

Contents

Preface *xi*

Part I Reactions via Nickelacycles 1

- 1 Formation of Nickelacycles and Reaction with Carbon Monoxide 3**
Sensuke Ogoshi
 - 1.1 Introduction 3
 - 1.2 Formation of Hetero-nickelacycles from Nickel(0) 3
 - 1.3 Stoichiometric Reaction of Hetero-nickelacycles with Carbon Monoxide 4
 - References 9

- 2 Transformation of Aldehydes via Nickelacycles 13**
Yoichi Hoshimoto
 - 2.1 Introduction and Scope of This Chapter 13
 - 2.2 Catalytic Transformation of Aldehydes Through Three-Membered Oxanickelacycle Complexes 14
 - 2.3 Catalytic Transformation of Aldehydes Through Five-Membered Oxanickelacycle Complexes 18
 - 2.4 Catalytic Transformation of Aldehydes Through Seven-Membered Oxanickelacycle Complexes 22
 - 2.5 Conclusion and Outlook 23
 - References 25

- 3 Transformation of Imines via Nickelacycles 29**
Masato Ohashi
 - 3.1 Introduction 29
 - 3.2 [2 + 2 + 1] Carbonylative Cycloaddition of an Imine and Either an Alkyne or an Alkene Leading to γ -Lactams 29
 - 3.3 [2 + 2 + 2] Cycloaddition Reaction of an Imine with Two Alkynes: Formation of 1,2-Dihydropyridine Derivatives 31

- 3.4 Three-Component Coupling and Cyclocondensation Reactions of an Imine, an Alkyne, and Alkylmetal Reagents 34
References 37
- 4 Asymmetric C—C Bond Formation Reactions via Nickelacycles 39**
Ravindra Kumar and Sensuke Ogoshi
- 4.1 Introduction 39
- 4.2 Enantioselective Reactions Involving Nickelacycles 39
- 4.2.1 Nickel-Catalyzed Asymmetric Coupling of Alkynes and Aldehydes 39
- 4.2.1.1 Nickel-Catalyzed Asymmetric Reductive Coupling of Alkynes and Aldehydes 40
- 4.2.1.2 Nickel-Catalyzed Asymmetric Alkylative Coupling of Alkynes and Aldehydes 43
- 4.2.2 Nickel-Catalyzed Asymmetric Coupling of Alkynes and Imines 44
- 4.2.3 Nickel-Catalyzed Asymmetric Coupling of 1,3-Enynes and Aldehydes 45
- 4.2.4 Nickel-Catalyzed Asymmetric Coupling of 1,3-Enynes and Ketones 46
- 4.2.5 Nickel-Catalyzed Asymmetric Coupling of 1,3-Dienes and Aldehydes 47
- 4.2.6 Nickel-Catalyzed Asymmetric Coupling of Enones and Alkynes 50
- 4.2.6.1 Nickel-Catalyzed Asymmetric Alkylative Coupling of Enones and Alkynes 50
- 4.2.6.2 Nickel-Catalyzed Asymmetric Coupling of Enones and Alkynes 51
- 4.2.7 Nickel-Catalyzed Asymmetric Coupling of Arylenoates and Alkynes 55
- 4.2.8 Nickel-Catalyzed Asymmetric Coupling of Diynes with Ketenes 56
- 4.2.9 Nickel-Catalyzed Asymmetric Coupling of Allenes, Aldehydes, and Silanes 57
- 4.2.10 Nickel-Catalyzed Asymmetric Coupling of Allenes and Isocyanates 58
- 4.2.11 Nickel-Catalyzed Asymmetric Coupling of Alkenes, Aldehydes, and Silanes 59
- 4.2.12 Nickel-Catalyzed Asymmetric Coupling of Formamide and Alkene 61
- 4.2.13 Nickel-Catalyzed Asymmetric Coupling of Alkynes and Cyclopropyl Carboxamide 63
- 4.3 Miscellaneous 64
- 4.3.1 Nickel-Catalyzed Asymmetric Annulation of Pyridones via Hydroarylation to Alkenes 64
- 4.3.2 Nickel-Catalyzed Asymmetric Synthesis of Benzoxasilole 65
- 4.4 Overview and Future Perspective 66
References 67

Part II Functionalization of Unreactive Bonds 69

- 5 Recent Advances in Ni-Catalyzed Chelation-Assisted Direct Functionalization of Inert C—H Bonds 71**
Yan-Hua Liu, Fang Hu, and Bing-Feng Shi
- 5.1 Introduction 71
- 5.2 Ni-Catalyzed Functionalization of Inert C—H Bonds Assisted by Bidentate Directing Groups 71
- 5.2.1 Arylation 72
- 5.2.2 Alkylation 76
- 5.2.3 Alkenylation 83
- 5.2.4 Alkynylation 85
- 5.2.5 Other C—C Bond Formation Reactions Directed by Bidentate Directing Group 88
- 5.2.6 C—N Bond Formation 89
- 5.2.7 C—Chalcogen (Chalcogen = O, S, Se) Bond Formation 89
- 5.2.8 C—Halogen Bond Formation 92
- 5.3 Ni-Catalyzed Functionalization of Inert C—H Bonds Assisted by Monodentate Directing Groups 94
- 5.3.1 Alkylation 94
- 5.3.2 Alkenylation 95
- 5.3.3 Alkynylation 96
- 5.3.4 C—Chalcogen Bond Formation 97
- 5.4 Summary 98
- References 98
- 6 C—C Bond Functionalization 103**
Yoshiaki Nakao
- 6.1 Introduction 103
- 6.2 C—C Bond Functionalization of Three-Membered Rings 103
- 6.3 C—C Bond Functionalization of Four- and Five-Membered Rings 110
- 6.4 C—C Bond Functionalization of Less Strained Molecules 113
- 6.5 C—CN Bond Functionalization 115
- 6.6 Summary and Outlook 116
- References 117
- 7 C—O Bond Transformations 123**
Mamoru Tobisu
- 7.1 Introduction 123
- 7.2 C(aryl)—O Bond Cleavage 124
- 7.2.1 Aryl Esters, Carbamates, and Carbonates 124
- 7.2.2 Aryl Ethers 132
- 7.2.3 Arenols 136
- 7.3 C(benzyl)—O Bond Cleavage 138

- 7.3.1 Benzyl Esters and Carbamates 138
- 7.3.2 Benzyl Ethers 140
- 7.4 C(acyl)—O Bond Cleavage 141
- 7.5 Summary and Outlook 144
- References 145

Part III Coupling Reactions via Ni(I) and/or Ni(III) 151

8 Photo-Assisted Nickel-Catalyzed Cross-Coupling

Processes 153

Christophe Lévéque, Cyril Ollivier, and Louis Fensterbank

- 8.1 Introduction 153
- 8.2 Development of Visible-Light Photoredox/Nickel Dual Catalysis 154
 - 8.2.1 For the Formation of Carbon–Carbon Bonds 154
 - 8.2.1.1 Starting from Organotrifluoroborates 154
 - 8.2.1.2 Starting from Carboxylates or Keto Acids or from Methylanilines 157
 - 8.2.1.3 Starting from Alkylsilicates 160
 - 8.2.1.4 Starting from 1,4-Dihydropyridines 166
 - 8.2.1.5 Starting from Alkylsulfonates 168
 - 8.2.1.6 Starting from Alkyl Bromides 168
 - 8.2.1.7 Starting from Xanthates 169
 - 8.2.1.8 Starting from Sp^3 CH Bonds 169
 - 8.2.2 For the Formation of Carbon–Heteroatom Bonds 170
 - 8.2.2.1 Formation of C–O Bond 170
 - 8.2.2.2 Formation of C–P Bond 171
 - 8.2.2.3 Formation of C–S Bond 171
- 8.3 Energy-Transfer-Mediated Nickel Catalysis 173
- 8.4 Conclusion 175
- References 176

9 Cross-Electrophile Coupling: Principles and New Reactions 183

Matthew M. Goldfogel, Liangbin Huang, and Daniel J. Weix

- 9.1 Introduction 183
- 9.2 Mechanistic Discussion of Cross-Electrophile Coupling 185
- 9.3 C(sp^2)—C(sp^3) Bond Formation 188
 - 9.3.1 Cross-Electrophile Coupling of Aryl-X and Alkyl-X 188
 - 9.3.2 Cross-Electrophile Coupling of ArX and Bn-X 195
 - 9.3.3 Cross-Electrophile Coupling of ArX and Allyl-X 196
 - 9.3.4 Vinyl-X with R-X 197
 - 9.3.5 Acyl-X with Alkyl-X 199
- 9.4 C(sp^2)—C(sp^2) Coupling 201
 - 9.4.1 Aryl-X/Vinyl-X + Aryl-X/Vinyl-X 201
 - 9.4.2 Aryl-X + Acyl-X 202
- 9.5 C(sp^3)—C(sp^3) Coupling 203

- 9.6 C(sp)–C(sp³) Coupling 205
- 9.7 Multicomponent Reactions 206
- 9.8 Future of the Field 208
- References 209
- 10 Organometallic Chemistry of High-Valent Ni(III) and Ni(IV) Complexes 223**
Liviu M. Mirica, Sofia M. Smith, and Leonel Griego
- 10.1 Introduction 223
- 10.2 Organometallic Ni(III) Complexes 223
- 10.3 Organometallic Ni(IV) Complexes 234
- 10.4 Other High-Valent Ni Complexes 239
- 10.4.1 Additional Ni^{III} Complexes 239
- 10.4.2 Additional Ni^{IV} Complexes 241
- 10.5 Conclusions and Outlook 243
- References 244
- Part IV Carbon Dioxide Fixation 249**
- 11 Carbon Dioxide Fixation via Nickelacycle 251**
Ryohei Doi and Yoshihiro Sato
- 11.1 Introduction: Carbon Dioxide as a C1 Building Block 251
- 11.2 Formation, Structure, and Reactivity of Nickelalactone 252
- 11.2.1 Formation and Characterization of Nickelalactone via Oxidative Cyclization with CO₂ 252
- 11.2.1.1 Reaction with Alkene 252
- 11.2.1.2 Reaction with Allene 255
- 11.2.1.3 Reaction with Diene 256
- 11.2.1.4 Reaction with Alkyne 257
- 11.2.1.5 Other Related Reactions 260
- 11.2.1.6 Generation of Nickelalactone Without CO₂ 261
- 11.2.2 Reactivity of Nickelalactone 261
- 11.2.2.1 Transmetalation with Organometallic Reagent 261
- 11.2.2.2 β-Hydride Elimination 263
- 11.2.2.3 Insertion of Another Unsaturated Molecule 264
- 11.2.2.4 Retro-cyclization 265
- 11.2.2.5 Nucleophilic Attack 265
- 11.2.2.6 Oxidation 267
- 11.2.2.7 Ligand Exchange 267
- 11.3 Catalytic Transformation via Nickelalactone 1: Reactions of Alkynes 268
- 11.3.1 Synthesis of Pyrone 268
- 11.3.1.1 Initial Finding 268
- 11.3.1.2 Reaction of Diynes with CO₂ 268
- 11.3.2 Synthesis of α,β-Unsaturated Ester 269

- 11.3.2.1 Electrochemical Reactions 269
- 11.3.2.2 Reduction with Organometallic Reagents 270
- 11.4 Catalytic Transformation via Nickelalactone 2: Reactions of Alkenes and Related Molecules 271
 - 11.4.1 Transformation of Diene, Allene, and Substituted Alkene 271
 - 11.4.1.1 Coupling of Diene with CO₂ 271
 - 11.4.1.2 Electrochemical Process 272
 - 11.4.1.3 Use of Reductant 272
 - 11.4.2 Synthesis of Acrylic Acid from Ethylene and CO₂ 274
 - 11.4.2.1 Before the Dawn 275
 - 11.4.2.2 Development of Catalytic Reaction 276
- 11.5 Concluding Remarks 278
- References 279

12 Relevance of Ni(II) in Catalytic Carboxylation Reactions 285

Rosie J. Somerville and Ruben Martin

- 12.1 Introduction 285
- 12.2 Mechanistic Building Blocks 287
 - 12.2.1 Additives 287
 - 12.2.2 Coordination of CO₂ 287
 - 12.2.3 Insertion/C—C Bond Formation 288
 - 12.2.4 Ligand Effects 289
 - 12.2.5 Oxidative Addition 290
 - 12.2.6 Oxidation State 290
 - 12.2.7 Single Electron Transfer (SET) 290
 - 12.2.8 Conclusion 290
- 12.3 Electrocarboxylation 291
 - 12.3.1 Introduction 291
 - 12.3.2 Phosphine Ligands 294
 - 12.3.3 Bipyridine and Related α -Diimine Ligands 296
 - 12.3.4 Salen Ligands 297
 - 12.3.5 Conclusion 298
- 12.4 Non-electrochemical Methods 298
 - 12.4.1 Aryl Halides 300
 - 12.4.2 Benzyl Electrophiles 304
 - 12.4.3 Carboxylation of Unactivated Alkyl Electrophiles 306
 - 12.4.4 Carboxylation of Allyl Electrophiles 312
 - 12.4.5 Unsaturated Systems 315
- 12.5 Conclusions 318
- References 319

Index 331