Contents

Preface xix Supramolecular Catalysis: An Introduction xxi |v

Part I Ligand-Ligand Interactions 1

1 Supramolecular Construction of Bidentate Ligands Through Self-assembly by Hydrogen Bonding 3

Felix Bauer and Bernhard Breit

- 1.1 Introduction 3
- 1.2 Formation of Bidentate Ligands Through Self-assembly via Hydrogen Bonding and Application in Hydroformylation 5
- 1.2.1 2-Hydroxypyridine/2-Pyridone Platform 5
- 1.2.2 Complementary Hydrogen Bonding for the Construction of Heterodimeric Self-assembling Ligands 9
- 1.3 Asymmetric Hydrogenation 13
- 1.3.1 P-chiral Self-assembly Ligands in Asymmetric Hydrogenation 13
- 1.3.2 Inducing Axial Chirality in a Supramolecular Catalyst 14
- 1.4 Other Catalytic Applications 17
- 1.4.1 Hydration of Alkynes 17
- 1.4.2 Hydration of Nitriles 19
- 1.4.3 Allylic Substitution with Allylic Alcohols 20
- 1.4.4 Hydrocyanation 20
- 1.5 Concluding Remarks 21 References 22
- 2 Self-Assembled Bidentate Ligands in Transition Metal Catalysis; From Fundamental Invention to Commercial Application 27

Alexander M. Kluwer, Xavier Caumes, and Joost N. H. Reek

- 2.1 Introduction 27
- 2.2 Metal–Ligand Interactions, the SUPRAphos Library 28

vi Contents

- 2.3 Supramolecular Bidentate Ligands Based on Hydrogen Bonds, a Toolbox for Evolutionary Catalyst Design 30
- 2.4 Formation of Supramolecular Pincer-Type Complexes 34
- 2.5 From a Supramolecular Bidentate Ligand to a Catalyst with Substrate Pre-organization *36*
- 2.6 Outlook 37 References 38

Part II Self-Assembled Nanostructures and Multi-component Assemblies 41

3	Assembled Ionic Molecular Catalysts and Ligands 43
	Kohsuke Ohmatsu, Daisuke Uraguchi, and Takashi Ooi
3.1	Introduction 43
3.2	Concept of Ion-Paired Chiral Ligand 44
3.2.1	Design and Synthesis of Ion-Paired Chiral Ligand 45
3.2.2	Application of Ion-Paired Chiral Ligand for Palladium-Catalyzed
	Asymmetric Allylations 45
3.2.3	In situ Generation of Ion-Paired Chiral Ligands and Their
	Combinatorial Screening 46
3.3	Hydrogen-Bond-Assisted Ion-Pairing for Supramolecule
	Formation 47
3.3.1	Discovery of Supramolecular Ion-Pair Catalysis 48
3.3.2	Supramolecular Ion-Pair Catalysis for Michael Addition of
	2-Unsubstituted Azlactone to Nitroolefins 50
3.4	Conclusion 51
	References 51
4	Self-amplification of Enantioselectivity in Asymmetric
	Catalysis by Supramolecular Recognition and
	Stereodynamics 55
	Oliver Trapp
4.1	Introduction 55
4.2	Design of an Enantioselective Self-amplifying Catalyst Based on
	Noncovalent Product–Catalyst Interactions 57
4.3	The Stereodynamics of the Ligand Core 57
4.4	Design of Product–Catalyst Adducts and Catalyst Synthesis 59
4.5	Noncovalent Interaction Studies via NMR Spectroscopy 61
4.6	Self-amplifying Hydrogenation of 3,5-DNB-ΔAla-OEt 63
4.7	Concluding Remarks 64
	Acknowledgments 64
	References 64

5 Interlocked Molecules in Enantioselective Catalysis 69

Carel Kwamen and Jochen Niemeyer

- 5.1 Introduction 69
- 5.2 Rotaxanes in Enantioselective Catalysis 70
- 5.3 Catenanes in Enantioselective Catalysis 75
- 5.4 Molecular Knots in Enantioselective Catalysis 77
- 5.5 Conclusion 78 References 78

6 Catalytic Supramolecular Gels 81

Beatriu Escuder

- 6.1 Introduction *81*
- 6.2 Catalytic LMWGs 82
- 6.3 LMWGs in Organocatalysis 82
- 6.4 LMWGs in Metallocatalysis *86*
- 6.5 Multicomponent Supramolecular Materials Involving Catalytic LMWGs *87*
- 6.6 Concluding Remarks 89 Acknowledgments 90 References 90

7	Supramolecular	Helical	Catalys	ts g	93

Laurent Bouteiller and Matthieu Raynal

- 7.1 Introduction 93
- 7.2 Concept: Induction of Chirality to Metal Centers Connected to Supramolecular Helices 94
- 7.3 Amplification of Chirality in Two-Component Supramolecular Helical Catalysts 97
- 7.4 Amplification of Chirality in Three-Component Helical Catalysts 98
- 7.5 Switchable Asymmetric Catalysis by Reversible Assembly of Helical Catalysts *100*
- 7.6 Dual Stereocontrol of an Asymmetric Reaction by Switchable Helical Catalysts *101*
- 7.7 Concluding Remarks 103 Acknowledgments 104 References 104
- 8 Self-Assembled Multi-Component Supramolecular Catalysts for Asymmetric Reactions 107 Guanghui Ouyang, Jian Jiang, and Minghua Liu References 114

Part III Ligand-Substrate Interactions 117

9 Harnessing Ligand-Substrate Non-covalent Interactions for Control of Site-Selectivity in Transition Metal-Catalyzed C-H Activation and Cross-Coupling 119 Robert J. Phipps

9.1 Introduction *119*

- 9.2 C–H Borylation *120*
- 9.3 Cross-Coupling 126
- 9.4 Concluding Remarks 128 Acknowledgments 129 References 129

10 Supramolecular Interactions in Distal C–H Activation of (Hetero)arenes 133

Jyoti P. Biswas and Debabrata Maiti

- 10.1 Introduction 133
- 10.2 Distal C–H Activation of Arenes 133
- 10.2.1 meta C-H Activation 134
- 10.2.2 para C-H Activation 136
- 10.3 Distal C-H Activation of Heterocycles 137
- 10.3.1 Tridentate Approach 138
- 10.3.2 Bidentate Approach 140
- 10.4 Conclusion 141 Acknowledgments 141 References 141
- 11 Transition-Metal-Catalyzed, Site- and Enantioselective Oxygen and Nitrogen Transfer Enabled by Lactam Hydrogen Bonds 145

Finn Burg and Thorsten Bach

- 11.1 Chiral Lactams as Hydrogen Bonding Sites for Enantioselective Catalysis 145
- 11.2 Enantioselective Addition to Olefins 147
- 11.3 Enantioselective $C(sp^3)$ -H Functionalization 150
- 11.4 Enantioselective Oxidation of Sulfur Centers 156
- 11.5 Concluding Remarks 157 Acknowledgments 158 References 158
- 12 Supramolecular Substrate Orientation as Strategy to Control Selectivity in Transition Metal Catalysis 161 Joost N.H. Reek and Bas de Bruin
- 12.1 Introduction 161
- 12.2 Asymmetric Hydrogenation *161*

Contents ix

- 12.3 Substrate Orientation in Hydroformylation Catalysis 164
- 12.4 Substrate Orientation in C—H Borylation 168
- 12.5 Second Coordination Sphere Control in Enantioselective Cobalt-catalyzed Carbene and Nitrene Transfer Reactions *170*
- 12.5.1 Applications 172
- 12.6 Concluding Remarks and Outlook 174 References 174
- **13 Phosphine Ligands with Acylguanidinium Groups as Substrate-directing Unit** 179 *Felix Bauer and Bernhard Breit*
- 13.1 Introduction 179
- 13.2 Hydroformylation of Alkenoic and Alkynoic Acids 179
- 13.3 Aldehyde Reduction and Tandem Hydroformylation–Hydrogenation *188*
- 13.4 Concluding Remarks 197 References 198
- 14 Chemical Reactions Controlled By Remote Zn···N Interactions Between Substrates and Catalysts 201

Jonathan Trouvé and Rafael Gramage-Doria

- 14.1 Introduction 201
- 14.2 Organic Reactions 202
- 14.3 Transition Metal Catalysis 204
- 14.4 Conclusion 207 Acknowledgments 207 References 207

Part IV Catalysis Promoted by Discrete Cages, Capsules, and Other Confined Environments 211

15 Artificial Enzymes Created Through Molecular Imprinting of Cross-Linked Micelles 213

Yan Zhao

- 15.1 Introduction 213
- 15.2 Surface-Cross-Linked Micelles (SCMs) 213
- 15.3 Molecularly Imprinted Nanoparticles (MINPs) via Double Cross-Linking of Micelles 215
- 15.4 MINP-Based Artificial Esterase 217
- 15.5 MINP-Based Artificial Glycosidase 219
- 15.6 MINP-Based Artificial Enzymes for Asymmetric Catalysis and Tandem Catalysis 223
- 15.7 Concluding Remarks 225 Acknowledgments 226 References 226

x Contents

16	Bioinspired Catalysis Using Innately Polarized Pd ₂ L ₄
	Coordination Cages 229
	Paul J. Lusby
16.1	Introduction 229
16.2	A Coordination-Cage Host–Guest Method Based on Polar
	Interactions 229
16.3	From Guest Binding to Catalysis; an Artificial "Diels–Alderase" 231
16.4	Base-Free Michael Addition Catalysis 235
16.5	Turning Cage-Catalysis Inside Out 238
16.6	Concluding Remarks 239
	Acknowledgments 239
	References 239
17	Supramolecular Catalysis with a Cubic Coordination Cage:
	Contributions from Cavity and External-Surface Binding 241
	Christopher G. P. Taylor and Michael D. Ward
17.1	Introduction: The Host Cage and Its Structure 241
17.2	Binding of Organic Guests in the Central Cavity in Water 242
17.3	Surface Binding of Anions 244
17.4	The Paradigm: Catalysis of the Kemp Elimination 245
17.5	Effects of Anion Accumulation Around the Surface: Autocatalysis 247
17.6	Catalysis with Noncavity-Bound Guests: Phosphate Ester
	Hydrolysis and an Aldol Condensation 249
17.7	Conclusion 251
	Acknowledgments 252
	References 252
18	Transition Metal Catalysis in Confined Spaces 255
	Joost N.H. Reek and Sonja Pullen
18.1	Introduction 255
18.2	Template Ligand Strategies for Encapsulation of Transition Metal
	Catalysts 255
18.3	Catalyst Encapsulation Strategies for Solar Fuel-Related Reactions 258
18.3.1	Molecular Cages for Water Oxidation Catalysis 260
18.3.2	Molecular Cages for Proton Reduction Catalysis 261
18.3.3	Proton Reduction Catalysis Using MOFs 266
18.4	Concluding Remarks and Outlook 268
	References 268
19	Catalysis by Metal–Organic Cages: A Computational
	Perspective 271
	Giuseppe Sciortino, Gantulga Norjmaa, Jean Didier Maréchal, and Gregori
	Ujaque
19.1	Introduction 271
19.2	Looking for a Robust Computational Framework to Study MOCs 272

- 19.3 Applications of Modeling to Confined Catalysis 274
- 19.4 Future Directions 281 References 281
- 20 N-heterocyclic Carbene (NHC)-Capped Cyclodextrins for Cavity-Controlled Catalysis 287 Sylvain Roland and Matthieu Sollogoub
- 20.1 Introduction: NHC-Capped Cyclodextrin Metal Complexes 287
- 20.2 Orientation of Cyclization Reactions Five vs. Six-Membered Cycle 289
- 20.3 Control of Regioselectivity 291
- 20.4 Control of Enantioselectivity by the CD Chiral Cavity 293
- 20.5 Substrate Selectivity 296
- 20.6 Protection of Metal Centers and Promotion of Reactive Species 297
- 20.7 Concluding Remarks 299 Acknowledgments 299 References 299
- 21 Supramolecular Catalysis by Metallohosts Based on Glycoluril 303
 - Jeroen PJ. Bruekers, Johannes A.A.W. Elemans, and Roeland J.M. Nolte
- 21.1 Introduction 303
- 21.2 Rhodium-Based Catalytic Baskets 304
- 21.3 Copper-Based Catalytic Baskets 306
- 21.4 Porphyrin Cage Catalysts 307
- 21.4.1 Epoxidation of Low-Molecular-Weight Alkenes 307
- 21.4.2 Epoxidation of Polymeric Alkenes 311
- 21.4.3 Carbenoid Transfer Reactions with α-Diazoesters 315
- 21.5 Outlook 316 Acknowledgments 317 References 317
- 22 Catalysis Inside the Hexameric Resorcinarene Capsule: Toward Addressing Current Challenges in Synthetic Organic Chemistry 321

Leonidas-Dimitrios Syntrivanis and Konrad Tiefenbacher

- 22.1 Introduction 321
- 22.2 Background 321
- 22.3 Application to Terpene Cyclization 323
- 22.4 Elucidating the Prerequisites for Catalytic Activity Inside the Resorcinarene Capsule 328
- 22.5 Further Applications of Capsule I as Catalyst 329
- 22.6 Concluding Remarks *330*
 - Acknowledgments 331
 - References 331

xii Contents

23	Supramolecular Organocatalysis Within the Nanospace of Resorcinarene Capsule 335
	Carmine Gaeta, Carmen Talotta, Margherita De Rosa, Annunziata Soriente,
23.1	Introduction 335
23.2	The Hexameric Resorcinarene Capsule 337
23.3	The Hexameric Capsule as H-bonding Organocatalyst 338
23.4	The Hexameric Capsule as Brønsted Acid Organocatalyst 339
23.5	Iminium Catalysis with a Coencapsulated Cocatalyst 341
23.6	Halogen-bond (XB) Catalysis with a Coencapsulated Cocatalyst 343
23.7	Concluding Remarks 343
	Acknowledgment 344
	References 344
24	Resorcin[4]arene Hexamer: From Nanocontainer to
	Nanocatalyst 347
	Giorgio Strukul, Fabrizio Fabris, and Alessandro Scarso
24.1	Introduction 347
24.2	Resorcinarene Capsule as Nanoreactor 348
24.3	Resorcin[4]arene Capsule as Nanocatalyst 352
24.4	Concluding Remarks 357
	Acknowledgments 358

References 358

Part V Supramolecular Organocatalysis and Non-classical Interactions 361

- 25 The Aryl-Pyrrolidine-*tert*-Leucine Motif as a New Privileged Chiral Scaffold: The Role of Noncovalent Stabilizing Interactions 363 Daniel A. Strassfeld and Eric N. Jacobsen
- 25.1 Introduction 363
- 25.2 Foundational Studies *364*
- 25.3 Development of the Aryl-Pyrrolidino-tert-Leucine Catalyst Motif 366
- 25.4 Scope of Enantioselective Reactions and Mechanisms Promoted Effectively by Aryl-Pyrrolidine-*tert*-Leucine HBD Catalysts 368
- 25.5 Mechanisms of Enantioinduction by Aryl-Pyrrolidine*tert*-Leucino-H-Bond-Donor Catalysts: Case Studies 374
- 25.6 Concluding Remarks 380 Acknowledgments 381 References 382

26	Chiral Triazole Foldamers in Enantioselective Anion-Binding
	Catalysis 387
	Alica C. Keuper and Olga García Mancheño
26.1	Introduction 387
26.2	Triazoles as Anion Receptors 387
26.3	Design of Foldamer Triazoles as Hydrogen Bond Donors for
	Anion-Binding Catalysis 388
26.4	Anion-Binding-Catalyzed Enantioselective Reissert-Type Reaction with
	Silylketene Acetals 389
26.5	Reaction with Different Nucleophiles 391
26.6	Nucleophilic Dearomatization of Pyrylium Derivatives 392
26.7	Folding and Cooperative Multi-Recognition Mechanism 393
26.8	Design of Catalytic Transformations Based on Anion-Template
	Strategies 394
26.9	Concluding Remarks 395
	Acknowledgments 396
	References 396
27	Supramolecular Catalysis via Organic Solids: Templates to
	Mechanochemistry to Cascades 401
	Shweta P. Yelgaonkar and Leonard R. MacGillivray
27.1	Template Approach for [2+2] Photocycloadditions 401
27.2	State of Mechanochemistry 402
27.2.1	Our Studies in Mechanochemistry 403
27.3	Organic Catalysis and Mechanochemistry 403
27.3.1	Supramolecular Catalysis by Ditopic Receptors 404
27.3.2	Our Studies in Supramolecular Catalysis and Mechanochemistry 405
27.4	Cascade Reactions and Mechanochemistry 407
27.5	Concluding Remarks 409
	Acknowledgments 409
	References 409
28	Exploration of Halogen Bonding for the Catalysis of Organic
	Reactions 413
	Revannath L. Sutar and Stefan M. Huber
28.1	Introduction 413
28.2	Halide Abstraction Reactions 415
28.3	A stimution of Operanic Frenchica of Operand 110
	Activation of Organic Functional Groups 418
28.4	Activation of Organic Functional Groups 418 Activation of a Metal–Halogen Bond 421
28.4 28.5	Activation of a Metal–Halogen Bond 421 Conclusion 421
28.4 28.5	Activation of Organic Functional Groups 418 Activation of a Metal–Halogen Bond 421 Conclusion 421 References 422
28.4 28.5	Activation of Organic Functional Groups 418 Activation of a Metal–Halogen Bond 421 Conclusion 421 References 422

xiv Contents

29 Chalcogen-Bonding Catalysis 427 Wei Wang and Yao Wang

- 29.1 Introduction 427
- 29.2 Challenges in Chalcogen-Bonding Catalysis 428
- 29.3 Discovery of Efficient Chalcogen-Bonding Catalysts 428
- 29.4 Chalcogen–Chalcogen Bonding Catalysis 431
- 29.5 Dual Chalcogen–Chalcogen Bonding Catalysis 433
- 29.6 Conclusion Remarks 436 Acknowledgments 437 References 437

30 Asymmetric Supramolecular Organocatalysis: The Fourth Pillar of Catalysis 441 Kengadarane Anebouselvy, Kodambahalli S. Shruthi,

- and Dhevalapally B. Ramachary
- 30.1 Introduction 441
- 30.2 Asymmetric Michael Additions 442
- 30.3 Concluding Remarks 448 Acknowledgments 448 References 448

Part VI Supramolecular Catalysis in Water 451

31 Metal Catalysis in Micellar Media 453

Giorgio Strukul, Fabrizio Fabris, and Alessandro Scarso

- 31.1 Introduction 453
- 31.2 Oxidation Reactions 454
- 31.3 C—C and C—X Bond Forming Reactions 457
- 31.4 Metal Nanoparticles in Micellar Media 461
- 31.5 Catalyst Surfactant Interactions 463
 Acknowledgments 465
 References 465

32 Surfactant Assemblies as Nanoreactors for Organic Transformations 467

Margery Cortes-Clerget, Joseph R.A. Kincaid, Nnamdi Akporji, and Bruce H. Lipshutz

- 32.1 Introduction 467
- 32.2 Micellar Catalysis: Concepts 468
- 32.3 Ligand Design 471
- 32.4 The "Nano-to-Nano" Effect 475
- 32.5 Reservoir Effect 476
- 32.6 Access to Opportunities for Telescoping Sequences 478
- 32.7 Industrial Applications 481

- 32.8 Conclusions 483 References 484
- 33 Compartmentalized Polymers for Catalysis in Aqueous Media 489

Fabian Eisenreich and Anja R.A. Palmans

- 33.1 Introduction 489
- 33.2 Folding a Polymer Chain in Water into a Compact Structure 491
- 33.3 Polymer-Supported Ru(II) Catalysis in Water 495
- 33.4 Polymer-Supported Cu(I) and Pd(II) Catalysis in Water 496
- 33.5 Polymer-Supported Organocatalysis in Water 498
- 33.6 Polymer-Supported Photocatalysis in Water 500
- 33.7 Outlook and Conclusions 501
 Acknowledgments 502
 References 502

34 Phosphines Modified by Cyclodextrins for Supramolecular Catalysis in Water 507

Sébastien Tilloy and Eric Monflier

- 34.1 Introduction 507
- 34.2 Synthesis and Properties of CD-Phosphine 1 (CD-P-1) 508
- 34.3 Synthesis and Properties of CD-Phosphine 2 (CD-P-2) 510
- 34.4 Synthesis and Properties of CD-Phosphine 3 (CD-P-3) 512
- 34.5 Synthesis and Properties of CD-Phosphine 4 (CD-P-4) 513
- 34.6 Concluding Remarks 514 References 515
- 35 Water-Soluble Yoctoliter Reaction Flasks 519
 - Yahya A. Ismaiel and Bruce C. Gibb
- 35.1 Introduction 519
- 35.2 Deep-Cavity Cavitands 520
- 35.3 The Thermodynamic and Kinetic Features of the Capsular Complexes *520*
- 35.4 Assembly State of OA 1 and TEMOA 2 and Guest Packing Motifs Within *521*
- 35.5 Photochemistry 523
- 35.6 Thermal Reactions 528
- 35.7 Summary and Conclusions 533 Acknowledgments 533 References 533

36 Chemical Catalyst-Promoted Regioselective Histone Acylation 537

Yuki Yamanashi and Motomu Kanai

- 36.1 Introduction 537
- 36.2 Chemical Catalyst-Mediated Synthetic Epigenetics 537

xvi Contents

36.3 36.4	Supramolecular Catalyst Strategy for Protein Modification 538 Supramolecular Catalyst Strategy for Histone Acetylation In Vitro 538
36.5	Catalyst-Promoted Selective Acylation Targeting Proteins in Living Cells 540
36.6	Chemical Catalyst-Promoted Regioselective Histone Acylation in Living Cells 543
36.7	Concluding Remarks 544 References 544
37	Protein–Substrate Supramolecular Interactions for the Shape-Selective Hydroformylation of Long-Chain α-Olefins 547 Peter J. Deuss and Amanda G. Jarvis
37.1	Introduction 547
37.1.1	Introduction on Aqueous Phase Hydroformylation of Long-Chain α -Olefins 547
37.1.2	Shape Selective Artificial Metalloenzyme Catalyst Design 549
37.2	Design of Protein Templates for Shape-Selective ArMs 551
37.3	Introduction of a Metal–Ligand Environment into SCP-2L 552
37.4	SCP-2L as a Catalytic Scaffold 553
37.5	Phosphine Modification of Proteins 554
37.6	Application in Biphasic Hydroformylation 555
37.7	Structural Studies on the Rhodium Hydroformylases 557
37.8	Concluding Remarks 558
	Acknowledgments 558
	References 559
38	Supramolecular Assembly of DNA- and Protein-Based
	Artificial Metalloenzymes 561
	Gerard Roelfes
38.1	Introduction 561
38.2	DNA-Based Artificial Metalloenzymes 562
38.3	Protein-Based Artificial Metalloenzymes 564
38.4	Synergistic Catalysis with Artificial Metalloenzymes 567
38.5	In Vivo Assembly and Application of LmrR-Based Artificial
	Metalloenzymes 568
38.6	Conclusions 569
	References 569

Part VII Supramolecular Allosteric Catalysts and Replicators 573

- **39** Switchable Catalysis Using Allosteric Effects 575
 - Michael Schmittel
- 39.1 Introduction 575
- 39.2 Allosteric Regulation at Zinc Porphyrin Stations by Catalyst Release 576
- 39.3 Allosteric Regulation of Catalysis at Copper(I) Sites 580
- 39.4 Dynamic Allosteric Regulation of Catalysis 583
- 39.5 The Future: From Allosteric Regulation of Catalysis in a Network to Smart and Autonomous Mixtures 585
- 39.6 Concluding Remarks 586
- Acknowledgments 586 References 587

40 Supramolecularly Regulated Enantioselective Catalysts 591

- Anton Vidal-Ferran
- 40.1 Introduction 591
- 40.2 Seminal Work 592
- 40.3 Supramolecular Regulation of a Preformed Enantioselective Catalyst 593
- 40.4 Supramolecular Regulation of a Prochiral Ligand or Catalyst 597
- 40.5 Concluding Remarks 600 Acknowledgments 601 References 601

41 Emergent Catalysis by Self-Replicating Molecules 605

Kai Liu, Jim Ottelé, and Sijbren Otto

- 41.1 Introduction 605
- 41.2 Implementation of Organocatalysis in Self-Replicating Systems 607
- 41.3 The Implementation of Photocatalysis in Self-Replicating Systems 610
- 41.4 Conclusions and Outlook *612* References *612*

.....

Index 615