Ferrocenes: Ligands, Materials and Biomolecules

Editor

PETR ŠTĚPNIČKA Charles University, Prague



Ferrocenes

Ferrocenes: Ligands, Materials and Biomolecules

Editor

PETR ŠTĚPNIČKA Charles University, Prague



John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England

Telephone (+44) 1243 779777

Email (for orders and customer service enquiries): cs-books@wiley.co.uk Visit our Home Page on www.wileyeurope.com or www.wiley.com

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except under the terms of the Copyright, Designs and Patents Act 1988 or under the terms of a licence issued by the Copyright Licensing Agency Ltd, 90 Tottenham Court Road, London W1T 4LP, UK, without the permission in writing of the Publisher. Requests to the Publisher should be addressed to the Permissions Department, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, or emailed to permreq@wiley.co.uk, or faxed to (+44) 1243 770620.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The Publisher is not associated with any product or vendor mentioned in this book.

This publication is designed to provide accurate and authoritative information in regard to the subject matter covered. It is sold on the understanding that the Publisher is not engaged in rendering professional services. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

The Publisher and the Author make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of fitness for a particular purpose. The advice and strategies contained herein may not be suitable for every situation. In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. The fact that an organization or Website is referred to in this work as a citation and/or a potential source of further information does not mean that the author or the publisher endorses the information the organization or Website may make. Further, readers should be aware that Internet Websites listed in this work may have changed or disappeared between when this work was written and when it is read. No warranty may be created or extended by any promotional statements for this work. Neither the Publisher nor the Author shall be liable for any damages arising herefrom.

Other Wiley Editorial Offices

John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 42 McDougall Street, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 6045 Freemont Blvd, Mississauga, Ontario, L5R 4J3, Canada

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Library of Congress Cataloging-in-Publication Data

Stepnicka, Petr.
Ferrocenes : ligands, materials and biomolecules / Petr Stepnicka. p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-03585-6 (cloth)
I. Ferrocene. 2. Ligands. 3. Biomolecules. I. Title.
QD412.F4S84 2008
547'.05621 - dc22

2007044547

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library ISBN 978-0-470-03585-6

Typeset in 10/12pt Times by Laserwords Private Limited, Chennai, India Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

Contents

Prej	face	vii
Con	tributors	xi
PART I FERROCENE LIGANDS		1
1	Monodentate Ferrocene Donor Ligands Robert C.J. Atkinson and Nicholas J. Long	3
2	The Coordination and Homogeneous Catalytic Chemistry of 1,1'-Bis(diphenylphosphino)ferrocene and its Chalcogenide Derivatives <i>Sheau W. Chien and T.S. Andy Hor</i>	33
3	Synthesis, Coordination Chemistry and Catalytic Use of dppf Analogs Thomas J. Colacot and Sébastien Parisel	117
4	Other Symmetric 1,1'-Bidentate Ferrocene Ligands Ulrich Siemeling	141
5	1'-Functionalised Ferrocene Phosphines: Synthesis, Coordination Chemistry and Catalytic Applications Petr Štěpnička	177
6	Chiral 1,2-Disubstituted Ferrocene Diphosphines for Asymmetric Catalysis Hans-Ulrich Blaser, Weiping Chen, Francesco Camponovo and Antonio Togni	205
7	Synthesis and Catalytic Use of Planar Chiral and Polydentate Ferrocene Donors Petr Štěpnička and Martin Lamač	237
PA	RT II MATERIALS, MOLECULAR DEVICES AND BIOMOLECULES	279
8	Ferrocene Sensors Simon R. Bayly, Paul D. Beer and George Z. Chen	281

Vİ	Contents	
9	Ferrocene-Based Electro-Optical Materials Jürgen Heck and Markus Dede	319
10	Ferrocene-Containing Polymers and Dendrimers Nicholas J. Long and Konrad Kowalski	393
11	Ferrocene-Containing Thermotropic Liquid Crystals <i>Robert Deschenaux</i>	447
12	Crystal Engineering with Ferrocene Compounds Dario Braga, Marco Curzi, Stefano Luca Giaffreda, Fabrizia Grepioni, Lucia Maini, Anna Pettersen and Marco Polito	465
13	The Bioorganometallic Chemistry of Ferrocene Nils Metzler-Nolte and Michèle Salmain	499
Index		641

Preface

Ferrocene, the first known and archetypal metallocene, stirred up a great deal of attention immediately after its discovery in the early 1950s.^{1,2} However, after the vigorous era of pioneering research aimed predominantly at understanding its basic properties and reactivity had subsided, research activity did not cease in the slightest. Instead, it spread further into many fields of chemistry and also to related neighbouring disciplines, where it continues with still increasing publication activity (Figure 1).

Nowadays, ferrocene is no longer considered a chemical curiosity, but serves as a widely applicable organometallic scaffold for the preparation of functional derivatives that are finding use in very many areas. These range from mostly academic research aimed at exploring its use in the preparation of various organometallic compounds, to practically directed applications in catalysis, material science and, more recently, also in biomedicinal chemistry.

About twelve years have already passed since the legendary book *Ferrocenes* edited by A. Togni and T. Hayashi was published.³ This, together with the recent developments, certainly justifies publication of a new guide to ferrocene chemistry. Although the areas originally highlighted in the subtitle of the book (Homogeneous Catalysis, Organic Synthesis, Materials Science) still represent the major research fields in ferrocene chemistry, there have emerged some additional, rapidly developing areas with a strong practical relevance, such as organometallic crystal engineering and, above all, bioorganometallic chemistry, which are also included in this book. Consequently, the book is formally divided into parts, dealing with ferrocene ligands, material aspects of ferrocene chemistry and, finally, with bioorganometallic chemistry involving ferrocene compounds. However, in view of the amount of literature concerning ferrocene and its derivatives, particularly in the popular areas, this book can no longer provide any kind of an exhaustive literature survey. Therefore, it is conceived for the most part as a combination of the necessary introductory information and a summary of important recent results published up to about the end of the year 2006. For readers seeking



Figure 1 The number of research articles published per year on 'ferrocene' according to CAS

more exhaustive literatures sources, references to literature reviews focusing on particular research areas have been included where appropriate. The book should not only provide a timely summary of important findings in each particular field covered but should also be of help for newcomers (or even random visitors) to ferrocene chemistry who simply make use of some property of a ferrocene derivative. I believe that this book may also serve as a starting point for those who want to become really 'involved' with ferrocene.

Finally, I wish to thank all the authors for the preparation of their individual contributions that really *make* this book. Their work, which often nearly turned to a Herculean task because of the enormous amount of recent literature, was always reliable and accurate. My sincere thanks go also to Paul Deards, a commissioning editor at Wiley in Chichester, and his whole editorial team for their encouragement in the initial stages, continuing support during the manuscript preparation and smooth guidance through the entire production process. I hope that the readers will enjoy reading this book and find it useful in their own work.

> Petr Štěpnička Prague, summer 2007

References

(a) T.J. Kealy, P.L. Pauson, *Nature*, 1951, **168**, 1039–1040; (b) S.A. Miller, J.A. Tebboth, J.F. Tremaine, *J. Chem. Soc.*, 1952, 632–635; (c) G. Wilkinson, M. Rosenblum, M.C. Whiting,

R.B. Woodward, J. Am. Chem. Soc., 1952, 74, 2125–2126; (d) E.O. Fischer, W. Pfab, Z. Naturforsch., 1952, 7b, 377–379.

- 2 For historical essays, see: G. Wilkinson, J. Organomet. Chem., 1975, **100**, 273–278; and historical notes published in the special issue of J. Organomet. Chem. dedicated to the 50th anniversary of the discovery of ferrocene, J. Organomet. Chem., 2001, **637–639**.
- 3 A. Togni, T. Hayashi (Eds), *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*, VCH, Weinheim, Germany (1995).

Note

Since the use of abbreviated symbols for ferrocene and ferrocenyl groups is somewhat confusing in the literature, in this book the ferrocenyl group $[Fe(\eta^5-C_5H_4)(\eta^5-C_5H_5)]$ is denoted as Fc and the ferrocene-1,1'-diyl group $[Fe(\eta^5-C_5H_4)_2]$ as fc. By using these abbreviations, ferrocene $[Fe(\eta^5-C_5H_5)_2]$ can be formulated either as FcH or fcH₂. Definitions of the frequently or chapter-specific abbreviations are provided in the individual parts.

Contributors

Robert C. J. Atkinson and Nicholas J. Long

Department of Chemistry, Imperial College London, South Kensington, London, United Kingdom

Sheau W. Chien and T. S. Andy Hor

Department of Chemistry, National University of Singapore, Singapore

Thomas J. Colacot^a and Sébastien Parisel^b

^aJohnson Matthey Catalysts, Catalysis and Chiral Technologies, West Deptford (NJ), United States of America ^bJohnson Matthey Catalysts, Catalysis and Chiral Technologies, Royston, United Kingdom.

Ulrich Siemeling

Institute of Chemistry, University of Kassel, Kassel, Germany

Petr Štěpnička

Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Czech Republic

Hans-Ulrich Blaser,^a Weiping Chen,^a Francesco Camponovo^b and Antonio Togni^b

^aSolvias AG, Basel, Switzerland ^bDepartment of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Zurich, Zurich, Switzerland

Petr Štěpnička and Martin Lamač

Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Czech Republic

Simon R. Bayly,^a Paul D. Beer^a and George Z. Chen^b

^aDepartment of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom

^bSchool of Chemical and Environmental Engineering, University of Nottingham Nottingham, United Kingdom

Jürgen Heck and Markus Dede

Institute of Inorganic and Applied Chemistry, University of Hamburg, Hamburg, Germany

Nicholas J. Long^a and Konrad Kowalski^b

^aDepartment of Chemistry, Imperial College London, South Kensington, London, United Kingdom

^bDepartment of Organic Chemistry, Institute of Chemistry, University of Łódź, Łódź, Poland

Robert Deschenaux

Institut de Chimie, Université de Neuchâtel, Neuchâtel, Switzerland

Dario Braga, Marco Curzi, Stefano Luca Giaffreda, Fabrizia Grepioni, Lucia Maini, Anna Pettersen and Marco Polito

Dipartimento di Chimica G. Ciamician, Università degli Studi di Bologna, Bologna, Italy

Nils Metzler-Nolte^a and Michèle Salmain^b

^aDepartment of Chemistry and Biochemistry, Ruhr-Universität Bochum, Bochum, Germany

^bEcole Nationale Supérieure de Chimie de Paris, Laboratoire de chimie et biochimie des complexes moléculaires, UMR CNRS 7576, Paris, France

PART I Ferrocene Ligands