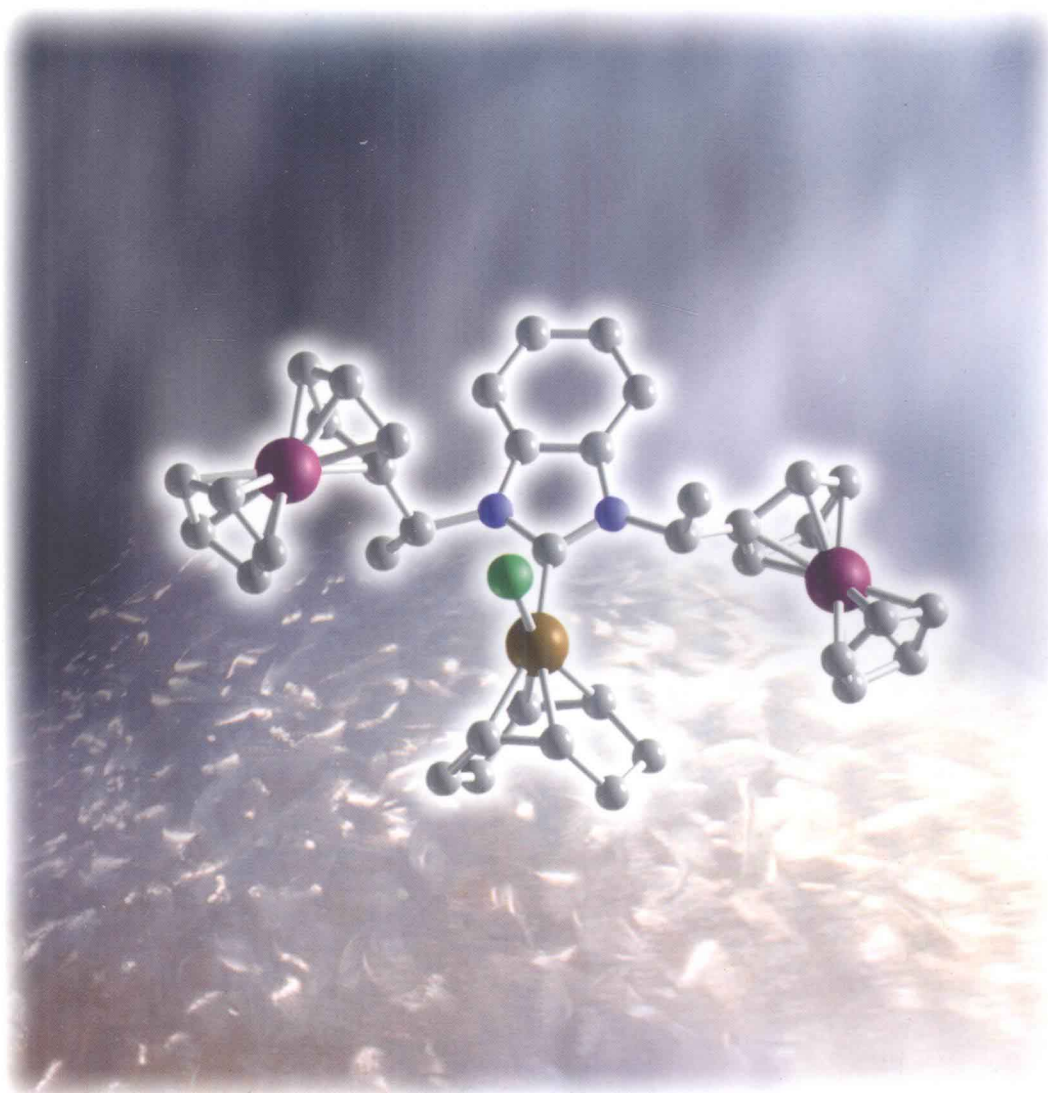


Edited by
Luis A. Oro and Carmen Claver

 WILEY-VCH

Iridium Complexes in Organic Synthesis



Iridium Complexes in Organic Synthesis

Edited by

Luis A. Oro and Carmen Claver



WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. Dr. Luis A. Oro

University of Zaragoza-CSIC
Dep. Inorganic Chemistry, Faculty of
Science-ICMA
Instituto Universitario de Catálisis Homogénea
Pedro Cerbuna 12
50009 Zaragoza
Spain

Prof. Dr. Carmen Claver

Universitat Rovira i Virgili
Dept. de Química Física i Inorgànica
Facultat de Química
c/ Marcel·lí Domingo, s/n
43007 Tarragona
Spain

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>>.

© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

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.

Composition SNP Best-set Typesetter Ltd., Hong Kong

Printing Strauss GmbH, Mörlenbach

Bookbinding Litges & Dopf GmbH, Heppenheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-31996-1

**Iridium Complexes in
Organic Synthesis**

*Edited by
Luis A. Oro and
Carmen Claver*

Further Reading

Hashmi, A. S. K., Toste, D. F. (Eds.)

Modern Gold Catalyzed Synthesis

2009

ISBN: 978-3-527-31952-7

Yamamoto, H., Ishihara, K. (Eds.)

Acid Catalysis in Modern Organic Synthesis

2 Volumes

2008

ISBN: 978-3-527-31724-0

Ding, K., Uozumi, Y. (Eds.)

Handbook of Asymmetric Heterogeneous Catalysis

2008

ISBN: 978-3-527-31913-8

Toru, T., Bolm, C. (Eds.)

Organosulfur Chemistry in Asymmetric Synthesis

2008

ISBN: 978-3-527-31854-2

Bolm, C., Hahn, F. E. (Eds.)

Activating Unreactive Substrates

The Role of Secondary Interactions

2009

ISBN: 978-3-527-31823-0

Preface

The impressive developments of organometallic chemistry during the past 50 years have allowed the preparation of a wide variety of soluble metal complexes useful for organic transformations under mild conditions. Among these metals, the noble triad of ruthenium, rhodium and palladium has played the major role, with rhodium being the most relevant when acquiring knowledge of the mechanisms of metal-mediated organic transformations. In fact, the discovery and application of Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$, proved to be a major milestone during the mid-1960s, mainly because it led to the initiation of many successful applications, including rhodium-catalyzed olefin hydroformylation, the Monsanto production of acetic acid, and industrial asymmetric hydrogenations. Details of some of the major applications of rhodium complexes were updated in a recent book, *Rhodium-Catalyzed Organic Reactions* (edited by P. A. Edwards, published by Wiley-VCH in 2006). In contrast, iridium complexes have been most often used as model compounds to acquire an understanding of the elementary steps of transition metal-catalyzed reactions. A good example of this was 'Vaska's compound', the details of which were first reported in 1965, and which has since provided valuable information on the oxidative addition reactions that serve as key steps in almost every catalytic cycle. Unfortunately, the $\text{IrCl}(\text{PPh}_3)_3$ complex—which can be seen as analogous to Wilkinson's catalyst—is not a good hydrogenation catalyst, due mainly to the inability of the $\text{IrH}_2\text{Cl}(\text{PPh}_3)_3$ to lose hydrogen. Nonetheless, a variety of cationic iridium complexes with a phosphine:iridium ratio of 1 to 2 have been used extensively as efficient catalysts for alkene hydrogenation, including the industrial enantioselective hydrogenation of imines. Although iridium complexes are less frequently used than their rhodium analogues, in some processes they may be more effective—the carbonylation of methanol being an excellent example in the arena of bulk chemistry. Perhaps the most important catalytic applications of iridium complexes, however, are in the manufacture of fine chemicals, most notably in areas of chemoselective and enantioselective hydrogenation. Iridium complexes have also been shown to play an important role in the enantioselective hydrogenation of $\text{C}=\text{N}$, which is used widely in the fine chemicals industry, and also of non-functionalized $\text{C}=\text{C}$ bonds, with particular interest being centered on the creation of intermediates and building blocks in organic synthesis.

Today, although the value of iridium is becoming increasingly recognized in many organic transformations, it is still not used to any great degree by the chemicals industry. So, it is the aim of this book not only to evaluate the potential of the most promising reactions that involve iridium complexes, but also to provide an account of the role of these materials in important organic transformations such as hydrogenation, hydroamination, hydroboration, C—C bond formation, carbonylation and cycloadditions. The use of relevant ligands as carbenes or pincer ligands, as well as recent catalytic systems using iridium nanoparticles, are also described.

We, the editors, believe that organoiridium chemistry has not only a rich past, but that the application of iridium complexes in organic transformations also has a brilliant future!

October, 2008

*Luis A. Oro, Zaragoza
Carmen Claver, Tarragona*

List of Contributors

Martin Albrecht

University of Fribourg
Department of Chemistry
Chemin du Musée 9
1700 Fribourg
Switzerland

Claudio Bianchini

Institute of Chemistry of
Organometallic Compounds
National Research Council
(ICCOM-CNR)
Via Madonna del Piano 10
50019 Sesto Fiorentino
Firenze
Italy

Hans-Ulrich Blaser

Solvias AG
P.O. Box
4002 Basel
Switzerland

Carmen Claver

Universitat Rovira i Virgili
Dept. de Química Física i Inorgànica
Facultat de Química
c/ Marcel·lí Domingo, s/n
43007 Tarragona
Spain

Robert H. Crabtree

Yale University
Department of Chemistry
225 Prospect Street
New Haven, CT 06520-8107
USA

Romano Dorta

Universidad Simón Bolívar
Departamento de Química
Valle de Sartenejas
1080 A Baruta – Caracas
Venezuela

Jairton Dupont

Laboratory of Molecular Catalysis
Institute of Chemistry
UFRGS Av. Bento Gonçalves
9500 Porto Alegre 91501-970 RS
Brazil

Elena Fernández

Facultat de Químicas
Universitat Rovira i Virgili
Campus Sescelades
C. Marcel·lí Domingo
43007 Tarragona
Spain

Ken-ichi Fujita

Graduate School of Human and
Environmental Studies
Kyoto University
Yoshida
Sakyo-ku
Kyoto 606-8501
Japan

Luca Gonsalvi

Institute of Chemistry of
Organometallic Compounds
National Research Council
(ICCOM-CNR)
Via Madonna del Piano 10
50019 Sesto Fiorentino
Firenze
Italy

Günter Helmchen

Universität Heidelberg
Organisch-Chemisches Institut
Im Neuenheimer Feld 270
69120 Heidelberg
Germany

Yasutaka Ishii

Kansai University
Department of Chemistry and
Materials Engineering
Faculty of Chemistry
Materials and Bioengineering
Suita
Osaka 564-8680
Japan

Philippe Kalck

Université de Toulouse
Laboratoire de Chimie de
Coordination du CNRS
UPR 8241
Equipe Catalyse et Chimie Fine
Composante INP-ENSIACET
118 route de Narbonne
31077 Toulouse
France

Ireneusz Kownacki

Adam Mickiewicz University
Department of Organometallic
Chemistry
Faculty of Chemistry
Grunwaldzka 6
60-780 Poznan
Poland

Bogdan Marciniak

Adam Mickiewicz University
Department of Organometallic
Chemistry
Faculty of Chemistry
Grunwaldzka 6
60-780 Poznan
Poland

David Morales-Morales

Universidad Nacional Autonoma de
México
Instituto de Quimica
Circuito Exterior S/N
Ciudad Universitaria
Mexico D.F. Coyoacan
C. P. 04510
Mexico

Yasushi Obora

Kansai University
Department of Chemistry and
Materials Engineering
Faculty of Chemistry
Materials and Bioengineering
Suita
Osaka 564-8680
Japan

Luis A. Oro

Instituto Universitario de Catálisis
Homogénea
Department of Inorganic Chemistry
Faculty of Science-ICMA
University of Zaragoza-CSIC
50009 Zaragoza
Spain

Eduardo Peris

Universitat Jaume I
 Department of Química Inorgánica y
 Orgánica
 Avenue Vicente Sos Baynat s/n,
 12080 Castellón
 Spain

Maurizio Peruzzini

Institute of Chemistry of
 Organometallic Compounds
 National Research Council
 (ICCOM-CNR)
 Via Madonna del Piano 10
 50019 Sesto Fiorentino
 Firenze
 Italy

Satoshi Sakaguchi

Kansai University
 Department of Chemistry and
 Materials Engineering
 Faculty of Chemistry
 Materials and Bioengineering
 Suita
 Osaka 564-8680
 Japan

Jackson D. Scholten

Laboratory of Molecular Catalysis
 Institute of Chemistry
 UFRGS Av. Bento Gonçalves
 9500 Porto Alegre 91501-970 RS
 Brazil

Anna M. Segarra

Escola Técnica Superior d'Enginyeria
 Química
 Universitat Rovira i Virgili
 Campus Sescelades
 C. Marcel·lí Domingo
 43007 Tarragona
 Spain

Philippe Serp

Université de Toulouse
 Laboratoire de Chimie de
 Coordination du CNRS
 UPR 8241
 Equipe Catalyse et Chimie Fine
 Composante INP-ENSIACET
 118 route de Narbonne
 31077 Toulouse
 France

Takanori Shibata

Waseda University
 Department of Chemistry
 School of Advanced Science &
 Engineering
 Ohkubo
 Shinjuku Tokyo 169-8555
 Japan

Ryohei Yamaguchi

Graduate School of Human and
 Environmental Studies
 Kyoto University
 Yoshida
 Sakyo-ku
 Kyoto 606-8501
 Japan

Contents

Preface XIII

List of Contributors XV

1	Application of Iridium Catalysts in the Fine Chemicals Industry	1
	<i>Hans-Ulrich Blaser</i>	
1.1	Introduction	1
1.2	Industrial Requirements for Applying Catalysts	1
1.2.1	Characteristics of the Manufacture of Enantiomerically Pure Products	1
1.2.2	Process Development: Critical Factors for the Application of Catalysts	2
1.2.3	Requirements for Practically Useful Catalysts	3
1.2.3.1	Preparation Methods	3
1.2.3.2	Catalysts Cost	3
1.2.3.3	Availability of the Catalysts	3
1.2.3.4	Catalytic Performance	3
1.2.3.5	Separation	4
1.3	Enantioselective Hydrogenation of C=N Bonds	4
1.3.1	Catalysts and Scope	4
1.3.2	Industrial Applications	6
1.4	Enantioselective Hydrogenation of C=C Bonds	8
1.4.1	Catalysts and Scope	8
1.4.2	Industrial Applications	9
1.5	Miscellaneous Catalytic Applications with Industrial Potential	10
1.6	Conclusions and Outlook	13
	References	13
2	Dihydrido Iridium Triisopropylphosphine Complexes: From Organometallic Chemistry to Catalysis	15
	<i>Luis A. Oro</i>	
2.1	Introduction	15
2.2	[Ir(COD)(NCMe)(PR ₃)]BF ₄ (PR ₃ = P ⁱ Pr ₃ , PMe ₃) and Related Complexes as Catalyst Precursors: Is 1,5-Cyclo-Octadiene an Innocent and Removable Ligand?	16

2.3	The Dihydrido Iridium Triisopropylphosphine Complex [IrH ₂ (NCMe) ₃ (P ⁱ Pr ₃)]BF ₄ as Alkene Hydrogenation Catalysts	21
2.4	The Dihydrido Iridium Triisopropylphosphine Complex [IrH ₂ (NCMe) ₃ (P ⁱ Pr ₃)]BF ₄ as Alkyne Hydrogenation Catalysts	26
2.5	Dihydrido Arene Iridium Triisopropylphosphine Complexes	29
2.6	Dihydrido Iridium Triisopropylphosphine Complexes as Imine Hydrogenation Catalysts	34
2.7	Conclusions	37
	Acknowledgments	37
	References	37
3	Iridium N-Heterocyclic Carbene Complexes and Their Application as Homogeneous Catalysts	39
	<i>Eduardo Peris and Robert H. Crabtree</i>	
3.1	Introduction	39
3.2	Types of Ir—NHC and Reactivity	40
3.2.1	Mono-NHCs and Intramolecular C—H Activation	40
3.2.2	Chelating bis-NHCs	43
3.2.3	Abnormal NHCs	46
3.3	Catalysis with Ir—NHCs	49
3.4	Conclusions	52
	References	52
4	Iridium-Catalyzed C=O Hydrogenation	55
	<i>Claudio Bianchini, Luca Gonsalvi and Maurizio Peruzzini</i>	
4.1	Introduction	55
4.2	Homogeneous C=O Hydrogenations	55
4.2.1	Chemoselective Hydrogenations	56
4.2.2	Enantioselective Hydrogenations	63
4.2.3	Transfer Hydrogenation (TH)	69
4.2.4	Asymmetric Transfer Hydrogenation (ATH)	81
4.3	Heterogeneous, Supported and Biocatalytic Hydrogenations	99
	References	103
5	Catalytic Activity of Cp* Iridium Complexes in Hydrogen Transfer Reactions	107
	<i>Ken-ichi Fujita and Ryohei Yamaguchi</i>	
5.1	Introduction	107
5.2	Hydrogen Transfer Oxidation of Alcohols (Oppenauer-Type Oxidation)	108
5.3	Transfer Hydrogenation of Unsaturated Compounds	112
5.3.1	Transfer Hydrogenation of Quinolines	112
5.3.2	Transfer Hydrogenation of Ketones and Imines	113
5.4	Asymmetric Synthesis Based on Hydrogen Transfer	113
5.4.1	Asymmetric Transfer Hydrogenation of Ketones	113
5.4.2	Dynamic Kinetic Resolution	118

5.5	Hydrogen Transfer Reactions in Aqueous Media	119
5.6	Carbon–Nitrogen Bond Formation Based on Hydrogen Transfer	123
5.6.1	N-Alkylation of Amines with Alcohols	123
5.6.2	Cyclization of Amino Alcohols	126
5.6.3	Cyclization of Primary Amines with Diols	127
5.6.4	Amidation of Alcohols with Hydroxylamine	128
5.7	Carbon–Carbon Bond Formation Based on Hydrogen Transfer	130
5.7.1	β -Alkylation of Secondary Alcohols	130
5.7.2	Alkylation of Active Methylene Compounds with Alcohols	131
5.8	Carbon–Oxygen Bond Formation Based on Hydrogen Transfer	135
5.8.1	Oxidative Lactonization of Diols	135
5.8.2	Inter- and Intra-Molecular Tishchenko Reactions	137
5.9	Dehydrogenative Oxidation of Alcohols	138
5.10	Conclusions	140
	References	140

6 Iridium-Catalyzed Hydroamination 145

Romano Dorta

6.1	Introduction	145
6.2	Iridium-Catalyzed Olefin Hydroamination (OHA)	146
6.2.1	The Ir(III)/Secondary Amines/Ethylene System	146
6.2.2	The Ir(I)/ZnCl ₂ /Aniline/Norbornene System	146
6.2.3	The Chiral Ir(I)/‘Naked Fluoride’/Norbornene/Aniline System	147
6.2.4	The Chiral Ir(I)/Organic Base/Anilines/Olefins System	150
6.2.5	The Ir(I)/Piperidine/Methacrylonitrile System	151
6.3	Iridium-Catalyzed Alkyne Hydroamination (AHA)	152
6.3.1	Intramolecular Aliphatic Systems	152
6.3.2	Indoles via Intramolecular AHA	153
6.3.3	Intermolecular Alkyne Hydroamination	153
6.4	Proposed Mechanisms	156
6.4.1	Olefin Hydroamination	156
6.4.2	Alkyne Hydroamination	158
6.5	Complexes and Reactions of Ir Relevant to Hydroamination	160
6.5.1	Ir(I)–Amine Complexes	160
6.5.2	Ir(I)–Anilido complexes	161
6.5.3	N–H Bond Activation Leading to Ir(III)–Amido-Hydrido Complexes	162
6.5.4	Alkyl–Amino-Hydrido Complexes of Ir(III)	165
6.5.5	Iridium–Fluoride Complexes	168
6.6	Conclusions	169
	References	170

7 Iridium-Catalyzed Boron-Addition 173

Elena Fernández and Anna M. Segarra

7.1	Introduction	173
7.2	Iridium–Boryl Complexes	173

- 7.3 Hydroboration 176
- 7.4 Diboration 184
- 7.5 Borylation 185
- References 191

8 Iridium-Catalyzed Methanol Carbonylation 195

Philippe Kalck and Philippe Serp

- 8.1 Introduction 195
- 8.2 Rhodium-Based Processes 197
 - 8.2.1 The Monsanto Process 197
 - 8.2.2 The Celanese Process 199
- 8.3 Iridium Reactivity in the Methanol Carbonylation Reaction 200
- 8.4 The Iridium-Based Cativa Process 204
- 8.5 The Iridium–Platinum-Based Process 206
- 8.6 The Iridium–Cocatalyst Mechanism, and Conclusions 207
- Acknowledgments 207
- References 208

9 Iridium-Catalyzed Asymmetric Allylic Substitutions 211

Günter Helmchen

- 9.1 Introduction 211
- 9.2 Ir-Catalyzed Allylic Substitutions: Fundamentals 212
 - 9.2.1 Reactivity and Regioselectivity 212
 - 9.2.2 Steric Course 214
 - 9.2.3 Asymmetric Catalysis: The Beginnings with Phosphinooxazolines as Chiral Ligands 215
 - 9.2.4 Phosphoramidites as Ligands for the Ir-Catalyzed Allylic Substitution 216
 - 9.2.4.1 Survey 216
 - 9.2.4.2 Catalyst Preparation, Reaction Conditions and Catalytic Cycle 217
 - 9.2.4.3 Preparation of Phosphoramidites 219
 - 9.2.4.4 Variation of the Phosphoramidite Ligands 219
 - 9.2.4.5 Further Ligands Used in Ir-Catalyzed Allylic Substitutions 220
- 9.3 C-Nucleophiles 221
 - 9.3.1 Stabilized Enolates as Nucleophiles 221
 - 9.3.1.1 Malonates and Related Pronucleophiles 221
 - 9.3.1.2 Aliphatic Nitro Compounds as Pronucleophiles 224
 - 9.3.1.3 A Glycine Equivalent as Pronucleophile 225
 - 9.3.2 Allylic Substitutions with Nonstabilized Enolates, Enamines and Organozinc Compounds 226
 - 9.3.2.1 Ketone Enolates Derived from Silyl Enol Ethers as Nucleophiles 226
 - 9.3.2.2 Allylation of Enamines 227
 - 9.3.2.3 Decarboxylative Allylic Alkylation 227
 - 9.3.2.4 Reactions with Aryl Zinc Compounds 228
- 9.4 N-Nucleophiles 229

9.4.1	Inter- and Intramolecular Reactions with Aliphatic Amines and Ammonia as Nucleophiles	229
9.4.2	Arylamines as Nucleophiles	232
9.4.3	Amination of Allylic Alcohols	232
9.4.4	Pronucleophiles Serving as Ammonia Surrogates: N,N-Diacylamines, Trifluoroacetamide and N-Sulfonylamines	233
9.4.5	Decarboxylative Allylic Amidation	236
9.4.6	Dihydropyrroles and γ -Lactams via Allylic Substitution and Ring-Closing Metathesis	237
9.4.7	Hydroxylamine Derivatives as N-Nucleophiles	238
9.5	O-Nucleophiles	239
9.5.1	Phenolates as Nucleophiles	239
9.5.2	Alkoxides as Nucleophiles	241
9.5.3	Hydroxylamine Derivatives as O-Nucleophiles	242
9.5.4	Silanolates as Nucleophiles	242
9.5.5	Dihydrofurans via Allylic Etherification in Combination with RCM	244
9.6	Synthesis of Biologically Active Compounds via Allylic Substitution	244
9.7	Conclusions	246
	Acknowledgments	247
	References	247

10 Iridium-Catalyzed Coupling Reactions 251

Yasutaka Ishii, Yasushi Obora and Satoshi Sakaguchi

10.1	Introduction	251
10.2	Iridium-Catalyzed Dimerization and Cyclotrimerization of Alkynes	251
10.3	Iridium-Catalyzed, Three-Component Coupling Reactions of Aldehydes, Amines and Alkynes	253
10.4	Head-to-Tail Dimerization of Acrylates	256
10.5	A Novel Synthesis of Vinyl Ethers via an Unusual Exchange Reaction	258
10.6	Iridium-Catalyzed Allylic Substitution	260
10.7	Alkylation of Ketones with Alcohols	262
10.8	N-Alkylation of Amines	264
10.9	Oxidative Dimerization of Primary Alcohols to Esters	266
10.10	Iridium-Catalyzed Addition of Water and Alcohols to Terminal Alkynes	266
10.11	Iridium-Catalyzed Direct Arylation of Aromatic C—H Bonds	267
10.12	Iridium-Catalyzed Anti-Markovnikov Olefin Arylation	267
10.13	Iridium-Catalyzed Silylation and Borylation of Aromatic C—H Bonds	268
10.14	Miscellaneous Reactions Catalyzed by Iridium Complexes	269
	References	271

11	Iridium-Catalyzed Cycloadditions	277
	<i>Takanori Shibata</i>	
11.1	Introduction	277
11.2	[2+2+2] Cycloaddition	278
11.3	Enantioselective [2+2+2] Cycloaddition	281
11.4	[2+2+1] Cycloaddition	283
11.5	[4+2] and [5+1] Cycloadditions	288
11.6	Cycloisomerization	289
11.7	Ir(III)-Catalyzed Cyclizations	291
11.8	Miscellaneous Cycloadditions	293
11.9	Conclusions	295
	References	296
12	Pincer-Type Iridium Complexes for Organic Transformations	299
	<i>Martin Albrecht and David Morales-Morales</i>	
12.1	Introduction	299
12.2	Iridium PCP-Catalyzed Activation of C(sp ³)—H Bonds in Unfunctionalized Alkanes	300
12.2.1	Scope of the Reaction	300
12.2.2	Mechanistic Considerations	302
12.2.3	Catalyst Optimization	307
12.2.4	Application of Alkane Functionalization	309
12.2.4.1	Alkane Metathesis	309
12.2.4.2	Polymer Functionalization	310
12.3	Arene C(sp ²)—H and Alkyne C(sp ¹)—H Bond Activation	311
12.3.1	Activation of C(sp ²)—H Bonds	312
12.3.2	Activation of C(sp ¹)—H Bonds	315
12.4	C—E Bond Activation	317
12.4.1	Activation of Carbon–Halogen Bonds	317
12.4.2	Activation of Carbon–Oxygen Bonds	318
12.4.3	Activation of Carbon–Carbon Bonds	318
12.5	Ammonia Borane Dehydrogenation	319
12.6	Conclusions	321
	Acknowledgments	321
	References	321
13	Iridium-Mediated Alkane Dehydrogenation	325
	<i>David Morales-Morales</i>	
13.1	Introduction	325
13.1.1	The Beginning	326
13.2	Alkane C—H Activation with Ir Derivatives	327
13.3	Alkane Dehydrogenation with Ir Complexes	328
13.4	Alkane Dehydrogenation Catalyzed by Ir Pincer Complexes	333
13.4.1	Ir-PCP Pincer Compounds	333
13.4.2	Ir-POCOP Pincer Compounds	336

13.5	Final Remarks	342
	Acknowledgments	342
	References	342
14	Transformations of (Organo)silicon Compounds Catalyzed by Iridium Complexes	345
	<i>Bogdan Marciniec and Ireneusz Kownacki</i>	
14.1	Introduction	345
14.2	Hydrosilylation and Dehydrogenative Silylation of Carbon–Carbon Multiple Bonds	346
14.2.1	Hydrosilylation and Dehydrogenative Silylation of Alkenes	346
14.2.2	Application of Hydrosilylation in Polymer Chemistry	348
14.2.3	Hydrosilylation and Dehydrogenative Silylation of Alkynes	349
14.3	Asymmetric Hydrosilylation of Ketones and Imines	352
14.4	Transformation of Organosilicon Compounds in the Presence of Carbon Monoxide	356
14.4.1	Hydroformylation of Vinylsilanes	356
14.4.2	Silylcarbonylation of Alkenes and Alkynes	357
14.5	Silylation of Aromatic Carbon–Hydrogen Bonds	359
14.6	Silylation of Alkenes with Vinylsilanes	360
14.7	Alcoholysis and Oxygenation of Hydrosilanes	361
14.8	Isomerization of Silyl Olefins	361
14.9	Addition of silylacetylenes $\equiv\text{C}-\text{H}$ Bonds into Imines	362
14.10	Conclusions	364
	References	365
15	Catalytic Properties of Soluble Iridium Nanoparticles	369
	<i>Jackson D. Scholten and Jairton Dupont</i>	
15.1	Introduction	369
15.2	Synthesis of Soluble Iridium Nanoparticles	369
15.2.1	Polyoxoanions	369
15.2.2	Surfactants	370
15.2.3	Imidazolium Ionic Liquids	372
15.3	Kinetic Studies of Iridium Nanoparticle Formation: The Autocatalytic Mechanism	377
15.4	Catalytic Applications of Soluble Iridium Nanoparticles	380
15.5	Conclusions	387
	References	388
	Index	391