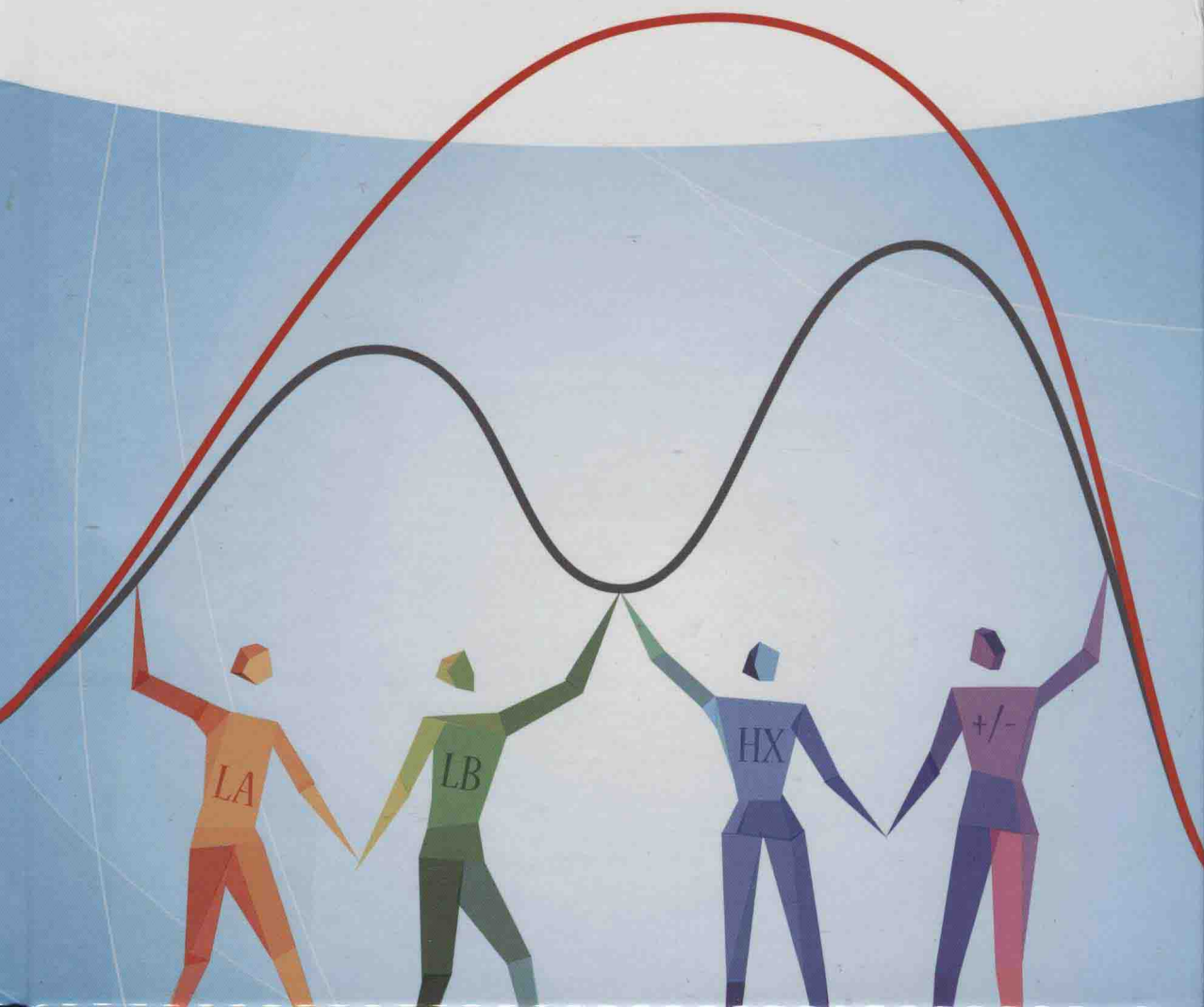


Edited by René Peters

Cooperative Catalysis

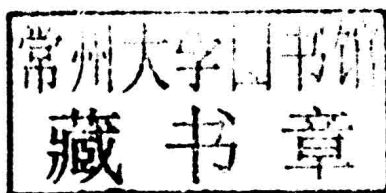
Designing Efficient Catalysts for Synthesis



Edited by René Peters

Cooperative Catalysis

Designing Efficient Catalysts for Synthesis



WILEY-VCH
Verlag GmbH & Co. KGaA

Editor

Prof. Dr. René Peters

Universität Stuttgart
Institut für Organische Chemie
Pfaffenwaldring 55
70569 Stuttgart
Germany
www.peters.oc.uni-stuttgart.de

Cover

The title picture was designed based on an idea commonly developed by Prof. René Peters and his (former) Ph.D. students Melanie Mechler, Carmen Schrapel, Dr. Manuel Weber and Marcel Weiss.

■ All books published by **Wiley-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-33689-0

ePDF ISBN: 978-3-527-68105-1

ePub ISBN: 978-3-527-68104-4

Mobi ISBN: 978-3-527-68103-7

oBook ISBN: 978-3-527-68102-0

Typesetting Laserwords Private Limited, Chennai, India

Printing and Binding Markono Print Media Pte Ltd, Singapore

Printed on acid-free paper

Edited by
René Peters

Cooperative Catalysis

Related Titles

Vedejs, E., Denmark, S.E. (eds.)

Lewis Base Catalysis in Organic Synthesis

2015

ISBN: 978-3-527-33618-0

Christmann, M., Bräse, S. (eds.)

Asymmetric Synthesis II More Methods and Applications

2012

ISBN: 978-3-527-32921-2

Dalko, P.I. (ed.)

Comprehensive Enantioselective Organocatalysis Catalysts, Reactions, and Applications

2013

ISBN: 978-3-527-33236-6

Zhou, Q. (ed.)

Privileged Chiral Ligands and Catalysts

2011

ISBN: 978-3-527-32704-1

Drauz, K., Gröger, H., May, O. (eds.)

Enzyme Catalysis in Organic Synthesis 3rd Edition

2012

ISBN: 978-3-527-32547-4

Caprio, V., Williams, J.M.

Catalysis in Asymmetric Synthesis 2e

2008

ISBN: 978-1-405-19091-6

Andersson, P.G. (ed.)

Innovative Catalysis in Organic Synthesis Oxidation, Hydrogenation, and C-X Bond Forming Reactions

2012

ISBN: 978-3-527-33097-3

Preface

The field of asymmetric catalysis has witnessed an amazing progress during the last decades. Even so, technical scale applications are still largely limited to few catalytic asymmetric reaction types [1]. From a technical point of view the large majority of traditional catalytic asymmetric methodologies is not proficient enough in terms of various fundamental aspects such as catalytic activity, substrate scope, selectivity, and cost efficiency.

In order to develop asymmetric catalysts of considerably improved activity, selectivity, and general applicability, the research field of cooperative catalysis is currently intensively studied by a large number of research groups worldwide, following the seminal marks of pioneers in that field like E. J. Corey, Eric Jacobsen, Ryoji Noyori, Masakatsu Shibasaki, or Hisashi Yamamoto to mention just a few. Their research strategy has mimicked the catalytical principles used by Nature to design artificial tailor-made catalysts: like Nature's catalysts – enzymes – these artificial catalyst systems make use of the synergistic and often sophisticated interplay of two or more functional groups. By simultaneous activation of the reactants using different catalyst functional groups cooperative catalysts can decrease the energy of the transition states of the rate-limiting steps to a much greater degree compared to either functional group working independently. Cooperative catalysts can thus notably accelerate and precisely control a chemical reaction, at the same time reducing the amount of side products and accordingly the production of waste. Dual/multiple activation catalysts consequently very often accomplish higher efficiencies than conventional monofunctional catalysts in terms of reactivity, substrate scope, regio-, diastereo- or enantioselectivity and potentially also cost-efficiency. Cooperative catalysis is arguably the most promising strategy to realize high reactivity and selectivity in chemical transformations. It thus appears likely that the different strategies of cooperative catalysis will streamline organic synthesis in general and will in the future also enable a growing number of technical scale applications for catalytic asymmetric C–C, C–N and C–O bond formations. Cooperative catalysis is hence expected to significantly strengthen asymmetric catalysis as a key technology for our society.

Like mentioned, cooperative catalysis makes use of two or even more functional groups present in a catalytic system, which simultaneously work in concert to accelerate and control a chemical reaction. In the definition utilized in

most chapters of this book these activating functional groups might be part of the same bi- or multifunctional catalyst entity or of two or more separate (co)catalyst molecules. This implicates that terms like bi(multi)functional catalysis, dual (multiple) activation catalysis, contemporaneous dual catalysis, synergistic catalysis or catalyzed catalysis are all covered by the general title of this book – ‘*Cooperative Catalysis*’. Examples for cascade catalysis will thus usually (with some exceptions where suitable) not be presented, because in cascade catalysis the different activating catalyst functionalities do not collectively team up in a way that they decrease the energy of the same transition state by their simultaneous action. An exception has, e.g., been made for Chapter 11, in which the intriguing cooperation of enzymes and metal(–complexes) is described, albeit both catalysts do not activate the substrates simultaneously.

The present book is considered to provide an overview of the most intensively studied concepts of cooperative catalysis, their historical development, their mode of operation and important applications. Advantages of these concepts, and sometimes also pitfalls that need to be overcome in the future, are described and illustrated. A central but not limiting aspect of this book is asymmetric catalysis. The book is subdivided in 13 chapters – each one written by scientific experts in the corresponding field – and classified by the types of the activating principles. It needs to be mentioned though that the transition between different concepts is often floating. For example, the areas of bimetallic catalysis and Lewis acid/Brønsted base catalysis are to a certain degree related concepts and it sometimes depends on your standpoint which classification might be preferred. To avoid a large overlap, this book thus contains a chapter about bimetallic catalysis with carbophilic Lewis acids, but there is no additional chapter for azo- or oxophilic bimetallic catalysts, as the arguably most important systems are already discussed in the chapter about Lewis acid/Brønsted base catalysis. In addition, as theoretically almost every traditional catalytic activation principle may be combined with another one in a cooperative sense, a huge variability appears to be possible. For that reason the title of some chapters specifies only one of the activating principles.

Summing up the most important – often complementary – concepts of cooperative catalysis in one book is expected to support the further development of this important field by both sharpening and extending our perception. It is not very risky to predict that the future of catalysis will be cooperative! Emil Fischer described a related vision already more than 100 years ago, when he stated: *If we wish to catch up with Nature, we shall use the same methods as she does, and I can foresee a time in which physiological chemistry will not only make greater use of natural enzymes but will actually resort to creating new synthetic ones* [2].

René Peters
Universität Stuttgart, 2014

References

1. H. U. Blaser, E. Schmidt, *Asymmetric Catalysis on Industrial Scale*, Wiley-VCH, 2004.
2. E. Fischer: *Synthesen in der Purin- und Zuckergruppe* In *Les Prix Nobel en 1902* (ed. P. T. Cleve, C.-B. Hasselberg, K.-A.-H. Morner), P.-A. Norstedt & Fils, 1905.

Acknowledgments

René Peters sincerely thanks all authors of this book for their valuable contributions. Moreover, he is very grateful to Dr. Anne Brennführer of Wiley-VCH for her suggestion to edit a book about cooperative catalysis and for her excellent support during its preparation. In addition, the editor is indebted to Dr. Waltraud Wüst of Wiley-VCH for her very valued help during the whole editing process. René Peters also gratefully acknowledges the generous financial funding of his research on cooperative catalysis by the Deutsche Forschungsgemeinschaft (DFG, PE 818/3-1, PE 818/4-1, PE 818/6-1). He warmly thanks his former and present coworkers for their high commitment and enthusiasm.

List of Contributors

Li Deng

Brandeis University
Department of Chemistry
Waltham, MA 02454-9110
USA

Yongming Deng

Miami University
Department of Chemistry and
Biochemistry
Oxford, OH 45056
USA

Liu-Zhu Gong

University of Science and
Technology of China
Hefei National Laboratory for
Physical Sciences at the
Microscale and Department of
Chemistry
Hefei 230026
China

Katharina Gratzner

Johannes Kepler University
Institute of Organic Chemistry
Altenbergerstrasse 69
4040 Linz
Austria

Harald Gröger

Bielefeld University
Faculty of Chemistry
Universitätsstr. 25
33615 Bielefeld
Germany

Hansjörg Grützmacher

ETH Zürich
Laboratorium für Anorganische
Chemie
Vladimir-Prelog-Weg 1
8093 Zürich
Switzerland

Yu-Ping He

University of Science and
Technology of China
Hefei National Laboratory for
Physical Sciences at the
Microscale and Department of
Chemistry
Hefei 230026
China

Alexander Katz

University of California
Department of Chemical and
Biomolecular Engineering
Berkeley, CA 94720
USA

Naoya Kumagai

Microbial Chemistry Research
Foundation
Institute of Microbial Chemistry
Laboratory of Synthetic Organic
Chemistry
3-14-23, Kamioosaki
Shinagawa-ku
Tokyo 141-0021
Japan

Xiaojie Lu

Brandeis University
Department of Chemistry
Waltham, MA 02454-9110
USA

Fabrizio Mancin

University of Padova
Department of Chemical
Sciences
via Marzolo 1
35131 Padova
Italy

Christina Moberg

KTH Royal Institute of
Technology
Department of Chemistry
Organic Chemistry
10044 Stockholm
Sweden

Michael M. Nigra

University of California
Department of Chemical and
Biomolecular Engineering
Berkeley, CA 94720
USA

Johanna Novacek

Johannes Kepler University
Institute of Organic Chemistry
Altenbergerstrasse 69
4040 Linz
Austria

Jan Paradies

University of Paderborn
Institute for Organic Chemistry
Warburger Strasse 100
33098 Paderborn
Germany

René Peters

Universität Stuttgart
Institut für Organische Chemie
Pfaffenwaldring 55
70569 Stuttgart
Germany

Leonard J. Prins

University of Padova
Department of Chemical
Sciences
via Marzolo 1
35131 Padova
Italy

Bernhard Rieger

Wacker Chair of
Macromolecular Chemistry
Department of Chemistry
Technische Universität München
Lichtenbergstr. 4
85748 Garching b. München
Germany

Paolo Scrimin

University of Padova
Department of Chemical
Sciences
via Marzolo 1
35131 Padova
Italy

Masakatsu Shibasaki

Microbial Chemistry Research
Foundation
Institute of Microbial Chemistry
Laboratory of Synthetic Organic
Chemistry
3-14-23, Kamioosaki
Shinagawa-ku
Tokyo 141-0021
Japan

Mónica Trincado

ETH Zürich
Laboratorium für Anorganische
Chemie
Vladimir-Prelog-Weg 1
8093 Zürich
Switzerland

Sergei Vagin

Wacker Chair of
Macromolecular Chemistry
Department of Chemistry
Technische Universität München
Lichtenbergstr. 4
85748 Garching b. München
Germany

Hong Wang

Miami University
Department of Chemistry and
Biochemistry
Oxford, OH 45056
USA

Mario Waser

Johannes Kepler University
Institute of Organic Chemistry
Altenbergerstrasse 69
4040 Linz
Austria

Marcel Weiss

Universität Stuttgart
Institut für Organische Chemie
Pfaffenwaldring 55
70569 Stuttgart
Germany

Malte Winnacker

Wacker Chair of
Macromolecular Chemistry
Department of Chemistry
Technische Universität München
Lichtenbergstr. 4
85748 Garching b. München
Germany

Hua Wu

University of Science and
Technology of China
Hefei National Laboratory for
Physical Sciences at the
Microscale and Department of
Chemistry
Hefei 230026
China

Contents

Preface *XIII*

Acknowledgments *XVII*

List of Contributors *XIX*

1	Lewis Acid–Brønsted Base Catalysis	1
	<i>Masakatsu Shibasaki and Naoya Kumagai</i>	
1.1	Introduction	1
1.2	Lewis Acid–Brønsted Base Catalysis in Metalloenzymes	1
1.3	Hard Lewis Acid–Brønsted Base Cooperative Catalysis	3
1.3.1	Cooperative Catalysts Based on a 1,1'-Binaphthol Ligand Platform	3
1.3.1.1	Heterobimetallic Catalysts	3
1.3.1.2	Cooperative Catalysts Based on Linked-BINOL	8
1.3.2	Cooperative Catalysts Based on a Salen and Schiff Base Ligand Platform	11
1.3.3	Cooperative Catalysts Based on a Ligand Platform Derived from Amino Acids	17
1.4	Soft Lewis Acid–Brønsted Base Cooperative Catalysis	21
1.5	Conclusion	24
	References	25
2	Lewis Acid–Lewis Base Catalysis	35
	<i>Christina Moberg</i>	
2.1	Introduction	35
2.2	Lewis Acid and Lewis Base Activation	35
2.2.1	Modes of Activation	35
2.2.2	Self-Quenching	37
2.3	Addition to Carbonyl Compounds	38
2.3.1	Reduction of Ketones	38
2.3.2	Alkylation of Aldehydes and Ketones	39
2.3.3	Allylation of Aldehydes and Ketones	41
2.3.3.1	Lewis Acid/Lewis Base Activation	41
2.3.3.2	Lewis Base Nucleophilic/Electrophilic Activation of Allylsilanes	42

2.3.4	Cyanation of Aldehydes, Ketones, and Imines	43
2.3.4.1	Silylcyanation	43
2.3.4.2	Cyanoformylation and Cyanophosphorylation	45
2.3.4.3	Cyanoacylation	46
2.4	Condensation Reactions	47
2.4.1	Aldol Reactions	47
2.4.2	Mannich Reactions	48
2.5	Morita-Baylis-Hillman Reactions	48
2.6	Epoxide Openings	50
2.6.1	Coupling with CO ₂ and CS ₂	50
2.7	Cyclization Reactions	51
2.7.1	[2+2] Cycloadditions	51
2.7.2	[3+2] Cycloadditions	56
2.7.3	[4+2] Additions	58
2.8	Polymerizations	60
2.9	Conclusions and Outlook	61
	References	62
3	Cooperating Ligands in Catalysis	67
	<i>Mónica Trincado and Hansjörg Grützmacher</i>	
3.1	Introduction	67
3.2	Chemically Active Ligands Assisting a Metal-Localized Catalytic Reaction	67
3.2.1	Cooperating Ligands with a Pendant Basic Site	67
3.2.1.1	Functional Sites Located in the First Coordination Sphere of a Metal Complex	68
3.2.1.2	Basic Functional Sites Located in the Outer Coordination Sphere	83
3.2.2	Remote Pendant Basic Sites and Reorganization of π Systems as Driving Forces for Metal–Ligand Cooperativity	89
3.2.3	Metal–Ligand Cooperation with a Pendant Acid Site	94
3.3	Redox-Active Ligands Assisting Metal-Based Catalysts	96
3.3.1	Redox-Active Ligands as Electron Reservoirs	96
3.3.2	Redox-Active Ligands Participating in Direct Substrate Activation	101
3.4	Summary	104
	References	105
4	Cooperative Enamine-Lewis Acid Catalysis	111
	<i>Hong Wang and Yongming Deng</i>	
4.1	Introduction	111
4.1.1	Challenge in Combining Enamine Catalysis with Lewis Acid Catalysis	112
4.2	Reactions Developed through Cooperative Enamine-Lewis Acid Catalysis	113