

Book Review

EDITED BY WILLIAM B. TOLMAN

Activation of small molecules, organometallic and bioinorganic perspectives

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The problem of catalytic activation of small molecules by transition metal complexes is long-standing and highly demanding. If the research has yet to yield new large-scale processes for activation of methane or nitrogen, it can nevertheless boast many advances and it is these that are the subject of this book. This is an edited volume with chapters on the activation of each of CO₂, NO and N₂O, N₂, H₂, O₂, CH₄, H₂O and CO. As expected from interests of the editor, W. B. Tolman, several of the chapters have a bioinorganic flavour, but there is also plenty here for the mainstream organometallic chemist. The book has a subject index, but no author index. I particularly recommend the chapters on methane, nitrogen and carbon dioxide. I was surprised that Tolman does not contribute directly at all: there would have been a great opportunity for a chapter drawing the threads together.

The book starts with a chapter on CO₂ reduction by Aresta, who brings his long-standing expertise to bear on the problem. He provides an excellent guide for beginners with a discussion of the molecular orbitals of CO₂, its Walsh diagram and the thermodynamics of reduction. His span of topics is very wide, ranging from CO₂ complexes to cyclic carbonate formation and transesterification of carbonates through to advances in syn-gas production. I particularly welcomed his section on photoreduction of CO₂.

Lee, Mondal and Karlin introduce NO complexes via the Enemark and Feltham notation and describe some of the advances made recently in bridging nitrosyls and side-on nitrosyls, though the photocrystallography deserved more space. Appropriately, however, they place considerable emphasis on the biological reduction of NO and the associated biomimetic chemistry. The paucity of transition metal chemistry of N₂O is still striking. The most remarkable advance is the elucidation of the structure of the copper centre of N₂O reductase, the enzyme that catalyses the reduction of N₂O to N₂ and water.

The chapter on 'Bio-organometallic approaches to nitrogen fixation' introduces the uninitiated to this subject in fine style, putting appropriate emphasis on the nitrogenase structure, the Chatt cycle, Schrock's recent advances and the cluster models

for nitrogen fixation. The author's own work and that of Holland *et al.* on high-spin iron complexes have advanced the subject considerably.

The chapter on activation of H₂ by Tye, Darensbourg and Hall reviews dihydrogen complexes, hydrogenase and its models. While these topics are important and fascinating, they give a one-sided picture of the activation of dihydrogen. Hydride complexes are barely mentioned and there is nothing about their commercial importance.

The succeeding chapter on oxidation catalysis by Cornell and Sigman targets metal-centred catalysts for aerobic oxidation. They successfully apply the distinction between oxidase, oxygenase and dioxygenase activity, transferred from enzyme catalysis, to inorganic catalysts such as salen complexes. Their emphasis is on classification of reactions rather than mechanism. Borovik, Zinn and Zart treat dioxygen complexes and associated reactivity in a separate chapter with stress on the structures of proteins and their mimics. It is here that you find a brief mention of methane mono-oxygenase. The lack of a molecular orbital approach, in contrast to Aresta or Karlin, is disappointing. I also missed mention of metal phosphine peroxo complexes and of Theopold's work, which has put into the question some of the distinctions between superoxo and peroxo complexes.

The chapter by Periana *et al.* on methane functionalization brings out the industrial context more clearly than any other chapter. As the leading figure in methane conversion, he writes authoritatively on the mercury and platinum catalysts that he has developed, including the problems of product inhibition. He also describes his remarkable oxidation of methane to acetic acid catalysed by Pd(II) in sulfuric acid. This is a thought-provoking chapter that breaks down the challenges into key steps. It is only in this chapter that the bioinorganic perspective is overlooked.

Water activation may not come to mind as a key challenge, but this is the topic of Berreau's review. She takes a bioinorganic perspective, but organometallic aqua complexes do receive a brief mention.

The final chapter by van Leeuwen and Freixa treats carbonylation catalysis. Although carbonylation catalysed by group 9 metals supports a mature industry, there have been major advances in recent years. Van Leeuwen describes the progress in hydroformylation and methanol carbonylation expertly.

Robin N. Perutz

University of York, York, UK