Activation of Small Molecules: Organometallic and Bioinorganic Perspectives, edited by W. B. Tolman; Wiley-VCH: Weinheim, **2007**, hardcover, 563 pp, US$ 175, ISBN 978-3-527-31312-9

This book contains an up-to-date dossier of small-molecule activation that has had a tremendous impact on the fields of bioinorganic, organometallic, and catalytic chemistry. Dr. William Tolman, a highly recognized researcher in this field, in an effort with various academic and industrial research groups, has organized this valuable book for a select scientific readership.

The first of this book's nine chapters describes the use of carbon dioxide as the source of carbon generation at an industrial level. It also describes the physical, chemical, and spectroscopic properties of CO_2, its applications in industrial- and laboratory-scale carboxylation, and its extensive use in chemical reactions involving metal coordination. The second chapter highlights the importance of NO and NO_2 binding to transition-metal ions and biologically important metal centers, which process these nitrogen oxides. Numerous examples of complex reductive pathways are included. The third chapter describes bioorganometallic approaches to nitrogen fixation, the biochemistry of nitrogenases, the process of the nitrogen-fixation cycle, and monometallic complexes comprising a variety of N_xH_y-type ligands. The activation of a simple molecule, dihydrogen, is discussed in chapter four. Difficulties associated with the storage of dihydrogen for future applications are also addressed. The generation of dihydrogen would require materials that are expensive to process, yet its activation by synthetic complexes has recently been identified.

The following chapters cover the activation of oxygen, dioxygen, reactive intermediates, oxidation processes, and ligand-modified catalysts. The use of dioxygen (molecular oxygen, O_2) as the most favored oxidant is due to its abundance in nature. A number of aerobic oxidations, whether in biological or organometallic reaction settings, result in the incorporation of O_2 into the product, and thus have been classified as 'oxygenase-' or 'oxidase-' type reactions. The book cites many examples of catalytic oxidation from the scientific literature along with the reported data. Metal-induced dioxygen binding and its activation is given excellent coverage, with emphasis on 3d transition-metal chemistry and examples from the biological field. The chemistry of methane and several of its important transformations are discussed in chapter 7, including its use as a substitute for petroleum, economical methodologies for functionalization at low temperatures, and the design of hydroxylation catalysts. The catalytic oxidative functionalization of methane is skillfully presented with mechanistic details and supported by spectroscopic data.

The evaluation of ligand effects on water activation and catalytic hydrolysis leading to the recent development of synthetic systems are summarized in chapter 8. However, an interesting discussion on how the coordination number of a supporting ligand or an anionic donor affects the acidity of a metal-bound water molecule requires further exploration. The activation of carbon monoxide, which has reactivity unlike that of other small molecules, is discussed at length. Such information will be useful to those working in various applications of homogenous catalysts, particularly at the larger, industrial scale. The C–O bond remains intact in carbonylation reactions; however, it is cleaved in alcohol homologation chemistry and also quite commonly in heterogeneous catalytic reactions.

In summary, this book is appropriate as a manual for chemists, biochemists, and engineers involved in exploring various aspects of the activation of small molecules.

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SYNTHESIS 2007, No. 12, pp 1898–1898
Advanced online publication: 08.06.2007
Art ID: B11207SS