Contents

Preface xiii

1 Introduction: Carbon Monoxide as Synthon in Organic Synthesis 1 Bartolo Gabriele References 7

Part I Carbonylations Promoted by First Row Transition Metal Catalysts 13

2 Cobalt-Catalyzed Carbonylations 15

Jérôme Volkman and Philippe Kalck

- 2.1 Introduction 15
- 2.2 Carbon Monoxide and Its Surrogates 16
- 2.3 Hydroformylation of Alkenes 18
- 2.4 Carbonylation of Alkynes by the Pauson–Khand [2+2+1] Reaction 23
- 2.5 Carbonylation of Methanol 28
- 2.6 Carbonylation of Heterocycles 30
- 2.7 Carbonylation of Alkyl and Aryl Halides 36
- 2.8 C—H Bond Carbonylations 37
- 2.9 Miscellaneous Co-Catalyzed Carbonylations 39
- 2.10 Summary and Conclusions 40
 - References 41

3 Nickel-Catalyzed Carbonylations 51

Debarati Das and Bhalchandra M. Bhanage

- 3.1 Introduction 51
- 3.2 Nickel Halides in Carbonylation Reaction 52
- 3.3 Ni-Chelates as Precatalysts 56
- 3.4 Nanoparticles as Active Catalysts 60
- 3.5 Dinickel Complexes as Catalysts 62

- 3.6 Ni/AC as a Promising Heterogeneous Catalyst 63
- 3.7 Use of CO Surrogates with Nickel Catalysts 64
- 3.7.1 Metal Carbonyls as CO Surrogates 64
- 3.7.2 Formates as CO Surrogates 67
- 3.7.3 Acid or Acid Chlorides as CO Surrogates 69
- 3.8 Other Prominent Roles of Nickel in Carbonylation 73
- 3.9 Conclusion and Future Outlook 77 References 78
- 4 Carbonylations Catalyzed by Other First Row Transition-Metal Catalysts (Manganese, Iron, Copper) 83

Chong-Liang Li, Hai Wang, and Xiao-Feng Wu

- 4.1 Introduction 83
- 4.2 Synthesis of Ketones 83
- 4.3 Synthesis of Esters 90
- 4.4 Synthesis of Amides 95
- 4.5 Synthesis of Other Products 104
- 4.6 Summary and Conclusions 110 References 110

Part II Carbonylations Promoted by Second Row Transition Metal Catalysts 113

5 Ruthenium-Catalyzed Carbonylations 115

Helfried Neumann and Rajenahally V. Jagadeesh

- 5.1 Introduction 115
- 5.2 CH Activation of Nitrogen-Containing Arene Derivatives 116
- 5.3 Ruthenium-Catalyzed Carbonylations of Olefins and Nitroarenes 123
- 5.3.1 Ruthenium-Catalyzed Hydroformylations 123
- 5.3.2 Ruthenium-Catalyzed Alkoxycarbonylation of Olefins 126
- 5.3.3 Carbonylation of Nitroarenes 129
- 5.4 Ruthenium-Catalyzed Carbonylation of Amines and Alcohols 132
- 5.5 Ruthenium-Catalyzed Cyclocarbonylations 133
- 5.6 Ruthenium-Catalyzed Reactions Using Syngas 138
- 5.6.1 Fischer–Tropsch Synthesis 138
- 5.6.2 Synthesis of Oxo Products from Syngas 140
- 5.7 Synthesis of Oxo Products from H_2 and CO_2 142
- 5.8 Conclusions 144 References 144

6 Rhodium-Catalyzed Carbonylations 149

Oreste Piccolo and Stefano Paganelli

- 6.1 Introduction 149
- 6.2 Hydroformylation 151

Contents	ix

- 6.2.1 Catalyst Recovery 152
- 6.2.2 Aqueous Biphase Hydroformylation 156
- 6.2.3 Enantioselective Hydroformylation *161*
- 6.2.4 Tandem Hydroformylation 164
- 6.2.5 Syngas Surrogates 169
- 6.3 Carbonylation 171
- 6.4 Some Relevant Patents and Patent Applications (2015–2020) 184
- 6.4.1 Hydroformylation 184
- 6.4.2 Preparation of Acetic Acid and Similar Compounds and Derivatives *185*
- 6.4.3 Alcohols 185
- 6.5 Summary and Conclusions 185 References 186

7	Pall	adiu	m(0))-Cata	lyzed Carb	onylati	ons	197

- Jianming Liu, Chengtao Yue, and Fuwei Li
- 7.1 Introduction 197
- 7.2 Palladium(0)-Catalyzed Carbonylative Synthesis of Ester Derivatives *198*
- 7.2.1 Palladium(0)-Catalyzed Carbonylative Synthesis of Ester Derivatives from Aryl Halides *198*
- 7.2.2 Palladium(0)-Catalyzed Carbonylative Synthesis of Ester Derivatives from Alkynes 201
- 7.2.3 Palladium(0)-Catalyzed Carbonylative Synthesis of Ester Derivatives Using Benzyl Amines 208
- 7.3 Palladium(0)-Catalyzed Carbonylative Synthesis of Amide Derivatives 209
- 7.3.1 Palladium(0)-Catalyzed Carbonylative Synthesis of β-Lactams 209
- 7.3.2 Palladium(0)-Catalyzed Carbonylative Synthesis of Five, Six, Seven-Membered Cyclic Amides 211
- 7.3.3 Palladium(0)-Catalyzed Carbonylative Synthesis of Benzamide Derivatives *214*
- 7.4 Palladium(0)-Catalyzed Carbonylative Synthesis of Ketone Derivatives 217
- 7.4.1 Palladium(0)-Catalyzed Carbonylative Synthesis of Ketone Derivatives from Aryl Halides 217
- 7.4.2 Palladium(0)-Catalyzed Carbonylative Synthesis of Ketone Derivatives from Other Substrates 223
- 7.5 Palladium(0)-Catalyzed Carbonylative Synthesis of α,β-Alkynyl Ketones Derivatives 223
- 7.6 Palladium(0)-Catalyzed Carbonylative Synthesis of Other Carbonyl Compounds 225
- 7.7 Summary and Conclusions 232 References 232

x Contents

8	Palladium(II)-Catalyzed Carbonylations 235
	Bartolo Gabriele, Nicola Della Ca', Raffaella Mancuso, Lucia Veltri,
	and Ida Ziccarelli
8.1	Introduction 235
8.2	Palladium(II)-Catalyzed Carbonylation of Alkanes and Saturated C—H
	Bonds 236
8.3	Palladium(II)-Catalyzed Carbonylation of Arenes and
	Heteroarenes 239
8.4	Palladium(II)-Catalyzed Carbonylation of Alkenes 243
8.4.1	Palladium(II)-Catalyzed Carbonylation of Unfunctionalized Alkenes,
	Dienes, and Allenes 243
8.4.2	Palladium(II)-Catalyzed Carbonylation of Functionalized Alkenes and Allenes 250
8.5	Palladium(II)-Catalyzed Carbonylation of Alkynes 255
8.5.1	Palladium(II)-Catalyzed Carbonylation of Unfunctionalized Alkynes 255
8.5.2	Palladium(II)-Catalyzed Carbonylation of Functionalized Alkynes 264
8.6	Palladium(II)-Catalyzed Carbonylation of Punctionalized Aikynes 204 Palladium(II)-Catalyzed Carbonylation of Other Substrates 274
8.7	Summary and Conclusions 277
0.7	References 278
	References 276
9	Carbonylations Catalyzed by Other Second-Row Transition
	Metal Catalysts 295
	Francesca Foschi and Gianluigi Broggini
9.1	Introduction 295
9.2	Zirconium Compounds as Carbonylation Catalysts 295
9.2.1	Carbonylation with Carbon Monoxide on Sulfated-Doped Zirconia as the Solid Acid Catalyst 295
9.2.2	Carbonylation of Zirconocene Complexes 299
9.3	Silver Compounds in Carbonylation Reactions 307
9.3.1	Koch-Type Reactions in the Presence of Silver Carbonyl Ion Catalyst 307
9.3.2	Koch-Type Reactions in the Presence of Silver Lewis Acids under CO Atmosphere 309
9.3.3	Carbonylative Coupling Reactions Promoted by Metal–Silver Bimetallic
	Catalysts 309
9.4	Molybdenum Compounds in Carbonylation Reactions 312
9.4.1	Formal Carbonylation Processes: Carbonylation of Ethylene and
	Methanol 312
9.4.2	Molybdenum Carbonyl Complexes as Catalysts and CO Source in
	Intermolecular Carbonylation Coupling Reactions of Aryl or Alkenyl
	Halides 314
9.4.3	Molybdenum Carbonyl Complexes as Both Catalysts and CO Source in Intramolecular Carbonylation Coupling Reactions 317

- 9.4.4 Metal-Catalyzed Coupling Procedures Using Molybdenum as the CO Source *319*
- 9.4.4.1 Intermolecular Cross-Coupling Procedures 320
- 9.4.4.2 Cascade and Intramolecular Cross-Coupling Procedures 323
- 9.4.4.3 Carbonylative Cross-Coupling in the Presence of Transmetalation Partners 326
- 9.5 Summary and Conclusions 327 References 328

Part III Miscellaneous Carbonylation Reactions 333

10 Carbonylations Promoted by Third-Row Transition Metal Catalysts 335

- Anthony Haynes
- 10.1 Introduction 335
- 10.2 Methanol Carbonylation 336
- 10.2.1 Acetic Acid Production 336
- 10.2.2 Process Considerations and Mechanism for Rh Catalyst 337
- 10.2.3 Iridium Catalysts 339
- 10.2.3.1 Mechanism for Iridium Catalyst 339
- 10.2.3.2 Role of Promoters in Iridium-Catalyzed Methanol Carbonylation 342
- 10.2.3.3 Recent Developments 344
- 10.3 Hydroformylation 345
- 10.3.1 Iridium Catalysts 346
- 10.3.2 Platinum Catalysts 349
- 10.3.3 Osmium Catalysts 351
- 10.4 Other Carbonylation Reactions 351
- 10.4.1 Alkoxycarbonylation of Alkenes 352
- 10.4.2 Carbonylation Reactions Involving Alkynes 353
- 10.4.3 Oxidative Carbonylations 354
- 10.5 Summary and Conclusions 355 References 356

11 Transition Metal-Free Carbonylation Processes 363

Lu Cheng, Binbin Liu, Fangning Xu, and Wei Han

- 11.1 Introduction 363
- 11.2 Transition-Metal-Free Carbonylation for the Synthesis of Aldehydes and Ketones *364*
- 11.3 Transition-Metal-Free Carbonylation for the Synthesis of Esters and Lactones *375*
- 11.4 Transition-Metal-Free Carbonylation for the Synthesis of Amides 385
- 11.5 Transition-Metal-Free Carbonylation for the Synthesis of Acids and Anhydrides 386

xii Contents

- 11.6 Transition-Metal-Free Carbonylation for the Synthesis of Acyl Chlorides and Alcohols 388
- 11.7 Summary and Conclusions 392 References 393

12 Conclusions and Perspectives *397 Bartolo Gabriele*

Index 401