Contents

Preface ix

T	why is Organo/Metal Combined Catalysis Necessary? I
1.1	Introduction 1
1.2	Early Stage of Organo/Metal Combined Catalysis and General
	Principles 3
1.3	Organo/Metal Cooperative Catalysis 7
1.3.1	Control of Stereochemistry 7
1.3.2	Cooperative Activation of Chemical Bonds 9
1.4	Organo/Metal Relay and Sequential Catalysis 11
1.5	Conclusion 16
	References 16
2	Metal/Phase-Transfer Catalyst Combined Catalysis 19
2.1	Introduction 19
2.1.1	Early Racemic Examples: PTC and Transition Metal Co-catalyzed
	Reactions 19
2.2	Asymmetric Metal/Phase-Transfer Catalyst Combined Catalysis 20
2.2.1	Combination of Cationic PTC and Transition Metal in Asymmetric
	Catalysis 22
2.2.2	Combination of Anionic PTC and Transition Metal in Asymmetric
	Catalysis 29
2.3	Conclusion 33
	References 34
3	Enamine-Metal Combined Catalysis 39
3.1	Introduction: Combined Enamine Activation and Metal Catalysis 39
3.2	Catalytic Asymmetric α-Allylation of Carbonyls 39
3.2.1	Oxidative Addition-Initiated Allylic Alkylation 39
3.2.2	Metal Hydride-Initiated Allylic Alkylation 48
3.2.3	Lewis Acid-Mediated S _N 1 or S _N 2 Reaction 50
3 3	Catalytic Asymmetric Substitution 51



vi	Contents	
	3.4	Catalytic Asymmetric α -Alkenylation, α -Arylation, and α -Trifluoromethylation of Carbonyl Compounds 55
	3.5	Asymmetric Addition to Alkynes by Cooperative Catalysis with π -Lewis Acids 59
	3.6	Catalytic Asymmetric Propargylic Substitution Reaction of Carbonyl Compounds 61
	3.7	Catalytic Asymmetric α-Oxidation of Aldehydes 63
	3.8	Relay Catalysis 64
	3.8.1	Catalytic Asymmetric Cross Dehydrogenative Coupling 64
	3.8.2	Transformation of Olefins 68
	3.9	Conclusion 70
		References 71
	4	Iminium and Metal Combined Catalysis 75
	4.1	Introduction: Iminium Activation and Metal Combined Catalysis 75
	4.2	Iminium Activation and Palladium Catalysis 76
	4.2.1	Enantioselective Conjugate Addition Reaction 76
	4.2.2	Asymmetric [3+2] Cycloaddition Via Ring-Opening Oxidative Addition 77
	4.2.3	Asymmetric Michael Addition and Carbocyclization Cascade 81
	4.2.4	Asymmetric Oxidative Cascade Reaction 83
	4.3	Iminium Activation and Coinage Metal Catalysis 83
	4.4	Iminium Activation and Other Metal Catalysis 85
	4.5	Conclusion 87
		References 88
	5	Brønsted Acid and Transition Metal Cooperative Catalysis 91
	5.1	Introduction 91
	5.2	Early Stage of Metal/Brønsted Acid Cooperative Catalysis 93
	5.3	Metal Alkynylide-Mediated Transformations 93
	5.4	π-Allyl-Metal-Mediated Transformation 95
	5.5	Asymmetric Hydrogenation of C—N Double Bond 107
	5.6	Metal Carbene-Mediated Transformations 110
	5.7	π-Lewis Acid Mediated Transformations 116
	5.8	Summary and Outlook 119 References 120
	6	Metal-Brønsted Acid Relay Catalysis 125
	6.1	Introduction 125
	6.2	π-Lewis Acid-Chiral Brønsted Acid Relay Catalysis 125
	6.2.1	Hydroamination-Initiated Cascade Reaction 127
	6.2.2	Hydroalkoxylation Mediated Relay Catalysis 132
	6.2.3	Hydrosiloxylation Mediated Relay Catalysis 136
	6.2.4	Relay Catalysis Involving the Addition of Nitrone or Nitro Group to Alkynes 138

6.2.5	Relay Catalysis Involving the Addition of Carbon Nucleophiles to Alkynes 139			
6.3	Metal/Brønsted Acid Relay Catalysis Involving Alkene Metathesis 1			
6.4	Metal/Brønsted Acid Relay Catalysis Involving Alkene			
	Isomerization 144			
6.5	Metal/Brønsted Acid Relay Catalysis Involving Hydrogenation 151			
6.6	Palladium/Brønsted Acid Relay Catalytic Asymmetric Allylation of Carbonyls 155			
6.7	Metal/Brønsted Acid Relay Catalysis Involving Hydroformylation 15			
6.8	Metal/Brønsted Acid Relay Catalysis Involving Metal Carbene Formation 160			
6.8.1	Cascade Metal Carbene Formation and Asymmetric Protonation 160			
6.8.2	Multiple Cascade Reaction Initiated with Metal Carbene 165			
6.9	Lewis Acid/Chiral Brønsted Acid Relay Catalysis 167			
6.10	Miscellaneous 169			
6.11	Summary and Outlook 172			
0.11	References 173			
7	Lewis Base-Lewis Acid Cooperative Catalysis 179			
7.1	Introduction: Combined Lewis Base and Lewis Acid Activations 179			
7.1.1	Early Examples in Lewis Base–Lewis Acid Cooperative Catalysis 183			
7.2	Asymmetric Reactions Driven by Tertiary Amine-Mediated Ammonium Enolates 184			
7.2.1	Asymmetric Baylis–Hillman Reactions 184			
7.2.2	Asymmetric [2+2] Reactions 186			
7.2.3	Asymmetric [4+2] Reactions 192			
7.2.4	Asymmetric α-Functionalization of Carbonyl Compounds 196			
7.3	Asymmetric Reactions Driven by NHC-Mediated Homoenolates 198			
7.3.1	Asymmetric Annulation Reactions 201			
7.3.2	Asymmetric β-Protonation Reactions 211			
7.3.3	Asymmetric Kinetic Resolutions 215			
7.4	Asymmetric Reactions Driven by NHC-Mediated Azolium Enolates 216			
7.5	Asymmetric Reactions Driven by Ammonium Salts 221			
7.6	Asymmetric Reactions Driven by NHC-Mediated α,β -Unsaturated Acyl Azoliums 225			
7.6.1	Asymmetric [3+3] Reactions 225			
7.6.2	Asymmetric Cascade Reactions 229			
7.6.3	Asymmetric Kinetic Resolutions 231			
7.7	Conclusion 235			
	References 235			
8	Lewis Base-Transition Metal Cooperative Catalysis 241			
8.1	Introduction 241			
8.2	Phosphine and Transition Metal Cooperative Catalysis 243			

8.2

viii	Contents	
	8.3	N-Heterocyclic Carbene and Transition Metal Cooperative Catalysis 244
	8.3.1	π -Allyl Metal Mediated Transformations 245
	8.3.2	Alkynyl-metal Mediated Transformations 253
	8.3.3	Metal-allenylidene Mediated Transformations 254
	8.4	Tertiary Amine and Transition Metal Cooperative Catalysis 258
	8.4.1	π -Allyl Metal Mediated Transformations 258
	8.4.2	π-Benzyl-metal Mediated Transformations 263
	8.4.3	Metal-allenylidene Mediated Transformations 265
	8.4.4	Other Transition Metal Mediated Transformations 267
	8.5	Conclusions 271
		References 271
	9	Chiral Organocatalyst Combined with Transition Metal Based
		Photoredox Catalyst 277
	9.1	Introduction 277
	9.2	Covalent-Based Organocatalytic Activation in Combination with
		Transition Metal-Based Photoredox Catalyst 279
	9.2.1	Chiral Amine/Photoredox Combined Catalysis 279
	9.3	Photoredox-Mediated SOMO Catalysis 284
	9.4	Nucleophilic Organocatalyst in Combination with Photoredox Catalyst 288
	9.5	Noncovalent-Based Organocatalytic Activation in Combination with Transition Metal-Based Photoredox Catalyst 290
	9.5.1	Chiral Phosphate/Photoredox Combined Catalysis 290
	9.6	Asymmetric Ion-Pair/Photoredox Combined Catalysis 295
	9.7	Summary and Outlook 297
		References 297
	10	Applications in Organic Synthesis 301
	10.1	Introduction 301
	10.2	Applications of Chiral Phosphoric Acid-Metal Cooperative
		Catalysis 301
	10.3	Application of Transition Metal Catalysis Combined with Secondary
		Amine Catalysis 305
	10.4	Application of Photocatalysis Combined with Organocatalysis 310
	10.5	Application of Lewis Base-Lewis Acid Cooperative Catalysis 312
	10.6	Application of Lewis Base-Transition Metal Relay Catalysis 316
	10.7	Application of Metal-Brønsted Acid Relay Catalysis 316
	10.8	Conclusion 320
		References 320