

Contents

Preface XI

List of Authors XIII

- 1 Introduction to Supramolecular Catalysis 1**
Pablo Ballester and Anton Vidal-Ferran
- 1.1 Introduction 1
- 1.2 Design Approaches to Supramolecular Catalysis 3
- 1.2.1 Molecular Receptors that Place a Binding Site Close to a Catalytic Center 3
- 1.2.2 Molecular Receptors that Promote the Reaction of two Simultaneously Complexed Reactants 7
- 1.2.3 Preparation of the Catalyst Backbone via Supramolecular Interactions 16
- 1.3 Artificial Biomacromolecules for Asymmetric Catalysis 22
- 1.4 Summary and Outlook 24
- References 24
- 2 Supramolecular Construction of Chelating Bidentate Ligand Libraries through Hydrogen Bonding: Concept and Applications in Homogeneous Metal Complex Catalysis 29**
Bernhard Breit
- 2.1 Introduction 29
- 2.2 Emulation of Chelation through Self-Assembly of Monodentate Ligands 30
- 2.3 Tautomeric Self-Complementary Interligand Hydrogen Bonding 33
- 2.3.1 Hydroformylation 33
- 2.3.2 Room Temperature/Ambient Pressure Hydroformylation 37
- 2.3.3 Asymmetric Hydrogenation 37
- 2.4 A-T Base Pair Analogous Complementary Hydrogen Bonding for the Construction of Heterodimeric Self-Assembling Ligands 38

2.4.1	Aminopyridine/Isoquinolone Platform	38
2.4.1.1	Hydroformylation	38
2.4.1.2	Hydration of Alkynes	39
2.4.1.3	Hydration of Nitriles	45
2.4.1.4	Asymmetric Hydrogenation	46
2.4.2	Platform Variation	49
2.4.2.1	Hydroformylation	49
2.5	Conclusion and Outlook	52
	References	52
3	Bis-Azolyazine Derivatives as Supramolecular Synthons for Copper and Silver [2 × 2] Grids and Coordination Polymers	57
	<i>Félix A. Jalón, Blanca R. Manzano, M. Laura Soriano, and Isabel M. Ortiz</i>	
3.1	Introduction	57
3.2	“Planar” and “Non-Planar” Azolyl Azines	58
3.2.1	Synthesis	59
3.2.2	Crystallographic Evidence for the Planarity	61
3.3	Preparation of [2 × 2] Grids with Cu(I) or Ag(I)	63
3.3.1	Synthesis	64
3.3.2	X-Ray and other Techniques for Structural Characterization in the Solid State	65
3.3.3	Structural Characterization in Solution by NMR	69
3.3.4	Anion Exchange in the Solid State	71
3.4	Preparation of Coordination Polymers with 2,3-Pyrazolylquinoxalines or 2,3-Pyrazolylpyrazines and Cu(I) or Ag(I)	72
3.4.1	Preparation and Characterization of Dinuclear Building Blocks and Coordination Polymers	72
3.4.2	X-Ray and other Techniques for Structural Characterization	74
3.5	Preparation of Supramolecular Structures with 2,4-Diamino-6-R-1,3,5-triazines and Ag(I)	79
3.5.1	Synthesis	80
3.5.2	X-Ray Structure Determination	80
3.5.3	Structural Characterization in Solution by NMR	84
3.6	Conclusions	85
	References	86
4	Chiral Metalloacycles for Asymmetric Catalysis	93
	<i>Wenbin Lin</i>	
4.1	Introduction	93
4.2	Thermodynamically-Controlled Metalloacycles	94
4.3	Kinetically-Controlled Metalloacycles	95
4.4	General Synthetic Strategies for Chiral Metalloacycles	96
4.5	Self- and Directed-Assembly of Chiral Pt-Alkynyl Metalloacycles	101

- 4.6 Chiral Pt-Alkynyl Metalloacycles for Asymmetric Catalysis 107
- 4.7 Concluding Remarks 109
References 110
- 5 Catalysis of Acyl Transfer Processes by Crown-Ether Supported Alkaline-Earth Metal Ions 113**
Roberta Cacciapaglia, Stefano Di Stefano, and Luigi Mandolini
- 5.1 Introduction 113
- 5.2 Basic Facts and Concepts 113
- 5.2.1 Reactivity of Alkaline-Earth Metal Alkoxides 114
- 5.2.2 The Influence of Crown Ethers 115
- 5.2.3 Preorganized Systems 116
- 5.2.3.1 Selected Examples 116
- 5.3 Nucleophilic Catalysts with Transacylase Activity 118
- 5.3.1 Calixcrowns 119
- 5.3.1.1 Catalytic Efficiency vs. Ester Reactivity 121
- 5.3.1.2 Trifunctional Catalysis 123
- 5.3.1.3 *p*-*tert*-Butylcalix[5]arene Derivatives 123
- 5.3.2 Thiol-Pendant Crown Ethers 124
- 5.4 Bimetallic Catalysts 128
- 5.4.1 Azacrown Ligating Units 129
- 5.4.1.1 Azacrown Decorated Calixarenes 133
- 5.4.2 Stilbenobis(18-Crown-6) Ligands 133
- 5.4.3 A Phototunable Dinuclear Catalyst 135
- 5.4.4 Effective Molarity and Catalytic Efficiency 136
- 5.5 Concluding Remarks 139
References 140
- 6 Bio-Inspired Supramolecular Catalysis 143**
Johannes A.A.W. Elemans, Jeroen J.L.M. Cornelissen, Martinus C. Feiters, Alan E. Rowan, and Roeland J.M. Nolte
- 6.1 Introduction 143
- 6.2 Host-Guest Catalysis 144
- 6.2.1 Rhodium-based Receptors 145
- 6.2.2 Copper-based Receptors 146
- 6.2.3 Porphyrin-based Receptors 149
- 6.3 Cytochrome P450 Mimics 153
- 6.3.1 Membrane-based Catalysts 153
- 6.3.2 Single Molecule Studies on Epoxidation Catalysts 155
- 6.4 Biohybrid Catalytic Systems 157
- 6.4.1 Bioamphiphiles 157
- 6.4.2 Single Enzyme Catalysis 159
- 6.5 Outlook 161
References 162

- 7** **Selective Stoichiometric and Catalytic Reactivity in the Confines of a Chiral Supramolecular Assembly** 165
Michael D. Pluth, Robert G. Bergman, and Kenneth N. Raymond
- 7.1 Introduction 165
- 7.2 Chemistry of Organometallic Guests 167
- 7.3 The Assembly as a Catalyst 175
- 7.3.1 Electrocyclic Rearrangements 175
- 7.3.2 Acid-Catalyzed Reactions 183
- 7.4 Conclusions and Outlook 191
References 191
- 8** **New Supramolecular Approaches in Transition Metal Catalysis; Template-Ligand Assisted Catalyst Encapsulation, Self-Assembled Ligands and Supramolecular Catalyst Immobilization** 199
Joost N.H. Reek
- 8.1 Introduction 199
- 8.2 Template-Ligand Assisted Catalyst Encapsulation 200
- 8.3 Self-Assembled Ligands in Transition Metal Catalysis 210
- 8.3.1 Template Approach 212
- 8.3.2 Direct Approach 217
- 8.4 Supramolecular Anchoring of Catalysts to Support 225
- 8.5 Conclusion 228
References 229
- 9** **Chirality-Directed Self-Assembly: An Enabling Strategy for Ligand Scaffold Optimization** 235
James M. Takacs, Shin A. Moteki, and D. Sahadeva Reddy
- 9.1 Introduction 235
- 9.2 The Need for New Catalyst Systems 235
- 9.3 A Typical Modular Approach to Chiral Bidentate Ligand Design 236
- 9.4 A Further Rationale for Developing Combinatorial Approaches to Scaffold Optimization 237
- 9.5 Approaches to Scaffold Optimization 238
- 9.6 A Convergent Approach to the Formation of Heterobimetallic Catalyst Systems 239
- 9.7 Chirality-Directed Self-Assembly: Selective Formation of Neutral, Heteroleptic Zinc(II) Complexes 240
- 9.8 *In situ* SAL Preparation 244
- 9.9 Ligand Scaffold Optimization in Palladium-Catalyzed Asymmetric Allylic Amination 244
- 9.10 What has been Learned? 246
- 9.11 Why such Wide Variation in Enantiomeric Excess given the Relatively Small Changes in Scaffold Structure? 248
- 9.12 Ligand Scaffold Optimization in Rhodium-Catalyzed Asymmetric Hydrogenation 248

9.13	Concluding Remarks	250
	References	251
10	Supramolecular Catalysis: Refocusing Catalysis	255
	<i>Piet W. N. M. Van Leeuwen and Zoraida Freixa</i>	
10.1	Introduction: A Brief Personal History	255
10.2	Secondary Phosphines or Phosphites as Supramolecular Ligands	258
10.3	Host–Guest Catalysis	263
10.4	Ionic Interactions as a Means to Form Heterobidentate Assembly Ligands	269
10.5	Ditopic Ligands for the Construction of Bidentate Phosphine Ligands	276
10.6	Conclusions and Outlook	289
	References	291
	Index	301