Contents

Introduction and Preface 1 Laurel G. Habgood, Lutz Ackermann, and T. Brent Gunnoe References 3

1 Functionalization of Heteroaromatic Substrates using Groups 9 and 10 Catalysts 5 v

Pedro Villuendas, Sara Ruiz, and Esteban P. Urriolabeitia

- 1.1 Introduction 5
- 1.2 Thiophenes, furans, and Related Heterocycles 8
- 1.3 Pyrroles, Indoles, Pyridines, and Imidazopyridines 21
- 1.4 Azoles and Other Miscellaneous Heterocycles 31
- 1.5 Summary 39 References 40
- 2 Ruthenium Catalysts for the Alkylation of Functionalized Arenes and Heteroaromatic Substrates via Hydroarylation 49 David J. Burns, Sergei I. Kozhushkov, and Lutz Ackermann
- 2.1 Introduction 49
- 2.2 Alkylation by Ruthenium(0) Catalysts via Oxidative-Addition C–H Activation 50
- 2.2.1 Alkylation by Ruthenium(II) Catalysts via Carboxylate-Assisted C–H Activation *63*
- 2.3 Summary and Conclusions 70 Abbreviations 71 References 71
- 3 Alkylation of Arenes Without Chelation Assistance: Transition Metal Catalysts with d⁶ Electron Configurations 83 Bradley A. McKeown, Laurel Goj Habgood, Thomas R. Cundari, and T. Brent Gunnoe
- 3.1 Transition Metal-Mediated Arene Alkylation: Overview 83
- 3.2 Octahedral d⁶ Transition Metal Catalysts for Olefin Hydroarylation: Scorpionate Supported Ru(II) Catalysts 85

vi Contents

- Structure–Activity Relationships with TpRu(L)(NCMe)Ph: 3.2.1 Examination of Elementary Steps and Catalytic Hydrophenylation of Ethylene as a Function of Ligand L 90
- Ethylene Hydrophenylation Catalyzed by Cationic Ru(II) Complexes 3.2.2 Ligated by Poly(pyrazolyl)alkanes 93
- Olefin Hydroarylation Catalyzed by Octahedral d⁶ Ir(III) Supported by 3.3 the Acetylacetonate Ligand 95
- 3.3.1 Mechanism of Catalytic Olefin Hydrophenylation using Ir(III) Supported by the Acetylacetonate Ligand 96
- Other d⁶ Ir(III) Catalysts 98 3.3.2
- Summary: Comparison of Ru(II) and Ir(III) Catalysts for Olefin 3.4 Hvdroarvlation 99
- 3.5 Future Outlook: Extension of Olefin Hydroarylation using Hydrocarbons to Earth Abundant Metals 100 References 102

4 Hydroarylation of Olefins with Complexes Bearing d⁸ Metal Centers 107

Benjamin A. Suslick and T. Don Tilley

- 4.1Introduction 107
- Pt^{II} Catalyzed Hydroarylation 109 4.2
- Pt^{II} Hydroarylation Catalysts Bearing Anionic Bidentate (NN) 4.2.1Ligands 109
- Pt^{II} Hydroarylation Catalysts Bearing Neutral Bidentate (NN) 4.2.2 Ligands 114
- 4.2.3 Pt^{II} Hydroarylation Catalysts Supported by Nonnitrogen-based Ligands 119
- Summary of Pt^{II} Catalyzed Hydroarylations 123 4.2.4
- 4.3 Rh^I-Catalyzed Hydroarylation 124
- Reactions of Unfunctionalized Arenes with Rh^I Complexes Proceeding 4.3.1 via Hydroarylation-Like Mechanisms 124
- 4.3.2 Directed *ortho*-Hydroarylation Catalyzed by Rh^I Complexes 126
- 4.3.3 Rh^I-Catalyzed Hydroarylation with Fluorinated Arenes 142
- Summary of Rh^I-Catalyzed Hydroarylation 142 4.3.4
- Directed *ortho*-Hydroarylation Catalyzed by Ir^I Complexes 144 4.4
- Hydroarylation with Ni⁰ Complexes via Ni^{II} Intermediates 152 4.5
- 4.6 Formal Hydroarylation Reactions with Pd^{II} Catalysts via Heck-Like Mechanisms 155
- Formate-Assisted Pd^{II} Catalyzed Hydroarylation 155 4.6.1
- 4.6.2 Oxidatively Coupled Pd^{II}-Catalyzed Hydroarylation with Aryltin and Arylboronic Ester Substrates 160
- Summary of Pd^{II}-Catalyzed Formal Hydroarylation Reactions 163 4.6.3
- 4.7Conclusions 166 References 166

5	Hydroarylation of C–C Multiple Bonds Using Nickel		Nickel
	Catalysta 177	175	

Catalysts 175 Yoshiaki Nakao

- 5.1 Introduction 175
- 5.2 Hydroarylation of Alkynes *175*
- 5.3 Hydroheteroarylation of Alkynes 179
- 5.3.1 Hydroheteroarylation of Alkynes with five-Membered Heteroarenes *179*
- 5.3.2 Hydroheteroarylation of Alkynes with Azine-*N*-oxides 182
- 5.3.3 Hydroheteroarylation of Alkynes with Azines *182*
- 5.4 Hydroarylation of Alkenes 184
- 5.5 Hydroheteroarylation of Alkenes 185
- 5.5.1 Hydroheteroarylation of Alkenes with five-Membered Heteroarenes *185*
- 5.5.2 Hydroheteroarylation of Alkenes with Azines 188
- 5.6 Summary and Outlook *189* References *190*
- 6 Hydroarylation of Alkynes and Alkenes using Group 7–9 First-Row Transition Metal Catalysts 193 Naohiko Yoshikai

6.1 Introduction *193*

- 6.2 Hydroarylation of Alkynes and Alkenes using Cobalt Catalysts 194
- 6.2.1 Hydroarylation of Alkynes using Low-Valent Cobalt Catalysts 194
- 6.2.2 Hydroarylation of Alkenes using Low-Valent Cobalt Catalysts 199
- 6.2.3 Hydroarylation of Alkynes and Alkenes using Cp*Co^{III} Catalysts 206
- 6.3 Hydroarylation of Alkynes and Alkenes using Iron Catalysts 208
- 6.3.1 Hydroarylation of Alkynes and Alkenes using Low-Valent Iron Catalysts 208
- 6.3.2 Hydroarylation of Alkenes using Lewis Acidic Iron Catalysts 208
- 6.4 Hydroarylation of Alkynes using Low-Valent Manganese Catalyst 209
- 6.5 Conclusions 211
- 6.6 Abbreviations 211 References 212

7 Hydroarylation of Alkynes using Cu, Ag, and Au Catalysts 217

- Mariia S. Kirillova, Fedor M. Miloserdov, and Antonio M. Echavarren
- 7.1 Introduction 217
- 7.2 Intramolecular Hydroarylation of Alkynes 218
- 7.2.1 Alkyne Hydroarylation with Electron-Rich Arenes 218
- 7.2.1.1 Alkyne Hydroarylation with Aniline Derivatives 218
- 7.2.1.2 Alkyne Hydroarylation with Phenols and Phenol Ether Derivatives 225

- 7.2.2 Alkyne Hydroarylation with Other Arenes 231
- 7.2.3 Alkyne Hydroarylation with Indoles 237
- 7.2.3.1 Alkenylation of Indoles at the 2-Position 239
- 7.2.3.2 Alkenylation of Indoles at the 3-position 242
- 7.2.3.3 Spirocyclizations 244
- 7.2.3.4 More Complex Transformations Featuring a Hydroarylation of Alkynes 246
- 7.2.4 Alkyne Hydroarylation with Pyrroles 258
- 7.2.5 Alkyne Hydroarylation with Furans and Benzofurans 263
- 7.2.5.1 Alkenylation at the 2-Position of Furan 264
- 7.2.5.2 Alkenylation at the 3-Position of Furan 265
- 7.2.5.3 More Complex Transformations Featuring Hydroarylation of Alkynes 265
- 7.2.5.4 The Furan–Yne Cycloisomerization to Phenols 270
- 7.2.6 Alkyne Hydroarylation with Thiophenes and Benzothiophenes 276
- 7.3 Intermolecular Hydroarylation of Alkynes 277
- 7.3.1 Intermolecular Hydroarylation of Alkynes with Arenes 277
- 7.3.2 Intermolecular Hydroarylation of Alkynes with Heteroarenes 278
- 7.3.2.1 N-Heterocycles 279
- 7.3.2.2 O-Heterocycles 282
- 7.4 Metal-Supported Catalysts and Their Applications in Hydroarylation of Alkynes 284
- 7.5 Hydroarylation of Alkynes in Total Synthesis 288 References 291
- 8 Catalytic Alkyne Hydroarylation Using Arylboron Reagents, Aryl Halides, and Congeners 305
- Yoshihiko Yamamoto
- 8.1 Introduction 305
- 8.2 Catalyzed Alkyne Hydroarylations Using Arylboron and Arylsilicon Reagents 307
- 8.2.1 Rhodium-Catalyzed Reactions 308
- 8.2.2 Palladium-Catalyzed Reactions 315
- 8.2.3 Reactions Catalyzed by First Row Transition Metals 321
- 8.3 Catalyzed Alkyne Hydroarylations Using Aryl Halides and Arenediazonium Compounds 326
- 8.3.1 Intermolecular Reductive Heck Reactions 327
- 8.3.2 Intramolecular Reductive Heck Reactions 333
- 8.4 Synthetic Applications of Alkyne Hyaroarylations Using Arylboron Reagents and Aryl Halides 336
- 8.4.1 Sequential Processes Involving Alkyne Hydroarylations Using Arylboron Reagents and Aryl Halides 336
- 8.4.1.1 Synthesis of Oxygen Heterocycles 336
- 8.4.1.2 Synthesis of Nitrogen and Phosphorous Heterocycles 341
- 8.4.1.3 Synthesis of Carbocycles 346

- 8.4.2 Synthesis of Bioactive Compounds and Natural Products via Alkyne Hydroarylations Using Arylboron Reagents and Aryl Halides 348
- 8.5 Summary 352 References 354

9 Transition Metal-Catalyzed Hydroarylation of Allenes 361

- Ross A. Widenhoefer
- 9.1 Introduction 361
- 9.2 Intramolecular Hydroarylation 362
- 9.2.1 Indoles as Nucleophiles 362
- 9.2.1.1 6-exo-Hydroarylation 362
- 9.2.1.2 5-exo-Hydroarylation 363
- 9.2.1.3 6-endo-Hydroarylation 364
- 9.2.1.4 5-endo-Hydroarylation 365
- 9.2.1.5 Less Common Modes of Ring Closure 367
- 9.2.2 Other Nucleophiles 368
- 9.2.2.1 6-exo-Hydroarylation 368
- 9.2.2.2 6-endo-Hydroarylation 373
- 9.2.2.3 Less Common Modes of Ring Closure 376
- 9.3 Intermolecular Hydroarylation 378
- 9.3.1 Indoles as Nucleophiles 378
- 9.3.1.1 Monoaddition Processes 378
- 9.3.1.2 Tandem Addition Processes 378
- 9.3.2 Furans as Nucleophiles 379
- 9.3.3 Alkoxy Benzenes as Nucleophiles 381
- 9.3.4 Alkyl Benzenes as Nucleophiles 383
- 9.4 Enantioselective Hydroarylation 384
- 9.4.1 Intramolecular Hydroarylation 384
- 9.4.2 Intermolecular Hydroarylation 384
- 9.5 Summary and Outlook 385 References 386

Index 389