Contents

Preface *xvii*

1 **Application of Stimuli-Responsive and "Non-innocent" Ligands in Base Metal Catalysis** *1*
Andrei Chirila, Braja Gopal Das, Petrus F. Kuijpers, Vivek Sinha, and Bas de Bruin
1.1 Introduction *1*
1.2 Stimuli-Responsive Ligands *2*
1.2.1 Redox-Responsive Ligands *3*
1.2.2 pH-Responsive Ligands *5*
1.2.3 Light-Responsive Ligands *7*
1.3 Redox-Active Ligands as Electron Reservoirs *8*
1.3.1 Bis(imino)pyridine (BIP) *8*
1.3.1.1 Ethylene Polymerization with BIP *9*
1.3.1.2 Cycloaddition Reactions *10*
1.3.1.3 Hydrogenation and Hydro-addition Reactions *12*
1.3.2 Other Ligands as Electron Reservoirs *14*
1.4 Cooperative Ligands *15*
1.4.1 Cooperative Reactivity with Ligand Radicals *16*
1.4.1.1 Galactose Oxidase (GoAse) and its Models *16*
1.4.1.2 Alcohol Oxidation by Salen Complexes *18*
1.4.2 Base Metal Cooperative Catalysis with Ligands Acting as an Internal Base *18*
1.4.2.1 Fe–Pincer Complexes *19*
1.4.2.2 Ligands Containing a Pendant Base *20*
1.5 Substrate Radicals in Catalysis *21*
1.5.1 Carbene Radicals *22*
1.5.2 Nitrene Radicals *25*
1.6 Summary and Conclusions *26*
References *27*

2 **Computational Insights into Chemical Reactivity and Road to Catalyst Design: The Paradigm of CO_2 Hydrogenation** *33*
Bhaskar Mondal, Frank Neese, and Shengfa Ye
2.1 Introduction *33*

2.1.1 Chemical Reactions: Conceptual Thoughts *33*
2.1.2 Motivation Behind Studying CO_2 Hydrogenation *35*
2.1.3 Challenges of CO_2 Reduction *35*
2.1.4 CO_2 Hydrogenation *37*
2.1.5 Noble vs Non-noble Metal Catalysis *38*
2.1.6 CO_2 Hydrogenation: Basic Mechanistic Considerations *38*
2.2 Reaction Energetics and Governing Factor *39*
2.3 Newly Designed Catalysts and Their Reactivity *42*
2.4 Correlation Between Hydricity and Reactivity *43*
2.5 Concluding Remarks *45*
Acknowledgments *46*
References *47*

3 Catalysis with Multinuclear Complexes *49*
Neal P. Mankad
3.1 Introduction *49*
3.2 Stoichiometric Reaction Pathways *50*
3.2.1 Bimetallic Binding and Activation of Substrates *50*
3.2.1.1 Small-Molecule Activation *51*
3.2.1.2 Alkyne Activation *52*
3.2.2 Bimetallic Analogs of Oxidative Addition and Reductive Elimination *53*
3.2.2.1 E—H Addition and Elimination *54*
3.2.2.2 C—X Activation and C—C Coupling *56*
3.2.2.3 C=O Cleavage *57*
3.3 Application in Catalysis *57*
3.3.1 Catalysis with Reactive Metal–Metal Bonds *58*
3.3.1.1 Bimetallic Alkyne Cycloadditions *58*
3.3.1.2 Bimetallic Oxidative Addition/Reductive Elimination Cycling *59*
3.3.2 Bifunctional and Tandem Catalysis without Metal–Metal Bonds *59*
3.3.2.1 Cooperative Activation of Unsaturated Substrates *59*
3.3.2.2 Cooperative Processes with Bimetallic Oxidative Addition and/or Reductive Elimination *62*
3.4 Polynuclear Complexes *64*
3.5 Outlook *65*
Acknowledgments *66*
References *66*

4 Copper-Catalyzed Hydrogenations and Aerobic N—N Bond Formations: Academic Developments and Industrial Relevance *69*
Paul L. Alsters and Laurent Lefort
4.1 Introduction *69*
4.2 Cu-Promoted N—N Bond Formation *70*
4.2.1 Noncyclization N—N or N=N Bond Formations *71*

4.2.1.1 N—N Single-Bond-Forming Reactions *71*
4.2.1.2 N=N Double Bond-Forming Reactions *72*
4.2.2 Cyclization N—N Bond Formations *74*
4.2.2.1 Dehydrogenative Cyclizations *77*
4.2.2.2 Eliminative Cyclizations *80*
4.2.2.3 Eliminative Dehydrogenative Cyclizations *81*
4.3 Cu-Catalyzed Homogeneous Hydrogenation *82*
4.3.1 Hydrogenation of CO_2 to Formate and Derivatives *84*
4.3.2 Hydrogenation of Carbonyl Compounds *86*
4.3.3 Hydrogenation of Olefins and Alkynes *89*
4.4 Conclusions *91*
References *92*

5 C=C Hydrogenations with Iron Group Metal Catalysts *97*
Tim N. Gieshoff and Axel J. von Wangelin
5.1 Introduction *97*
5.2 Iron *99*
5.2.1 Introduction *99*
5.2.2 Pincer Complexes *100*
5.2.3 Others *106*
5.3 Cobalt *107*
5.3.1 Introduction *107*
5.3.2 Pincer Complexes *108*
5.3.3 Others *115*
5.4 Nickel *118*
5.4.1 Introduction *118*
5.4.2 Pincer Complexes *119*
5.4.3 Others *121*
5.5 Conclusion *122*
Acknowledgments *123*
References *123*

6 Base Metal-Catalyzed Addition Reactions Across C—C Multiple Bonds *127*
Rodrigo Ramírez-Contreras and Bill Morandi
6.1 Introduction *127*
6.2 Catalytic Addition to Alkenes Initiated Through Radical Mechanisms *128*
6.2.1 Hydrogen Atom Transfer as a General Approach to Hydrofunctionalization of Unsaturated Bonds *128*
6.2.2 Hydrazines and Azides via Hydrohydrazination and Hydroazidation of Olefins *128*
6.2.2.1 Co- and Mn-Catalyzed Hydrohydrazination *128*
6.2.2.2 Cobalt- and Manganese-Catalyzed Hydroazidation of Olefins *130*
6.2.3 Co-Catalyzed Hydrocyanation of Olefins with Tosyl Cyanide *133*
6.2.4 Co-Catalyzed Hydrochlorination of Olefins with Tosyl Chloride *133*

6.2.5 $Fe^{III}/NaBH_4$-Mediated Additions of Unactivated Alkenes *134*
6.2.6 Co-Catalyzed Markovnikov Hydroalkoxylation of Unactivated Olefins *135*
6.2.7 Fe-Catalyzed Hydromethylation of Unactivated Olefins *137*
6.2.8 Hydroamination of Olefins Using Nitroarenes to Obtain Anilines *137*
6.2.9 Dual-Catalytic Markovnikov Hydroarylation of Alkenes *139*
6.3 Other Catalytic Additions to Unsaturated Bonds Proceeding Through Initial $R^\cdot$ ($R \neq H$) Attack *139*
6.3.1 Cu-Catalyzed Trifluoromethylation of Unactivated Alkenes *139*
6.3.2 Mn-Catalyzed Aerobic Oxidative Hydroxyazidation of Alkenes *139*
6.3.3 Fe-Catalyzed Aminohydroxylation of Alkenes *141*
6.4 Catalytic Addition to Alkenes Initiated Through Polar Mechanisms *143*
6.4.1 Cu-Catalyzed Hydroamination of Alkenes and Alkynes *143*
6.4.2 Ni-Catalyzed, Lewis-acid-Assisted Carbocyanation of Alkynes *147*
6.4.3 Ni-Catalyzed Transfer Hydrocyanation *148*
6.5 Hydrosilylation Reactions *150*
6.5.1 Fe-Catalyzed, Anti-Markovnikov Hydrosilylation of Alkenes with Tertiary Silanes and Hydrosiloxanes *150*
6.5.2 Highly Chemoselective Co-Catalyzed Hydrosilylation of Functionalized Alkenes Using Tertiary Silanes and Hydrosiloxanes *151*
6.5.3 Alkene Hydrosilylation Using Tertiary Silanes with α-Diimine Ni Catalysts *151*
6.5.4 Chemoselective Alkene Hydrosilylation Catalyzed by Ni Pincer Complexes *154*
6.5.5 Fe- and Co-Catalyzed Regiodivergent Hydrosilylation of Alkenes *155*
6.5.6 Co-Catalyzed Markovnikov Hydrosilylation of Terminal Alkynes and Hydroborylation of α-Vinylsilanes *155*
6.5.7 Fe and Co Pivalate Isocyanide-Ligated Catalyst Systems for Hydrosilylation of Alkenes with Hydrosiloxanes *157*
6.6 Conclusion *159*
References *160*

7 Iron-Catalyzed Cyclopropanation of Alkenes by Carbene Transfer Reactions *163*
Daniela Intrieri, Daniela M. Carminati, and Emma Gallo
7.1 Introduction *163*
7.2 Achiral Iron Porphyrin Catalysts *165*
7.3 Chiral Iron Porphyrin Catalysts *172*
7.4 Iron Phthalocyanines and Corroles *176*
7.5 Iron Catalysts with N or N,O Ligands *180*
7.6 The $[Cp(CO)_2Fe^{II}(THF)]BF_4$ Catalyst *184*

7.7 Conclusions *186*
References *187*

8 Novel Substrates and Nucleophiles in Asymmetric Copper-Catalyzed Conjugate Addition Reactions *191*
Ravindra P. Jumde, Syuzanna R. Harutyunyan, and Adriaan J. Minnaard
8.1 Introduction *191*
8.2 Catalytic Asymmetric Conjugate Additions to α-Substituted α,β-Unsaturated Carbonyl Compounds *192*
8.3 Catalytic Asymmetric Conjugate Additions to Alkenyl-heteroarenes *196*
8.3.1 A Brief Overview of Asymmetric Nucleophilic Conjugate Additions to Alkenyl-heteroarenes *197*
8.3.2 Copper-Catalyzed Asymmetric Nucleophilic Conjugate Additions to Alkenyl-heteroarenes *198*
8.4 Conclusion *205*
References *207*

9 Asymmetric Reduction of Polar Double Bonds *209*
Raphael Bigler, Lorena De Luca, Raffael Huber, and Antonio Mezzetti
9.1 Introduction *209*
9.1.1 Catalytic Approaches for Polar Double Bond Reduction *209*
9.1.2 The Role of Hydride Complexes *210*
9.1.3 Ligand Choice and Catalyst Stability *211*
9.2 Manganese *211*
9.3 Iron *212*
9.3.1 Iron Catalysts in Asymmetric Transfer Hydrogenation (ATH) *213*
9.3.2 Iron Catalysts in Asymmetric Direct (H_2) Hydrogenation (AH) *218*
9.3.3 Iron Catalysts in Asymmetric Hydrosilylation (AHS) *220*
9.4 Cobalt *223*
9.4.1 Cobalt Catalysts in the AH of Ketones *223*
9.4.2 Cobalt Catalysts in the ATH of Ketones *224*
9.4.3 Cobalt Catalysts in Asymmetric Hydrosilylation *225*
9.4.4 Asymmetric Borohydride Reduction and Hydroboration *226*
9.5 Nickel *228*
9.5.1 Nickel Catalysts in Asymmetric H_2 Hydrogenation *228*
9.5.2 Nickel ATH Catalysts *228*
9.5.3 Nickel AHS Catalysts *229*
9.5.4 Nickel-Catalyzed Asymmetric Borohydride Reduction *230*
9.5.5 Ni-Catalyzed Asymmetric Hydroboration of α,β-Unsaturated Ketones *230*
9.6 Copper *231*
9.6.1 Copper-Catalyzed AH *231*
9.6.2 Copper-Catalyzed ATH of α-Ketoesters *232*
9.6.3 Copper-Catalyzed AHS of Ketones and Imines *232*
9.7 Conclusion *235*
References *235*

10 Iron-, Cobalt-, and Manganese-Catalyzed Hydrosilylation of Carbonyl Compounds and Carbon Dioxide *241*
Christophe Darcel, Jean-Baptiste Sortais, Duo Wei, and Antoine Bruneau-Voisine
10.1 Introduction *241*
10.2 Hydrosilylation of Aldehydes and Ketones *241*
10.2.1 Iron-Catalyzed Hydrosilylation *242*
10.2.2 Cobalt-Catalyzed Hydrosilylation *247*
10.2.3 Manganese-Catalyzed Hydrosilylation *248*
10.3 Reduction of Imines and Reductive Amination of Carbonyl Compounds *251*
10.4 Reduction of Carboxylic Acid Derivatives *252*
10.4.1 Carboxamides and Ureas *252*
10.4.2 Carboxylic Esters *254*
10.4.3 Carboxylic Acids *257*
10.5 Hydroelementation of Carbon Dioxide *258*
10.5.1 Hydrosilylation of Carbon Dioxide *258*
10.5.2 Hydroboration of Carbon Dioxide *259*
10.6 Conclusion *260*
References *261*

11 Reactive Intermediates and Mechanism in Iron-Catalyzed Cross-coupling *265*
Jared L. Kneebone, Jeffrey D. Sears, and Michael L. Neidig
11.1 Introduction *265*
11.2 Cross-coupling Catalyzed by Simple Iron Salts *266*
11.2.1 Methods Overview *266*
11.2.2 Mechanistic Investigations *267*
11.3 TMEDA in Iron-Catalyzed Cross-coupling *273*
11.3.1 Methods Overview *273*
11.3.2 Mechanistic Investigations *275*
11.4 NHCs in Iron-Catalyzed Cross-coupling *276*
11.4.1 Methods Overview *276*
11.4.2 Mechanistic Investigations *279*
11.5 Phosphines in Iron-Catalyzed Cross-coupling *283*
11.5.1 Methods Overview *283*
11.5.2 Mechanistic Investigations *285*
11.6 Future Outlook *291*
Acknowledgments *291*
References *291*

12 Recent Advances in Cobalt-Catalyzed Cross-coupling Reactions *297*
Oriol Planas, Christopher J. Whiteoak, and Xavi Ribas
12.1 Introduction *297*
12.2 Cobalt-Catalyzed C—C Couplings Through a C—H Activation Approach *299*

12.2.1 Low-Valent Cobalt Catalysis *299*
12.2.2 High-Valent Cobalt Catalysis *302*
12.3 Cobalt-Catalyzed C—C Couplings Using a Preactivated Substrate Approach (Aryl Halides and Pseudohalides) *308*
12.3.1 Aryl or Alkenyl Halides, C(sp^2)–X *308*
12.3.2 Alkyl Halides, C(sp^3)–X *309*
12.3.3 Alkynyl Halides, C(sp)–X *311*
12.3.4 Aryl Halides Without Organomagnesium *311*
12.4 Cobalt-Catalyzed C—X Couplings Using C—H Activation Approaches *312*
12.4.1 C—N Bond Formation *313*
12.4.2 C—O and C—S Bond Formation *317*
12.4.3 C—X Bond Formation (X = Cl, Br, I, and CN) *318*
12.5 Cobalt-Catalyzed C—X Couplings Using a Preactivated Substrate Approach (Aryl Halides and Pseudohalides) *320*
12.5.1 C(sp^2)–S Coupling *320*
12.5.2 C(sp^2)–N Coupling *321*
12.5.3 C(sp^2)–O Coupling *322*
12.6 Miscellaneous *322*
12.7 Conclusions and Future Prospects *323*
Acknowledgments *323*
References *324*

13 Trifluoromethylation and Related Reactions *329*
Jérémy Jacquet, Louis Fensterbank, and Marine Desage-El Murr
13.1 Trifluoromethylation Reactions *329*
13.1.1 Copper(I) Salts with Nucleophilic Trifluoromethyl Sources *329*
13.1.1.1 Reactions with Electrophiles *330*
13.1.1.2 Reactions with Nucleophiles: Oxidative Coupling *331*
13.1.2 Generation of $CF_3^\bullet$ Radicals Using Langlois' Reagent *332*
13.1.3 Copper and Electrophilic CF_3^+ Sources *333*
13.2 Trifluoromethylthiolation Reactions *341*
13.2.1 Nucleophilic Trifluoromethylthiolation *342*
13.2.1.1 Copper-Catalyzed Nucleophilic Trifluoromethylthiolation *342*
13.2.1.2 Nickel-Catalyzed Nucleophilic Trifluoromethylthiolation *344*
13.2.2 Electrophilic Trifluoromethylthiolation *345*
13.3 Perfluoroalkylation Reactions *348*
13.4 Conclusion *350*
References *350*

14 Catalytic Oxygenation of C=C and C—H Bonds *355*
Pradip Ghosh, Marc-Etienne Moret, and Robert J. M. Klein Gebbink
14.1 Introduction *355*
14.2 Oxygenation of C=C Bonds *356*
14.2.1 Manganese Catalysts *356*
14.2.2 Iron Catalysts *363*
14.2.3 Cobalt, Nickel, and Copper Catalysts *372*

14.3 Oxygenation of C—H Bonds *376*
14.3.1 Manganese Catalysts *376*
14.3.2 Iron Catalysts *377*
14.3.3 Cobalt Catalysts *380*
14.3.4 Nickel Catalysts *381*
14.3.5 Copper Catalysts *383*
14.4 Conclusions and Outlook *384*
Acknowledgment *385*
References *385*

15 Organometallic Chelation-Assisted C—H Functionalization *391*
Parthasarathy Gandeepan and Lutz Ackermann
15.1 Introduction *391*
15.2 C—C Bond Formation via C—H Activation *392*
15.2.1 Reaction with Unsaturated Substrates *392*
15.2.1.1 Addition to C—C Multiple Bonds *392*
15.2.1.2 Addition to C—Heteroatom Multiple Bonds *393*
15.2.1.3 Oxidative C—H Olefination *396*
15.2.1.4 C—H Allylation *397*
15.2.1.5 Oxidative C—H Functionalization and Annulations *397*
15.2.1.6 C—H Alkynylations *403*
15.2.2 C—H Cyanation *404*
15.2.3 C—H Arylation *404*
15.2.4 C—H Alkylation *407*
15.3 C—Heteroatom Formation via C—H Activation *409*
15.3.1 C—N Formation via C—H Activation *409*
15.3.1.1 C—H Amination with Unactivated Amines *409*
15.3.1.2 C—H Amination with Activated Amine Sources *409*
15.3.2 C—O Formation via C—H Activation *412*
15.3.3 C—Halogen Formation via C—H Activation *412*
15.3.4 C—Chalcogen Formation via C—H Activation *414*
15.4 Conclusions *415*
Acknowledgments *415*
References *415*

16 Catalytic Water Oxidation: Water Oxidation to O_2 Mediated by 3d Transition Metal Complexes *425*
Zoel Codolá, Julio Lloret-Fillol, and Miquel Costas
16.1 Water Oxidation – From Insights into Fundamental Chemical Concepts to Future Solar Fuels *425*
16.1.1 The Oxygen-Evolving Complex. A Well-Defined Tetramanganese Calcium Cluster *425*
16.1.2 Synthetic Models for the Natural Water Oxidation Reaction *428*
16.1.3 Oxidants in Water Oxidation Reactions *428*

16.2 Model Well-Defined Water Oxidation Catalysts *430*
16.2.1 Manganese Water Oxidation Catalysts *430*
16.2.1.1 Bioinspired Mn_4O_4 Models *430*
16.2.1.2 Biomimetic Models Including a Lewis Acid *432*
16.2.1.3 Catalytic Water Oxidation with Manganese Coordination Complexes *433*
16.2.2 Water Oxidation with Molecular Iron Catalysts *435*
16.2.2.1 Iron Catalysts with Tetra-Anionic Tetra-Amido Macrocyclic Ligands *436*
16.2.2.2 Mononuclear Complexes with Monoanionic Polyamine Ligands *437*
16.2.2.3 Iron Catalysts with Neutral Ligands *437*
16.2.2.4 Water Oxidation by a Multi-iron Catalyst *440*
16.2.3 Cobalt Water Oxidation Catalysts *440*
16.2.4 Nickel-Based Water Oxidation Catalysts *443*
16.2.5 Copper-Based Water Oxidation Catalysts *445*
16.3 Conclusion and Outlook *446*
References *448*

17 Base-Metal-Catalyzed Hydrogen Generation from Carbon- and Boron Nitrogen-Based Substrates *453*
Elisabetta Alberico, Lydia K. Vogt, Nils Rockstroh, and Henrik Junge
17.1 Introduction *453*
17.1.1 State of the Art of Hydrogen Generation from Carbon- and Boron Nitrogen-Based Substrates *453*
17.1.2 Development of Base Metal Catalysts for Catalytic Hydrogen Generation *458*
17.2 Hydrogen Generation from Formic Acid *460*
17.2.1 Iron *461*
17.2.2 Nickel *466*
17.2.3 Aluminum *467*
17.2.4 Miscellaneous *467*
17.3 Hydrogen Generation from Alcohols *469*
17.3.1 Hydrogen Generation with Respect to Energetic Application *469*
17.3.2 Hydrogen Generation Coupled with the Synthesis of Organic Compounds *470*
17.4 Hydrogen Storage in Liquid Organic Hydrogen Carriers *473*
17.5 Dehydrogenation of Ammonia Borane and Amine Boranes *474*
17.5.1 Overview on Conditions for H_2 Liberation from Ammonia Borane and Amine Boranes *474*
17.5.2 Non-noble Metal-Catalyzed Dehydrogenation of Ammonia Borane and Amine Boranes *476*
17.6 Conclusion *480*
References *481*

18 Molecular Catalysts for Proton Reduction Based on Non-noble Metals *489*
Catherine Elleouet, François Y. Pétillon, and Philippe Schollhammer
18.1 Introduction *489*
18.2 Iron and Nickel Catalysts *489*
18.2.1 Bioinspired Di-iron Molecules *490*
18.2.2 Mono- and Poly-iron Complexes *496*
18.2.3 Bioinspired [NiFe] Complexes and [NiMn] Analogs *501*
18.2.4 Other Nickel-Based Catalysts *506*
18.3 Other Non-noble Metal-Based Catalysts: Co, Mn, Cu, Mo, and W *508*
18.3.1 Cobalt *508*
18.3.2 Manganese *512*
18.3.3 Copper *514*
18.3.4 Group 6 Metals (Mo, W) *514*
18.4 Conclusion *518*
References *518*

19 Nonreductive Reactions of CO_2 Mediated by Cobalt Catalysts: Cyclic and Polycarbonates *529*
Thomas A. Zevaco and Arjan W. Kleij
19.1 Introduction *529*
19.2 Cocatalysts for CO_2/Epoxide Couplings: Salen-Based Systems *530*
19.3 Co–Porphyrins as Catalysts for Epoxide/CO_2 Coupling *537*
19.4 Cocatalysts Based on Other N_4-Ligated and Related Systems *540*
19.5 Aminophenoxide-Based Co Complexes *542*
19.6 Conclusion and Outlook *544*
Acknowledgments *545*
References *545*

20 Dinitrogen Reduction *549*
Fenna F. van de Watering and Wojciech I. Dzik
20.1 Introduction *549*
20.2 Activation of N_2 *550*
20.3 Reduction of N_2 to Ammonia *551*
20.3.1 Haber–Bosch-Inspired Systems *551*
20.3.2 Nitrogenase-Inspired Systems *555*
20.3.2.1 Early Mechanistic Studies on N_2 Reduction by Metal Complexes *556*
20.3.2.2 Iron–Sulfur Systems *557*
20.3.3 Catalytic Ammonia Formation *559*
20.3.3.1 Tripodal Systems *560*
20.3.3.2 Iron and Cobalt PNP Systems *566*
20.3.3.3 The Cyclic Aminocarbene Iron System *567*
20.3.3.4 The Diphosphine Iron System *568*
20.4 Reduction of N_2 to Silylamines *569*
20.4.1 Iron *570*

20.4.2 Cobalt *572*
20.5 Conclusions and Outlook *575*
Acknowledgments *576*
References *576*

Index *583*