

Contents

Preface *XIII*

List of Contributors *XV*

1	Chemistry of Metalated Container Molecules	1
	<i>Berthold Kersting</i>	
1.1	Introduction	1
1.2	Metalated Container Molecules: A Brief Overview	2
1.3	Metalated Container Molecules of Binucleating Supporting Ligands	2
1.3.1	Synthesis	3
1.3.2	Coordination Chemistry of Binucleating Supporting Ligands	4
1.3.3	Effects of <i>N</i> -alkylation on the Molecular and Electronic Structures of the Complexes	5
1.3.4	The Ligand Matrix as a Medium	6
1.3.5	Variation, Coordination Modes and Activation of Coligands	7
1.3.6	Reactivity of the Complexes	10
1.4	Conclusions	12
	References	13
2	The Chemistry of Superbasic Guanidines	17
	<i>Jörg Sundermeyer, Volker Raab, Ekatarina Gaoutchenova, Udo Garrelts, Nuri Abacilar, and Klaus Harms</i>	
2.1	Properties of the Guanidine Functionality	17
2.2	Design of Superbasic Proton Sponges	18
2.3	Some Perspectives in Proton Sponge Chemistry	20
2.4	Multidentate Superbasic Guanidine Ligands as Receptors for Metal Cations	22
2.5	The Chemistry of Guanidine Copper Complexes	24
2.6	The Chemistry of Guanidine Zinc Complexes	31
2.7	Conclusions	35
	References	35

3	Iron Complexes and Dioxygen Activation	39
	<i>Thomas Nebe, Jing-Yuan Xu, and Siegfried Schindler</i>	
3.1	Introduction	39
3.2	Dinuclear Iron Peroxo Complexes	40
3.3	Tripodal Tetradeятate Ligands and Derivatives	42
3.3.1	Tmpa	42
3.3.2	Uns-penp	44
3.4	Mononuclear Iron Peroxo Complexes	46
3.5	Mononuclear Iron Oxo Species	48
3.6	Work in Progress	49
3.7	Conclusions	49
	References	50
4	Tuning of Structures and Properties of Bispidine Complexes	53
	<i>Peter Comba and Marion Kerscher</i>	
4.1	Introduction	53
4.2	Jahn–Teller Isomerism with Copper(II) Bispidines	55
4.3	Stabilization of High-spin Ferryl Complexes	59
4.4	Jahn–Teller-distorted Cobalt(III) Complexes	61
4.5	Conclusions	62
	References	63
5	Novel Phosphorus and Nitrogen Donor Ligands Bearing Secondary Functionalities for Applications in Homogeneous Catalysis	65
	<i>Anna-Katharina Pleier, Yu Sun, Anett Schubert, Dirk Zabel, Claudia May, Andreas Reis, Gotthelf Wolmershäuser, and Werner R. Thiel</i>	
5.1	Introduction	65
5.2	Phosphine Ligands	66
5.2.1	Cooperative Effects for Ligand Self-organization	66
5.2.2	Phosphines with Pyrazole and Pyrimidine Substituents	72
5.3	Nitrogen Donor Ligands Without Phosphorus Sites	77
5.4	Conclusion	85
	References	85
6	Square-Pyramidal Coordinated Phosphine Iron Fragments: A Tale of the Unexpected	89
	<i>Andreas Grohmann and Stephan Kohl</i>	
6.1	Introduction	89
6.2	Polyphosphine Ligands with Three and Four Coordinating Arms	91
6.3	C–P Bond Activation and Agostic Interactions in Iron Complexes of Polypodal Phosphine Ligands	92
6.4	Mechanistic Considerations	99

6.5	Conclusion	100
	References	101
7	Regioselective Catalytic Activity of Complexes with NH,NR-substituted Heterocyclic Carbene Ligands	103
	<i>Siegfried R. Waldvogel, Anke Spurg, and F. Ekkehardt Hahn</i>	
7.1	Introduction	103
7.2	Concept of Regioselective Substrate Activation	103
7.3	Synthesis of Complexes with NH,NR-stabilized NHC Ligands	106
7.4	Preparation of Substrates for Catalytic Experiments	115
7.5	Catalysis Experiments	116
7.6	Conclusions and Summary	119
	References	120
8	Functionalized Cycloheptatrienyl-Cyclopentadienyl Sandwich Complexes as Building Blocks in Metallo-supramolecular Chemistry	123
	<i>Matthias Tamm</i>	
8.1	Introduction	123
8.2	Syntheses and Electronic Structures of Group 4 Cycloheptatrienyl-Cyclopentadienyl Sandwich Complexes	124
8.3	Syntheses and Reactivity of <i>ansa</i> -Cycloheptatrienyl-Cyclopentadienyl Complexes	130
8.4	Ring-opening Reactions of <i>ansa</i> -Cycloheptatrienyl-Cyclopentadienyl Complexes	135
8.5	Phosphine-functionalized Cycloheptatrienyl-Cyclopentadienyl Sandwich Complexes	140
	References	143
9	Monosaccharide Ligands in Organotitanium and Organozirconium Chemistry	147
	<i>Peter Kitaev, Daniela Zeysing, and Jürgen Heck</i>	
9.1	Introduction	147
9.2	Synthesis of Organotitanium Carbohydrate Compounds	147
9.3	Organotitanium Carbohydrate Compounds for Use in Catalytic Reactions: Polymerization of Ethylene	152
9.4	Intramolecular Hydroamination of Aminoalkenes	153
9.5	Organozirconium Carbohydrate Compounds	155
9.6	Amine Exchange	156
9.7	Chiral Recognition	157
9.7.1	Diels–Alder Reaction	159
9.7.2	Nucleophilic Addition	159
9.8	Conclusions	162
	References	163

10	Reactions of C–F Bonds with Titanocene and Zirconocene: From Secondary Interaction via Bond Cleavage to Catalysis	165
	<i>Uwe Rosenthal, Vladimir V. Burlakov, Perdita Arndt, Anke Spannenberg, Ulrike Jäger-Fiedler, Marcus Klahn, and Marko Hapke</i>	
10.1	Introduction and Background	165
10.2	Secondary Interactions with C–F Bonds	166
10.2.1	Reactions of Metallacycloprenes with $B(C_6F_5)_3$	166
10.2.2	Reactions of Five-membered Metallacycles with $B(C_6F_5)_3$	170
10.3	Formation of M–F Bonds	171
10.3.1	Stoichiometric Cleavage of C–F Bonds	171
10.3.2	Stoichiometric Formation by M–C Bond Cleavage and Exchange Reactions	174
10.4	Stoichiometric Formation of Zr–H Bonds	174
10.4.1	From Zr–F/Al–H to Zr–H/Al–F Bonds	174
10.5	Catalytic Formation of Zr–H Bonds	175
10.5.1	From Zr–F using Al–H to Zr–H and Al–F Bonds	175
10.5.2	Catalytic Ethene Polymerization	176
10.5.3	Catalytic Hydrodefluorination of Activated C–F Bonds	178
10.5.4	Hydrodefluorination of Nonactivated C–F Bonds by Diisobutylaluminumhydride via the Aluminum Cation $[iBu_2Al]^+$	178
10.6	Conclusion	179
	References	180
11	Bisazines in the Coordination Sphere of Early Transition Metals	183
	<i>Ruediger Beckhaus</i>	
11.1	Introduction	183
11.2	Results and Discussion	185
11.2.1	Formation of Molecular Architectures	185
11.2.2	Molecular Architectures Accompanied by Radical-induced C–C Coupling Reactions	195
11.2.3	Molecular Architectures Based on C–C Coupling Reactions Initiated by C–H Bond Activation Reactions	199
11.3	Conclusions and Future Directions	203
	References	204
12	Bifunctional Molecular Systems with Pendant Bis(pentafluorophenyl)boryl Groups: From Intramolecular CH-activation to Heterolytic Dihydrogen Splitting	209
	<i>Michael Hill, Christoph Herrmann, Patrick Spies, Gerald Kehr, Klaus Bergander, Roland Fröhlich, and Gerhard Erker</i>	
12.1	Introduction	209
12.2	Bifunctional Zirconium/Boron Systems	210
12.3	Bifunctional Group 9 Metal/Boron Systems	216

12.4	Bifunctional Phosphorus/Boron Systems	223
12.5	Conclusions	228
	References	228
13	Ruthenium-containing Polyoxotungstates: Structure and Redox Activity	<i>Ulrich Kortz</i>
13.1	Introduction	231
13.2	The Organoruthenium(II)-containing 49-Tungsto-8-Phosphate $\{[K(H_2O)]_3[Ru(p\text{-cymene})(H_2O)]_4P_8W_{49}O_{186}(H_2O)_2\}^{27-}$	232
13.3	The Mono-Ruthenium(III)-substituted Keggin-Type 11-Tungstosilicate $[\alpha\text{-SiW}_{11}O_{39}Ru^{III}(H_2O)]^{5-}$ and its Dimerization	236
13.4	Conclusions	241
	References	242
14	From NO to Peroxide Activation by Model Iron(III) Complexes	<i>Alicja Franke, Natalya Hessenauer-Ilicheva, Joo-Eun Jee, and Rudi van Eldik</i>
14.1	Introduction	245
14.2	NO Activation by Fe(III) Complexes	246
14.2.1	Fe(III)-Porphyrins	246
14.2.2	Cytochrome P450 and Model Complexes	254
14.3	Peroxide Activation by Fe(III) Complexes	260
14.3.1	Cytochrome P450	262
14.3.2	Fe(III) Porphyrins	263
14.3.3	Catalytic Oxidation Cycle	266
14.4	Conclusions	271
	References	272
15	Synthetic Nitrogen Fixation with Molybdenum and Tungsten Phosphine Complexes: New Developments	<i>Gerald Stephan and Felix Tuczek</i>
15.1	Introduction	273
15.2	Mechanistic Investigation of the Chatt Cycle	276
15.2.1	Protonation of N_2	276
15.2.2	N–N Cleavage	278
15.2.3	Reactivity of Nitrido and Imido Complexes	280
15.2.4	DFT Calculations of the Chatt Cycle	282
15.3	New Phosphine and Mixed P/N Ligands for Synthetic Nitrogen Fixation	285
15.3.1	Tetraphos Ligands	285
15.3.2	Pentaphosphine Complexes	287
15.3.3	Mixed P/N Ligands	291
15.4	Summary and Conclusions	294
	References	294

16	Directed C–H Functionalizations	297
	<i>Carsten Bolm</i>	
16.1	Introduction	297
16.2	Results and Discussion	300
16.3	Conclusions	307
	References	307
17	Development of Novel Ruthenium and Iron Catalysts for Epoxidation with Hydrogen Peroxide	313
	<i>Man Kin Tse, Bianca Bitterlich, and Matthias Beller</i>	
17.1	Introduction	313
17.2	Development of Epoxidation Catalysts Using H ₂ O ₂	314
17.2.1	Ruthenium-catalyzed Epoxidation	315
17.2.2	Biomimetic Iron-catalyzed Epoxidation	318
	References	332
18	Pentacoordinating Bis(oxazoline) Ligands with Secondary Binding Sites	339
	<i>Caroline A. Schall, Michael Seitz, Anja Kaiser, and Oliver Reiser</i>	
	References	348
19	Flavin Photocatalysts with Substrate Binding Sites	349
	<i>Harald Schmaderer, Jiri Svoboda, and Burkhard König</i>	
19.1	Introduction	349
19.2	Templated Flavin Photoreductions	351
19.3	Templated Flavin Photooxidations	353
19.4	Summary and Outlook	355
	References	356
20	New Catalytic Cu-, Pd- and Stoichiometric Mg-, Zn-Mediated Bond Activations	359
	<i>Tobias Thaler, Hongjun Ren, Nina Gommermann, Giuliano C. Clososki, Christoph J. Rohbogner, Stefan H. Wunderlich, and Paul Knochel</i>	
20.1	Introduction	359
20.2	Catalytic Activation	360
20.2.1	C–H Bond Activation for the Preparation of Condensed Polycyclic Alkaloids	360
20.2.2	Activation of Terminal Alkynes in a One-pot Three-component Enantioselective Synthesis of Propargylamines	363
20.3	Stoichiometric Activation	366
20.3.1	The Halogen-Magnesium Exchange	366
20.3.2	Selective Deprotonation Reactions with Magnesium and Zinc Amides	368
20.4	Summary	375
	References	375

21	From Cobalt(II)-activated Molecular Oxygen to Hydroxymethyl-substituted Tetrahydrofurans	379
	<i>Bárbara Menéndez Pérez, Dominik Schuch, and Jens Hartung</i>	
21.1	Introduction [1]	379
21.2	Thermochemical Considerations	381
21.3	Cobalt(II)-Diketonate Complexes	382
21.4	Reactivity	383
21.5	Stereoselectivity Survey	388
21.6	A Derivative of Magnosalicin	390
21.7	Expanding the Scope	391
21.8	Concluding Remarks	393
	References	395
22	Regiodivergent Epoxide Opening	397
	<i>Andreas Gansäuer, Florian Keller, Chun-An Fan, and Peter Karbaum</i>	
22.1	Epoxide Opening via Nucleophilic Substitution: Limitations Arising from the S _N 2-mechanism	397
22.2	Regiodivergent Epoxide Opening (REO): Mechanistic Implications, Synthetic Potential, and Aspects of Catalyst Design	398
22.3	Reductive Epoxide Opening via Electron Transfer from Titanocene(III) Reagents	400
22.3.1	Mechanism of Reductive Epoxide Opening: Predetermined for REO!	401
22.4	Synthetic Realization of Titanocene-catalyzed REO	402
	References and Notes	407
23	Supramolecular Containers: Host-guest Chemistry and Reactivity	411
	<i>Markus Albrecht</i>	
23.1	Introduction	411
23.2	M ₄ L ₄ Tetrahedra	412
23.2.1	Flexible Triangular Ligands	412
23.2.2	Rigid Triangular Ligands	415
23.3	Amino Acid-bridged Dinuclear Titanium(IV) Complexes as Metalloenzyme Mimicry	420
23.4	Conclusions	423
	References	423
24	Self-assembly of Dinuclear Helical Metallosupramolecular Coordination Compounds	427
	<i>Ulf Kiehne, Jens Bunzen, and Arne Lützen</i>	
24.1	Introduction	427
24.2	The Concept of Diastereoselective Self-assembly of Dinuclear Helicates	429
24.3	Synthesis of Building Blocks for the Covalent Assembly of Bis(chelating) Ligands	430

24.3.1	Synthesis of Dissymmetric Elements	430
24.3.2	Synthesis and Resolution of 9,9'-Spirobifluorenes	431
24.3.3	Synthesis and Resolution of Tröger's Base Derivatives	431
24.3.4	Synthesis of 2,2'-Bipyridines	432
24.4	Synthesis of Bis(chelating) Ligands and Their Dinuclear Metal Complexes	434
24.4.1	D-Isomannide-based Ligand and Its Complexes	434
24.4.2	9,9'-Spirobifluorene-based Ligand and Its Complexes	437
24.4.3	Tröger's Base Derivatives-based Ligands and Their Complexes	437
24.5	Conclusions	441
	References	442

Index 447