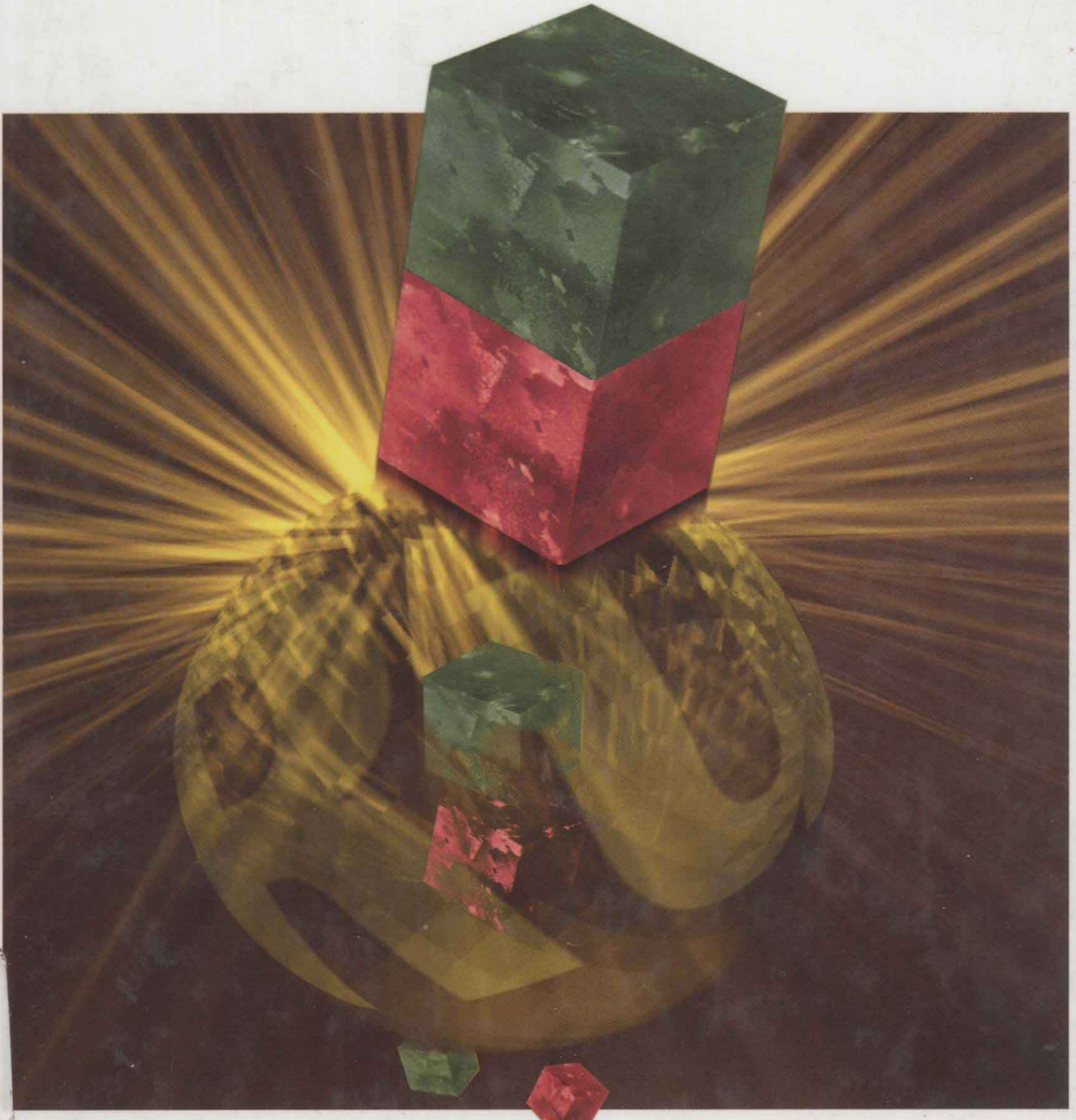
Edited by
S.-I. Murahashi

WILEY-VCH

Ruthenium in Organic Synthesis



Shun-Ichi Murahashi (Ed.)

Ruthenium in Organic Synthesis

WILEY-VCH Verlag GmbH & Co. KGaA

Editor

Professor Shun-Ichi Murahashi
Department of Applied Chemistry
Okayama University of Science
Ridai-cho, 1-1
Okayama, 700-0005
Japan

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 Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <http://dnb.ddb.de>.

Printed on acid-free paper.

Typesetting Kühn & Weyh, Satz und Medien, Freiburg
Printing Strauss GmbH, Mörlenbach
Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN 3-527-30692-7

Shun-Ichi Murahashi (Ed.)

Ruthenium in Organic Synthesis

Further Reading from Wiley-VCH

de Meijere, A., Diederich, F. (Eds.)

Metal-Catalyzed Cross-Coupling Reactions, 2 Vols., 2nd Ed.

2004. 3-527-30518-1

Shibasaki, M., Yamamoto, Y. (Eds.)

Multimetallic Catalysts in Organic Synthesis

2004. 3-527-30828-8

M. Beller, C. Bolm (Eds.)

Transition Metals for Organic Synthesis, 2 Vols., 2nd Ed.

Building Blocks and Fine Chemicals

2004. 3-527-30613-7

Grubbs, R. H. (Ed.)

Handbook of Metathesis, 3 Vols.

2003. 3-527-30616-1

Bäckvall, J.-E. (Ed.)

Modern Oxidation Methods

2004. 3-527-30642-0

Preface

In the recent past, transition metals have contributed extensively to organic synthesis, and this trend will continue in the future. Although ruthenium chemistry has lagged somewhat behind that of the other transition metals such as palladium, ruthenium complexes have a variety of useful characteristics including high electron transfer ability, high coordination ability to hetero-atoms, Lewis acid activity, low redox potentials, and unique reactivity of metal species and intermediates such as oxo-metals, metallacycles, and carbene complexes. Consequently, a large number of novel, useful reactions have begun to be developed using both stoichiometric and catalytic amounts of ruthenium complexes. Although several organic reactions using ruthenium catalysts have been reviewed separately, there is at present no comprehensive book available which details the field of ruthenium chemistry. Hence, the publication of this volume, *Ruthenium in Organic Synthesis,* is both interesting and timely, bearing in mind the recent developments in ruthenium chemistry and the practical application of ruthenium compounds. I hope that this book will provide valuable information to those researchers currently working on the chemistry of ruthenium – both in academia and industry – and will stimulate new developments in this fascinating area of chemistry.

I would like to thank the authors of the individual chapters, each of whom is acknowledged as a world expert in their area of ruthenium chemistry, for their cooperation in writing within the limited number of pages available. I would also like to thank the team at Wiley-VCH, especially Dr. Elke Maase and Dr. Romy Kirsten for their help and cooperation, not only for editing the manuscripts but also for providing valuable assistance during the publishing process.

Shun-Ichi Murahashi
Okayama,
February 2004

Ruthenium in Organic Synthesis. Shun-Ichi Murahashi (Ed.)

ISBN: 3-527-30692-7

List of Contributors

C. Bruneau
Institut de Chimie de Rennes,
UMR 6509 CNRS-Université de Rennes 1,
Campus de Beaulieu,
35042 Rennes,
France

Naoto Chatani
Department of Chemistry,
Faculty of Engineering,
Osaka University, Suita,
Osaka, 565-0871,
Japan

Pierre Dixneuf
Institut de Chimie de Rennes,
UMR 6509 CNRS-Université de Rennes 1,
Campus de Beaulieu,
35042 Rennes,
France

C. Fischmeister
Institut de Chimie de Rennes,
UMR 6509 CNRS-Université de Rennes 1,
Campus de Beaulieu,
35042 Rennes,
France

Robert H. Grubbs
Arnold and Mabel Beckman Laboratory
of Chemical Synthesis,
California Institute of Technology,
Division of Chemistry and Chemical
Engineering,
164-30, Pasadena,
CA 91125,
USA

Masafumi Hirano
Department of Applied Chemistry,
Faculty of Technology,
Tokyo University of Agriculture and
Technology,
Nakacho, 2-24-16, Koganei,
Tokyo, 184-8588,
Japan

Kenji Itoh
Department of Molecular Design and
Engineering,
Graduate School of Engineering,
Nagoya University,
Chikusa-ku, Furo-cho,
Nagoya, 464-8603,
Japan

Ruthenium in Organic Synthesis. Shun-Ichi Murahashi (Ed.)

ISBN: 3-527-30692-7

Rodolphe F. R. Jazzar
Department of Organic Chemistry,
University of Geneva,
30 Quai Ersermet,
1211 Geneva 4,
Switzerland

Fumitoshi Kakiuchi
Department of Chemistry,
Faculty of Engineering,
Osaka University, Suita,
Osaka, 565-0871,
Japan

Masato Kitamura
Department of Chemistry and
Research Center for Material Science,
Nagoya University, Chikusa-ku,
Nagoya, 464-8602,
Japan

Naruyoshi Komiya
Department of Chemistry,
Graduate School of Engineering
Science,
Osaka University,
1-3, Machikaneyama, Toyonaka,
Osaka 560-8531,
Japan

Sanshiro Komiya
Department of Applied Chemistry,
Faculty of Technology,
Tokyo University of Agriculture and
Technology,
Nakacho, 2-24-16, Koganei,
Tokyo, 184-8588,
Japan

Teruyuki Kondo
Department of Energy and
Hydrocarbon Chemistry,
Graduate School of Engineering,
Kyoto University, Sakyo-ku,
Kyoto, 615-8510,
Japan

E. Peter Kündig
Department of Organic Chemistry,
University of Geneva,
30 Quai Ersermet,
1211 Geneva 4,
Switzerland

Take-aki Mitsudo
Department of Energy and Hydrocarbon Chemistry,
Graduate School of Engineering,
Kyoto University, Sakyo-ku,
Kyoto, 615-8510,
Japan

Shun-Ichi Murahashi
Department of Applied Chemistry,
Okayama University of Science,
1-1, Ridai-cho, Okayama,
Okayama 700-0005,
Japan

Hideo Nagashima
Graduate School of Engineering
Sciences,
Institute of Advanced Material Science,
Kyushu University, Kasuga,
Fukuoka, 816-8580,
Japan

Hisao Nishiyama
Department of Applied Chemistry,
Graduate School of Engineering,
Nagoya University,
Chikusa, Furo-cho,
Nagoya, 464-8603,
Japan

Ryoji Noyori
Department of Chemistry and
Research Center for Material Science,
Nagoya University, Chikusa-ku,
Nagoya, 464-8602,
Japan

Hiroharu Suzuki
Department of Applied Chemistry,
Graduate School of Science and
Engineering,
Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku,
Tokyo, 152-8552,
Japan

Toshiro Takao
Department of Applied Chemistry,
Graduate School of Science and
Engineering,
Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku,
Tokyo, 152-8552,
Japan

Tina M. Trnka
Department of Chemistry and
Biochemistry,
University of California,
Santa Barbara,
CA 93106-9510,
USA

Yoshihiko Yamamoto
Department of Applied Chemistry,
Graduate School of Engineering,
Nagoya University, Chikusa,
Nagoya 464-8603,
Japan

Contents

Ruthenium in Organic Synthesis. Shun-Ichi Murahashi (Ed.)

ISBN: 3-527-30692-7

9 Ruthenium-Catalyzed Reactions via sp C–H, sp^2 C–H, sp^3 C–H, and C–Halogen Bond Activations *219*

F. Kakiuchi and N. Chatani

10 Ruthenium Lewis Acid-Catalyzed Reactions *257*

R. F. R. Jazzar and E. P. Kündig

1
Introduction

Shun-Ichi Murahashi

Metal-catalyzed reactions have made a great contribution to the recent growth of organic synthesis, and a variety of synthetic methods have been reported using mainly Group 8 transition metal complexes in stoichiometric or catalytic amounts. In particular, useful transformations bearing high chemo- and stereoselectivities have been discovered in the field of palladium chemistry. Of all elements of the Periodic Table, ruthenium has the widest scope of oxidation states (from –2 valent in $Ru(CO)_4^{2-}$ to octavalent in RuO_4), and various coordination geometries in each electron configuration, which is in contrast to the narrow scope of oxidation states and simple square planar structure of palladium. For instance, in the principal lower oxidation states of 0, II, and III, ruthenium complexes normally prefer trigonal-bipyramidal and octahedral structures, respectively. Such a variety of ruthenium complexes has great potential for the exploitation of novel catalytic reactions and synthetic methods; however, as a consequence of the difficulties of matching the catalysts and substrates, ruthenium chemistry has lagged behind palladium chemistry by almost decade. Indeed, until the 1980s the reported useful synthetic methods using ruthenium catalysts are limited to a few reactions which include oxidations with RuO_4, hydrogenation reactions, and hydrogen transfer reactions. As the coordination chemistry of ruthenium complexes has progressed, specific characters of ruthenium have been made clear.

Ruthenium is relatively inexpensive in comparison with the other Group 8 transition metals such as rhodium, and a wide variety of ruthenium complexes have been prepared. $RuCl_3 \cdot nH_2O$ is frequently used as the starting material in the preparation of most of these ruthenium complexes [1]. The ruthenium complexes can be roughly divided into five groups according to their supporting ligands: carbonyl, tertiary phosphines, cyclopentadienyl, arena/dienes, and carbenes. These ligands have proven to serve effectively as the activating factors such as generation of coordinatively unsaturated species by the liberation of ligands, and stabilization of reactive intermediates. It has been understood that the precise control of coordination sites and redox sequences of the intermediacies are especially important in the case of ruthenium to design specific organic transformations. Moreover, ruthenium complexes also demonstrate a variety of useful characteristics, which include low redox potential, high electron transfer ability, high coordination ability to heteroatoms, Lewis acid acidity, unique reactivity of metallic species and intermediates such as

Ruthenium in Organic Synthesis. Shun-Ichi Murahashi (Ed.)

ISBN: 3-527-30692-7

oxo-metals, metallacycles, and metal carbene complexes. Therefore, a large number of novel, useful reactions have begun to be developed using catalytic amounts of ruthenium complexes [2,3]. The great influence of ruthenium chemistry on organic synthesis in recent years has now elevated the metal's importance to the same level as palladium, or even higher. Indeed, some ruthenium-catalyzed reactions have become industrial processes, with typical examples including a combination of the ruthenium-catalyzed asymmetric hydrogenation of 2-benzamidomethyl-3-oxobutanate via kinetic resolution [4] and the ruthenium-catalyzed oxidation of (1*R*′,3*S*)-3-[1′-(*tert*-butyldimethylsilyloxy)ethyl]azetidin-2-one. The latter process provides an important industrial scheme for the synthesis of 4-acetoxyazetidinone, which is a versatile and key intermediate in the synthesis of cabapenem antibiotics [5]. Grubb's ruthenium carbene complexes have also been used for industrial ring-opening metathesis polymerization (ROMP) [6]. Recent progress in the ruthenium carbene complex-catalyzed carbon-carbon double bond formation for organic synthesis is outstanding, and has become extremely important [7].

The 13 chapters of this book survey a range of fields of organic syntheses promoted by ruthenium catalysts, which involve hydrogenation, oxidation, various carbon–carbon bond formations, C–H activation, carbonylation, isomerization, bond-cleavage reaction, metathesis reaction, and miscellaneous nucleophilic and electrophilic reactions.

References

1 (a) W. P. Griffith, *The Chemistry of the Rare Platinum Metals: Os, Ru, Ir, and Rh*, Wiley-Interscience, New York, **1967**; (b) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochman, *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons, New York, **1999**; (c) S. Komiya, M. Hirano, *Synthesis of Organometallic Compounds*, S. Komiya (Ed.), John Wiley & Sons, New York, **1997**; (d) *Comprehensive Inorganic Chemistry*, Volume 3, J. C. Bailar, H. J. Emeléus, R. Nyholm, A. F. Trotman-Dickenson (eds.), Pergamon Press, Oxford, **1973**.

2 T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599.

3 B. M. Trost, F. Đ. Toste, A. B. Pinkerton, *Cem. Rev.*, **2001**, *101*, 2067.

4 R. Noyori, T. Ikeda, T. Ohkuma, M. Widhalm, M. Kitamura, H. Takaya, S. Akutagawa, *J. Am. Chem. Soc.*, **1989**, *111*, 9134.

5 S.-I. Murahashi, T. Naota, T. Kuwabara, T. Saito, H. Kumobayashi, S. Akutagawa, *J. Am. Chem. Soc.*, **1990**, *112*, 7820.

6 R. H. Grubbs (Ed.), *Handbook of Metathesis, Volume 2*, Applications in Organic Synthesis, Wiley-VCH, **2003**.

7 R. H. Grubbs (Ed.), *Handbook of Metathesis, Volume 3*, Applications in Polymer Synthesis, Wiley-VCH, **2003**.