Contents

Preface XIII
List of Contributors XV

1 Metal-Catalyzed Cross-Couplings of Aryl Halides to Form C–C Bonds in Aqueous Media 1
Kevin H. Shaughnessy

1.1 Introduction 1

1.2 Aqueous-Phase Cross-Coupling Using Hydrophilic Catalysts 3
1.2.1 Hydrophilic Triarylphtosphines and Diarylalkylphosphines 3
1.2.2 Sterically Demanding, Hydrophilic Trialkyl and Dialkylbiarylphosphines 7
1.2.3 NHC Ligands 10
1.2.4 Nitrogen Ligands 13

1.3 Cross-Coupling in Aqueous Media Using Hydrophobic Ligands 17
1.3.1 Surfactant-Free Reactions 17
1.3.2 Surfactant-Promoted Reactions 20
1.3.2.1 Cationic Surfactants 21
1.3.2.2 Anionic Surfactants 22
1.3.2.3 Nonionic Surfactants 22

1.4 Heterogeneous Catalysts in Aqueous Media 25
1.4.1 Supported Palladium–Ligand Complexes 25
1.4.1.1 Polymer-Supported Palladium Complexes 25
1.4.1.2 Palladium Complexes Supported on Inorganic Materials 27
1.4.2 Nanoparticle-Catalyzed Coupling 29
1.4.2.1 Unsupported Palladium Nanoparticle Catalysts 29
1.4.2.2 Polymer-Supported Nanoparticles 30
1.4.2.3 Inorganic-Supported Nanoparticle Catalysts 33

1.5 Special Reaction Conditions 35
1.5.1 Microwave Heating 35
1.5.2 Ultrasound 36
1.5.3 Thermomorphic Reaction Control 36
1.6 Homogeneous Aqueous-Phase Modification of Biomolecules 37
1.6.1 Amino Acids and Proteins 37
1.6.2 Nucleosides and Nucleotides 38
1.7 Conclusion 39
References 39

2 Metal-Catalyzed C–H Bond Activation and C–C Bond Formation in Water 47
Bin Li and Pierre H. Dixneuf
2.1 Introduction 47
2.2 Catalytic Formation of C–C Bonds from spC–H Bonds in Water 48
2.2.1 Catalytic Nucleophilic Additions of Alkynes in Water 48
2.2.2 Addition of Terminal Alkynes to C= C Bonds in Water 49
2.2.3 The Sonogashira-Type Reactions in Water 49
2.3 Activation of sp²C–H Bonds for Catalytic C–C Bond Formation in Water 53
2.3.1 Homocoupling of sp²C–H Bonds 53
2.3.2 Direct C–H Bond Arylation of Alkenes and Aryl Boronic Acid Derivatives 55
2.3.3 Cross-Coupling Reactions of sp²C–H Bonds with sp²C-X Bonds in Water 56
2.3.3.1 Direct C–H Bond Arylations with Aryl Halides and Palladium Catalysts 56
2.3.3.2 Direct C–H Bond Arylations with Aryl Halides and Ruthenium Catalysts 62
2.3.4 Cross-Coupling Reactions of sp²C–H Bonds with Carbon Nucleophiles in Water 64
2.3.5 Oxidative Cross-Coupling of sp²C–H Bond Reactions in Water 65
2.3.5.1 Alkenylations of Arenes and Heteroarenes with Palladium Catalysts 65
2.3.5.2 Alkenylation of Heterocycles Using In(OTf)₃ Catalyst 68
2.3.5.3 Alkenylation of Arenes and Heteroarenes with Ruthenium(II) Catalysts 69
2.4 Activation of sp³C–H Bonds for Catalytic C–C Bond Formation in Water 73
2.4.1 Selective sp³C–H Activation of Ketones 73
2.4.2 Catalytic Enantioselective Alkynylation of sp³C–H Bonds 74
2.4.3 Cross-Dehydrogenative Coupling between sp³C–H Bonds Adjacent to a Heteroatom 75
2.4.4 Catalytic Enolate Carbon Coupling with (Arene) C–X Carbon 77
2.4.5 Arylation of sp³C–H Bonds with Aryl Halides or sp²C–H Bond 79
2.5 Conclusion 80
Acknowledgments 81
References 81
3 Catalytic Nucleophilic Additions of Alkynes in Water 87
Xiaoquan Yao and Chao-Jun Li

3.1 Introduction 87

3.2 Catalytic Nucleophilic Additions of Terminal Alkynes with Carbonyl Derivatives 88

3.2.1 Reaction with Acid Chlorides 89
3.2.2 Reaction with Aldehydes 89
3.2.3 Reaction with Ketones 95
3.3 Addition of Terminal Alkyne to Imine, Tosylimine, Iminium Ion, and Acyl Iminium Ion 96

3.3.1 Reaction with Imines 97
3.3.2 Reaction with Iminium Ions 99
3.3.3 Reaction with Acylimine and Acyliminium Ions 102

3.4 Direct Conjugate Addition of Terminal Alkynes 103
3.5 Conclusions 105

Acknowledgments 105

References 106

4 Water-Soluble Hydroformylation Catalysis 109
Duc Hanh Nguyen, Martine Urrutigoity, and Philippe Kalck

4.1 Introduction 109

4.2 Hydroformylation of Light C2–C5 Alkenes in the RCH/RP Process 110

4.3 Hydroformylation of Alkenes Heavier than C5 115

4.3.1 Water-Soluble and Amphiphilic Ligands 116
4.3.2 Phase-Transfer Agents: Cyclodextrins and Calixarenes 120
4.3.3 Supported Aqueous-Phase Catalysis 125

4.4 Innovative Expansions 128
4.4.1 Thermoregulated Catalytic Systems 128
4.4.2 Ionic Liquids and Carbon Dioxide Induced Phase Switching 129
4.4.3 Cascade Reactions 130

4.5 Conclusion 132

References 133

5 Green Catalytic Oxidations in Water 139
Roger A. Sheldon

5.1 Introduction 139

5.2 Examples of Water-Soluble Ligands 140

5.3 Enzymatic Oxidations 140

5.4 Biomimetic Oxidations 142

5.5 Epoxidation, Dihydroxylation, and Oxidative Cleavage of Olefins 143
5.5.1 Tungsten-Based Systems 144
5.5.2 Manganese- and Iron-Based Systems 145
5.5.3 Ruthenium and Platinum Catalysts 148
5.5.4 Other Systems 149
5.6 Alcohol Oxidations  151
  5.6.1 Tungsten (VI) Catalysts  151
  5.6.2 Palladium Diamine Complexes as Catalysts  153
  5.6.3 Noble Metal Nanoparticles as Quasi-Homogeneous Catalysts  156
  5.6.4 Ruthenium and Manganese Catalysts  158
  5.6.5 Organocatalysts: Stable N-Oxy Radicals and Hypervalent Iodine Compounds  158
  5.6.6 Enzymatic Oxidation of Alcohols  161
5.7 Sulfoxidations in Water  161
  5.7.1 Tungsten- and Vanadium-Catalyzed Oxidations  162
  5.7.2 Enantioselective Sulfoxidation with Enzymes  163
  5.7.3 Flavins as Organocatalysts for Sulfoxidation  165
5.8 Conclusions and Future Outlook  166
References  166

6 Hydrogenation and Transfer Hydrogenation in Water  173
  Xiaofeng Wu and Jianliang Xiao
  6.1 Introduction  173
  6.2 Water-Soluble Ligands  174
    6.2.1 Water-Soluble Achiral Ligands  175
    6.2.2 Water-Soluble Chiral Ligands  175
  6.3 Hydrogenation in Water  176
    6.3.1 Achiral Hydrogenation  176
      6.3.1.1 Hydrogenation of Olefins  176
      6.3.1.2 Hydrogenation of Carbonyl Compounds  183
      6.3.1.3 Hydrogenation of Aromatic Rings  185
      6.3.1.4 Hydrogenation of Other Organic Groups  187
      6.3.1.5 Hydrogenation of CO₂  188
    6.3.2 Asymmetric Hydrogenation  191
      6.3.2.1 Asymmetric Hydrogenation of Olefins  191
      6.3.2.2 Asymmetric Hydrogenation of Carbonyl and Related Compounds  194
      6.3.2.3 Asymmetric Hydrogenation of Imines  196
  6.4 Transfer Hydrogenation in Water  197
    6.4.1 Achiral Transfer Hydrogenation  198
      6.4.1.1 Achiral Transfer Hydrogenation of Carbonyl Compounds  198
      6.4.1.2 Achiral Transfer Hydrogenation of Imino Compounds  203
    6.4.2 Asymmetric Transfer Hydrogenation  204
      6.4.2.1 Asymmetric Transfer Hydrogenation of C=C Double Bonds  204
      6.4.2.2 Asymmetric Transfer Hydrogenation of Simple Ketones  204
      6.4.2.3 Asymmetric Transfer Hydrogenation of Functionalized Ketones  209
      6.4.2.4 Asymmetric Transfer Hydrogenation of Imines  213
    6.4.3 Asymmetric Transfer Hydrogenation with Biomimetic Catalysts  219
    6.4.4 Asymmetric Transfer Hydrogenation with Immobilized Catalysts  222
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>Role of Water</td>
<td>228</td>
</tr>
<tr>
<td>6.5.1</td>
<td>Coordination to Metals</td>
<td>228</td>
</tr>
<tr>
<td>6.5.2</td>
<td>Acid–Base Equilibrium</td>
<td>229</td>
</tr>
<tr>
<td>6.5.3</td>
<td>H–D Exchange</td>
<td>230</td>
</tr>
<tr>
<td>6.5.4</td>
<td>Participation in Transition States</td>
<td>231</td>
</tr>
<tr>
<td>6.6</td>
<td>Concluding Remarks</td>
<td>232</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>233</td>
</tr>
<tr>
<td>7</td>
<td>Catalytic Rearrangements and Allylation Reactions in Water</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>Victorio Cadierno, Joaquín García-Álvarez, and Sergio E. García-Garrido</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>243</td>
</tr>
<tr>
<td>7.2</td>
<td>Rearrangements</td>
<td>244</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Isomerization of Olefinic Substrates</td>
<td>244</td>
</tr>
<tr>
<td>7.2.1.1</td>
<td>Isomerization of Allylic Alcohols, Ethers, and Amines</td>
<td>244</td>
</tr>
<tr>
<td>7.2.1.2</td>
<td>Isomerization of Other Olefins</td>
<td>252</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Cycloisomerizations and Related Cyclization Processes</td>
<td>256</td>
</tr>
<tr>
<td>7.2.3</td>
<td>Other Rearrangements</td>
<td>261</td>
</tr>
<tr>
<td>7.3</td>
<td>Allylation Reactions</td>
<td>264</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Allylic Substitution Reactions</td>
<td>265</td>
</tr>
<tr>
<td>7.3.1.1</td>
<td>Palladium-Catalyzed Allylic Substitution Reactions (Tsuji–Trost Allylations)</td>
<td>265</td>
</tr>
<tr>
<td>7.3.1.2</td>
<td>Other Metal-Catalyzed Allylic Substitution Reactions</td>
<td>272</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Allylation Reactions of C=O and C=N Bonds</td>
<td>273</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Other Allylation Reactions in Aqueous Media</td>
<td>278</td>
</tr>
<tr>
<td>7.4</td>
<td>Conclusion</td>
<td>279</td>
</tr>
<tr>
<td></td>
<td>Acknowledgments</td>
<td>279</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>280</td>
</tr>
<tr>
<td>8</td>
<td>Alkene Metathesis in Water</td>
<td>291</td>
</tr>
<tr>
<td></td>
<td>Karol Grela, Łukasz Gułański, and Krzysztof Skowerski</td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>291</td>
</tr>
<tr>
<td>8.1.1</td>
<td>General Introduction to Olefin Metathesis</td>
<td>291</td>
</tr>
<tr>
<td>8.1.2</td>
<td>Metathesis of Water-Soluble Substrates</td>
<td>293</td>
</tr>
<tr>
<td>8.1.3</td>
<td>Metathesis of Water-Insoluble Substrates</td>
<td>300</td>
</tr>
<tr>
<td>8.1.3.1</td>
<td>&quot;Enabling Techniques&quot; for Olefin Metathesis in Aqueous Media</td>
<td>300</td>
</tr>
<tr>
<td>8.1.3.2</td>
<td>Other Additives and Techniques</td>
<td>305</td>
</tr>
<tr>
<td>8.2</td>
<td>Examples of Applications of Olefin Metathesis in Aqueous Media</td>
<td>308</td>
</tr>
<tr>
<td>8.2.1</td>
<td>Polymerizations</td>
<td>308</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Metathesis of Water-Soluble Substrates</td>
<td>312</td>
</tr>
<tr>
<td>8.2.2.1</td>
<td>Ring-Closing Metathesis and Enyne Cycloisomerization of Water-Soluble Substrates</td>
<td>312</td>
</tr>
<tr>
<td>8.2.2.2</td>
<td>Cross Metathesis of Water-Soluble Substrates</td>
<td>315</td>
</tr>
<tr>
<td>8.2.3</td>
<td>Cross Metathesis with Substrate Having an Allylic Heteroatom</td>
<td>316</td>
</tr>
<tr>
<td>8.2.4</td>
<td>Metathesis of Water-Insoluble Substrates</td>
<td>318</td>
</tr>
</tbody>
</table>