Preface

Familiar to anyone who has taken a basic chemistry course, simple small molecules like H_2, N_2 and O_2 are ubiquitous reservoirs of chemical energy. These energy sources may be used in many ways, such as for fueling biological systems and as synthons for the construction of more complex molecules. Moreover, they may serve as signaling agents in biological systems to trigger complex protein expression and regulation processes. Such small molecules are generally quite thermodynamically stable and their successful utilization depends on surmounting often quite significant kinetic barriers. It has long been recognized that metal ions play an important role in providing low-barrier reaction pathways through binding and activation events. Much fundamental chemistry research has therefore been aimed at addressing questions such as:

- How do metal ions coordinate to and modulate the reactivity of small, often rather inert molecules?
- What is the basis for the selectivity of natural and synthetic metal-containing systems for specific small-molecule substrates?
- Can one use knowledge of metal/small-molecule chemistry for the development of new catalytic processes useful in the laboratory and/or in industry?

These and other related questions have been addressed in the past 10–15 years through the application of creative synthetic strategies and advanced experimental and theoretical techniques. The aim of this book is to provide highlights of recent research, with emphasis on newly discovered fundamental chemistry involved in metal-mediated binding and activation of CO_2, CO, NO, N_2O, N_2, H_2, CH_4, H_2O and O_2. This work has led to a deep understanding that has significantly impacted the fields of bioinorganic, organometallic and catalytic chemistry. By bringing together concise, yet detailed reviews by experts in these wide-ranging fields into a single volume, cross-disciplinary insights are provided in a valuable resource for students and researchers. Importantly, by organizing each chapter by small molecule, organometallic and bioinorganic perspectives are discussed together, in comparative fashion, thus bridging the two disciplines and generating new, unifying concepts.

Industrial processes for the utilization of the greenhouse gas CO_2 are emphasized in Chapter 1 by M. Aresta, with comparisons also drawn to biological pro-

Activation of Small Molecules. Edited by William B. Tolman

ISBN: 3-527-31312-5

cesses. Chapter 2 by D. H. Lee, B. Mondal and K. D. Karlin focuses on NO and N_2O reduction using examples drawn broadly from coordination and organometallic chemistry, as well as biological systems. Mechanisms of reduction of N_2 by nitrogenase and synthetic model systems are discussed by J. Peters and M. Mehn in Chapter 3, while in Chapter 4, J. W. Tye and M. Hall provide a tutorial on H_2 binding and reduction by metal complexes and metalloproteins. The broad topic of O_2 coordination and activation is presented in Chapters 5 and 6 by C. N. Cornall and M. Sigman and A. Borovik, P. J. Zinn and M. K. Zart, respectively. Complementary views of metal–O_2 chemistry are provided in these chapters through discussion of mechanisms, oxidation catalysis and reactive intermediate characterization. The enormously important problem of methane functionalization is tackled in Chapter 7 by R. Periana. The role of metal–aquo complexes in bioinorganic catalysis is emphasized in Chapter 8 by L. Berreau, before turning back to industrial applications in the discussion of CO chemistry by P. W. N. M van Leeuwen and Z. Freixa in Chapter 9. Taken together, these chapters illustrate the diversity of, and provide detailed mechanistic insights into, metal systems that are used in the laboratory and by nature to capture and use small molecules. Challenges for the future are laced throughout, and it is hoped that the reader will be stimulated to address them in future research.

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June 2006