

Contents

Preface XIII

List of Contributors XV

1	Metal-Catalyzed Cross-Couplings of Aryl Halides to Form C–C Bonds in Aqueous Media	1
	<i>Kevin H. Shaughnessy</i>	
1.1	Introduction	1
1.2	Aqueous-Phase Cross-Coupling Using Hydrophilic Catalysts	3
1.2.1	Hydrophilic Triarylphosphines 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
1.2.5	Palladacyclic Complexes	15
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
	<i>Bin Li and Pierre H. Dixneuf</i>	
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 sp ² C–H Bonds for Catalytic C–C Bond Formation in Water	53
2.3.1	Homocoupling of sp ² C–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 sp ² C–H Bonds with sp ² C–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 sp ² C–H Bonds with Carbon Nucleophiles in Water	64
2.3.5	Oxidative Cross-Coupling of sp ² C–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 sp ³ C–H Bonds for Catalytic C–C Bond Formation in Water	73
2.4.1	Selective sp ³ C–H Activation of Ketones	73
2.4.2	Catalytic Enantioselective Alkynylation of sp ³ C–H Bonds	74
2.4.3	Cross-Dehydrogenative Coupling between sp ³ C–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 sp ³ C–H Bonds with Aryl Halides or sp ² C–H Bond	79
2.5	Conclusion	80
	Acknowledgments	81
	References	81

3	Catalytic Nucleophilic Additions of Alkynes in Water	87
	<i>Xiaoquan Yao and Chao-Jun Li</i>	
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
	<i>Duc Hanh Nguyen, Martine Urrutigoity, and Philippe Kalck</i>	
4.1	Introduction	109
4.2	Hydroformylation of Light C ₂ –C ₅ Alkenes in the RCH/RP Process	110
4.3	Hydroformylation of Alkenes Heavier than C ₅	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
	<i>Roger A. Sheldon</i>	
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
	<i>Xiaofeng Wu and Jianliang Xiao</i>	
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 CO ₂	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

6.5	Role of Water	228
6.5.1	Coordination to Metals	228
6.5.2	Acid–Base Equilibrium	229
6.5.3	H–D Exchange	230
6.5.4	Participation in Transition States	231
6.6	Concluding Remarks	232
	References	233
7	Catalytic Rearrangements and Allylation Reactions in Water	243
	<i>Victorio Cadierno, Joaquín García-Álvarez, and Sergio E. García-Garrido</i>	
7.1	Introduction	243
7.2	Rearrangements	244
7.2.1	Isomerization of Olefinic Substrates	244
7.2.1.1	Isomerization of Allylic Alcohols, Ethers, and Amines	244
7.2.1.2	Isomerization of Other Olefins	252
7.2.2	Cycloisomerizations and Related Cyclization Processes	256
7.2.3	Other Rearrangements	261
7.3	Allylation Reactions	264
7.3.1	Allylic Substitution Reactions	265
7.3.1.1	Palladium-Catalyzed Allylic Substitution Reactions (Tsuji–Trost Allylations)	265
7.3.1.2	Other Metal-Catalyzed Allylic Substitution Reactions	272
7.3.2	Allylation Reactions of C=O and C=N Bonds	273
7.3.3	Other Allylation Reactions in Aqueous Media	278
7.4	Conclusion	279
	Acknowledgments	279
	References	280
8	Alkene Metathesis in Water	291
	<i>Karol Grela, Łukasz Gułajski, and Krzysztof Skowerski</i>	
8.1	Introduction	291
8.1.1	General Introduction to Olefin Metathesis	291
8.1.2	Metathesis of Water-Soluble Substrates	293
8.1.3	Metathesis of Water-Insoluble Substrates	300
8.1.3.1	“Enabling Techniques” for Olefin Metathesis in Aqueous Media	300
8.1.3.2	Other Additives and Techniques	305
8.2	Examples of Applications of Olefin Metathesis in Aqueous Media	308
8.2.1	Polymerizations	308
8.2.2	Metathesis of Water-Soluble Substrates	312
8.2.2.1	Ring-Closing Metathesis and Enyne Cycloisomerization of Water-Soluble Substrates	312
8.2.2.2	Cross Metathesis of Water-Soluble Substrates	315
8.2.3	Cross Metathesis with Substrate Having an Allylic Heteroatom	316
8.2.4	Metathesis of Water-Insoluble Substrates	318

8.2.4.1	Ring-Closing Metathesis of Water-Insoluble Substrates	318
8.2.4.2	Enyne Cycloisomerization	328
8.2.4.3	Cross Metathesis of Water-Insoluble Substrates	328
8.3	Conclusions and Outlook	332
	Acknowledgments	333
	References	333
9	Nanocatalysis in Water	337
	<i>R. B. Nasir Baig and Rajender S. Varma</i>	
9.1	Introduction	337
9.2	Nanocatalysis	338
9.3	Effects of Size of Nanocatalysts	339
9.4	Transition-Metal Nanoparticles	340
9.4.1	Synthesis of Transition-Metal Nanoparticles	341
9.4.2	Greener Synthesis of Nanomaterials	341
9.4.3	Immobilization of M-NPs on a Solid Support	343
9.5	Catalytic Applications of Transition-Metal-Based Nanomaterials	343
9.6	Pd Nanoparticles in Organic Synthesis	344
9.6.1	Pd Nanoparticles in Suzuki Reactions	344
9.6.2	Pd Nanoparticles in the Heck Reactions	350
9.6.3	Pd Nanoparticles in the Sonogashira Reactions	354
9.6.4	Pd Nanoparticles in the Stille Coupling Reactions	359
9.6.5	Pd Nanoparticles in the Hiyama Couplings	360
9.6.6	Pd Nanoparticles in the Tsuji–Trost Reaction	361
9.7	Nanogold Catalysis	362
9.7.1	Coupling Reactions	362
9.7.1.1	The Suzuki–Miyaura Cross-Coupling Reaction	362
9.7.1.2	Homocoupling of Arylboronic Acid	365
9.7.2	Reduction Reactions	366
9.7.2.1	Hydrogenation of Benzene	366
9.7.2.2	Nitro group reduction	367
9.7.3	Oxidation Reactions	368
9.7.3.1	Benzylic and Allylic C–H Bonds Oxidation	368
9.7.3.2	Epoxidation of Propylene	369
9.7.3.3	Oxidation of Alcohols	370
9.7.4	Hydration of Alkynes	371
9.8	Copper Nanoparticles	372
9.8.1	Phenylselenylation of Aryl Iodides and Vinyl Bromides	372
9.8.2	Cu-Nanoparticle-Catalyzed Selective Synthesis of Phenols, Anilines, and Thiophenols	373
9.8.3	Hydrogenation of Azides over Copper Nanoparticles	373
9.8.4	Cu-Nanoparticle-Catalyzed Synthesis of Aryl Dithiocarbamate	374
9.8.5	Click Chemistry	375
9.9	Ruthenium Nanocatalysts	376
9.10	Magnetic Iron Oxide Nanoparticle	378

9.10.1	Synthesis of Heterocycles	378
9.10.2	Homocoupling of Arylboronic Acid	381
9.10.3	Rh Anchored on Fe ₃ O ₄ Nanoparticles	382
9.11	Cobalt Nanoparticles	384
9.12	Conclusion	386
	References	387

Index	395
--------------	-----

