Contents

List of Contributors *XI*
Preface *XV*

1 **Mechanisms of Metal-Mediated C–N Coupling Processes: A Synergistic Relationship between Gas-Phase Experiments and Computational Chemistry** *1*
Robert Kretschmer, Maria Schlangen, and Helmut Schwarz
1.1 Introduction *1*
1.2 From Metal-Carbon to Carbon–Nitrogen Bonds *2*
1.2.1 Thermal Reactions of Metal Carbide and Metal Methylidene Complexes with Ammonia *2*
1.2.2 How Metals Control the C–N Bond-Making Step in the Coupling of CH_4 and NH_3 *4*
1.2.3 C–N Coupling via S_N2 Reactions: Neutral Metal Atoms as a Novel Leaving Group *6*
1.3 From Metal-Nitrogen to Carbon-Nitrogen Bonds *8*
1.3.1 High-Valent Iron Nitride and Iron Imide Complexes *8*
1.3.2 Metal-Mediated Hydroamination of an Unactivated Olefin by $[Ni(NH_2)]^+$ *11*
1.4 Conclusion and Perspectives *12*
Acknowledgments *14*
References *14*

2 **Fundamental Aspects of the Metal-Catalyzed C–H Bond Functionalization by Diazocarbenes: Guiding Principles for Design of Catalyst with Non-redox-Active Metal (Such as Ca) and Non-Innocent Ligand** *17*
Adrian Varela-Alvarez and Djamaladdin G. Musaev
2.1 Introduction *17*
2.1.1 Electronic Structure of Free Carbenes *20*
2.1.2 Electronic Structure of Metallocarbenes *22*
2.2 Theoretical Models and Methods *25*

2.3 Design of Catalyst with Non-redox-Active Metal and Non-Innocent Ligand *26*
2.3.1 The Proposed Catalyst: a Coordinatively Saturated Ca(II) Complex *26*
2.3.2 Potential Energy Surface of the [(PDI)Ca(THF)$_3$] Catalyzed C–H Bond Alkylation of MeCH$_2$Ph by Unsubstituted N$_2$CH$_2$ Diazocarbene *27*
2.3.3 [(PDI)Ca(THF)$_3$]-Catalyzed C–H Bond Alkylation of MeCH$_2$Ph by *Donor–Donor* (D/D) Diazocarbene N$_2$CPh$_2$ *32*
2.4 Conclusions and Perspectives *35*
Acknowledgment *37*
References *37*

3 Using Metal Vinylidene Complexes to Probe the Partnership Between Theory and Experiment *41*
John M. Slattery, Jason M. Lynam, and Natalie Fey
3.1 Introduction *41*
3.1.1 The Partnership between Theory and Experiment *41*
3.1.2 Transition-Metal-Stabilized Vinylidenes *42*
3.2 Project Planning in Organometallic Chemistry *44*
3.2.1 Experimental Methodologies *44*
3.2.2 Computational Methodologies *46*
3.3 Case Studies *49*
3.3.1 Mechanism of Rhodium-Mediated Alkyne to Vinylidene Transformation *50*
3.3.2 Using Ligand Assistance to Form Ruthenium–Vinylidene Complexes *54*
3.3.3 Vinylidenes in Gold Catalysis *58*
3.3.4 Metal Effects on the Alkyne/Vinylidene Tautomer Preference *61*
3.4 The Benefits of Synergy and Partnerships *63*
References *64*

4 Ligand, Additive, and Solvent Effects in Palladium Catalysis – Mechanistic Studies *En Route* to Catalyst Design *69*
Franziska Schoenebeck
4.1 Introduction *69*
4.2 The Effect of Solvent in Palladium-Catalyzed Cross Coupling and on the Nature of the Catalytically Active Species *71*
4.3 Common Additives in Palladium-Catalyzed Cross-Coupling Reactions – Effect on (Pre)catalyst and Active Catalytic Species *75*
4.4 Pd(I) Dimer: Only Precatalyst or Also Catalyst? *79*
4.5 Investigation of Key Catalytic Intermediates in High-Oxidation-State Palladium Chemistry *81*
4.6 Concluding Remarks *87*
References *88*

5 **Computational Studies on Sigmatropic Rearrangements via π-Activation by Palladium and Gold Catalysts** *93*
Osvaldo Gutierrez and Marisa C. Kozlowski
5.1 Introduction *93*
5.1.1 Sigmatropic Rearrangements *93*
5.1.2 Metal-Catalyzed Sigmatropic Rearrangements *93*
5.2 Palladium as a Catalyst *94*
5.2.1 Palladium Alkene Activation *94*
5.2.1.1 [3,3]-Sigmatropic Rearrangements *94*
5.2.1.2 [2,3]-Sigmatropic Rearrangements *101*
5.2.2 Palladium Alkyne Activation *103*
5.3 Gold as a Catalyst *103*
5.3.1 Gold Alkene Activation *103*
5.3.1.1 [3,3]-Sigmatropic Rearrangements *103*
5.3.2 Gold Alkyne Activation *108*
5.3.2.1 [3,3]-Sigmatropic Rearrangements *108*
5.4 Concluding Remarks *117*
References *117*

6 **Theoretical Insights into Transition Metal-Catalyzed Reactions of Carbon Dioxide** *121*
Ting Fan and Zhenyang Lin
6.1 Introduction *121*
6.2 Theoretical Methods *122*
6.3 Hydrogenation of CO_2 with H_2 *122*
6.4 Coupling Reactions of CO_2 and Epoxides *127*
6.5 Reduction of CO_2 with Organoborons *131*
6.6 Carboxylation of Olefins with CO_2 *134*
6.7 Hydrocarboxylation of Olefins with CO_2 and H_2 *134*
6.8 Summary *137*
Acknowledgment *139*
References *139*

7 **Catalytically Enhanced NMR of Heterogeneously Catalyzed Hydrogenations** *145*
Vladimir V. Zhivonitko, Kirill V. Kovtunov, Ivan V. Skovpin, Danila A. Barskiy, Oleg G. Salnikov, and Igor V. Koptyug
7.1 Introduction *145*
7.2 Parahydrogen and PHIP Basics *146*
7.3 PHIP as a Mechanistic Tool in Homogeneous Catalysis *149*
7.3.1 PHIP-Enhanced NMR of Reaction Products *150*
7.3.2 PHIP Studies of Reaction Intermediates *152*
7.3.3 Activation of H_2 and Structure and Dynamics of Metal Dihydride Complexes *153*
7.4 PHIP-Enhanced NMR and Heterogeneous Catalysis *155*

7.4.1 PHIP with Immobilized Metal Complexes *155*
7.4.2 PHIP with Supported Metal Catalysts *164*
7.4.3 Model Calculations Related to Underlying Chemistry in PHIP *173*
7.5 Summary and Conclusions *180*
Acknowledgments *180*
References *181*

8 Combined Use of Both Experimental and Theoretical Methods in the Exploration of Reaction Mechanisms in Catalysis by Transition Metals *187*
Daniel Lupp, Niels Johan Christensen, and Peter Fristrup
8.1 Introduction *187*
8.1.1 Hammett Methodology *187*
8.1.2 Kinetic Isotope Effects *188*
8.1.3 Competition Experiments *189*
8.2 Recent DFT Developments of Relevance to Transition Metal Catalysis *190*
8.2.1 Computational Efficiency *191*
8.2.2 Dispersion Effects *193*
8.2.3 Solvation *195*
8.2.4 Effective Core Potentials *196*
8.2.5 Connecting Theory with Experiment *197*
8.3 Case Studies *197*
8.3.1 Rhodium-Catalyzed Decarbonylation of Aldehydes *198*
8.3.2 Iridium-Catalyzed Alkylation of Alcohols with Amines *203*
8.3.3 Palladium-Catalyzed Allylic C–H Alkylation *205*
8.3.4 Ruthenium-Catalyzed Amidation of Alcohols *209*
8.4 Conclusions *213*
Acknowledgments *214*
References *214*

9 Is There Something New Under the Sun? Myths and Facts in the Analysis of Catalytic Cycles *217*
Sebastian Kozuch
9.1 Introduction *217*
9.1.1 Prologue *217*
9.1.2 A Brief History of Catalysis *217*
9.2 Kinetics Based on Rate Constants or Energies *218*
9.2.1 Kinetic Graphs *220*
9.2.2 *TOF* Calculation of Any Cycle *222*
9.2.3 *TOF* in the *E*-Representation *225*
9.3 Application: Cross-Coupling with a Bidentate Pd Complex *227*
9.4 A Century of Sabatier's Genius Idea *230*
9.5 Theory and Practice of Catalysis, Including Concentration Effects *232*

9.5.1 Application: Negishi Cross-Coupling with a Ni Complex *233*
9.5.2 Can a Reaction Be Catalyzed in Both Directions? *236*
9.5.3 The Power Law *239*
9.6 *RDStep* ☒, *RDStates* ☑ *239*
9.6.1 Finding the *RDStates* *242*
9.6.2 Finding the Irreversible Steps *243*
9.7 Conclusion *244*
9.7.1 The Last Myth: Defining the *TOF* *244*
9.7.2 Final Words about the *E*-Representation *245*
References *246*

10 Computational Tools for Structure, Spectroscopy and Thermochemistry *249*
Vincenzo Barone, Malgorzata Biczysko, and Ivan Carnimeo
10.1 Introduction *249*
10.2 Basic Concepts *251*
10.2.1 Potential Energy Surface: Molecular Structure, Transition States, and Reaction Paths *251*
10.2.2 DFT and Hybrid Approaches for Organometallic Systems *254*
10.2.3 Description of Environment *257*
10.3 Spectroscopic Techniques *260*
10.3.1 Rotational Spectroscopy *261*
10.3.1.1 Identification of Conformers/Tautomers *263*
10.3.1.2 Accurate Equilibrium Structures *266*
10.3.2 Vibrational Spectroscopy *267*
10.3.2.1 Frequencies *267*
10.3.2.2 Infrared and Raman Intensities *270*
10.3.2.3 Effective Treatment of Fermi Resonances *273*
10.3.2.4 Thermochemistry *275*
10.3.2.5 Approximate Methods: Hybrid Force Fields *277*
10.3.2.6 Approximate Methods: Reduced Dimensionality VPT2 *279*
10.3.3 Electronic Spectroscopy *280*
10.3.3.1 General Framework for Time-Independent and Time-Dependent Computations of Vibronic Spectra *280*
10.3.3.2 Approximate Description of Excited State PES *283*
10.4 Applications and Case Studies *287*
10.4.1 Thermodynamics and Vibrational Spectroscopy Beyond Harmonic Approximation: Glycine and Its Metal Complexes *287*
10.4.1.1 Accurate Results for Isolated Glycine from Hybrid CC/DFT Computations *287*
10.4.1.2 Glycine Adsorbed on the (100) Silicon Surface *290*
10.4.1.3 Glycine–Metal Binding *291*
10.4.2 Optical Properties of Organometallic Systems *297*
10.4.2.1 Metal Complexation effects on the Structure and UV–Vis Spectra of Alizarin *297*

10.4.2.2 Luminescent Organometallic Complexes of Technological Interest *301*
10.4.3 Interplay of Different Effects: The Case of Chlorophyll-*a* *302*
10.5 Conclusions and Future Developments *308*
Acknowledgments *309*
References *309*

11 Computational Modeling of Graphene Systems Containing Transition Metal Atoms and Clusters *321*
Mikhail V. Polynski and Valentine P. Ananikov
11.1 Introduction *321*
11.2 Quantum Chemical Modeling and Benchmarking *322*
11.2.1 Electron Correlation Methods *322*
11.2.1.1 Truncated Coupled Cluster Methods *322*
11.2.1.2 Truncated Quadratic Configuration Interaction Methods *323*
11.2.1.3 Methods of Møller–Plesset Perturbation Theory *323*
11.2.2 Dispersion-Accounting DFT Methods *324*
11.2.2.1 Empirically Corrected DFT Methods *325*
11.2.2.2 Density Functionals with Nonlocal Correlation Term *330*
11.2.3 Database and Benchmarking Considerations *334*
11.2.3.1 S22, S66, and Related Databases *334*
11.2.3.2 Databases of Relatively Large Intermolecular Systems *337*
11.2.3.3 DFT Methods Benchmarking against Systems with Transition Metal Species *338*
11.2.4 Outlook on Database and Benchmarking *340*
11.3 Representative Studies of Graphene Systems with Transition Metals *341*
11.3.1 Graphene Models *341*
11.3.2 Pristine Graphene as a Substrate for Transition Metal Particles *342*
11.3.2.1 Transition Metal Adatoms on Pristine Graphene *342*
11.3.2.2 Metal Clusters or Nanoparticles on Pristine Graphene *343*
11.3.3 Defective or Doped Graphene as a Support for Transition Metal Particles *347*
11.3.3.1 Transition Metal Adatoms on Doped or Defective Graphene *347*
11.3.3.2 Transition Metal Clusters on Doped or Defective Graphene *349*
11.3.4 Studies of Complex Graphene Systems with Transition Metals *352*
11.3.5 Modeling Chemical Transformations in Graphene/Transition Metal Systems *355*
11.4 Conclusions *362*
Acknowledgments *363*
List of Abbreviations *363*
References *365*

Index *375*