ORGANOMETALLICS

Book Reviews

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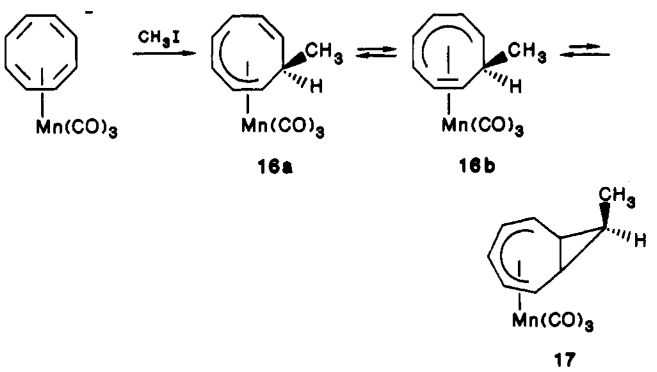

plexes with simple organic electrophiles are in marked contrast to isoelectronic neutral (diene)$Fe(CO)_3$ complexes.[12] Such reactivity differences and the ability to directly functionalize the complexed diene or polyene via reactions with electrophiles and to demetalate such complexes[2c,d] makes these manganese complexes potentially useful synthetic complements to the (diene)iron tricarbonyl systems.

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Supplementary Material Available: Spectroscopic characterization for **6**–**8**, **10**–**12**, **14a**,**b**, **15a**,**b**, and **16** and analytical data for **1b**–**3b**, **5b**, **6**, **7**, **10**, **15a**,**b**, and **16** (6 pages). Ordering information is given on any current masthead page.

Book Reviews

Tailored Metal Catalysts. Edited by Y. Iwasawa. D. Reidel Publishing Co., Dordrecht. 1986. xii + 333 pages. $59.00.

This book is about the chemistry of an increasingly important class of catalysts, metal complexes anchored to solids. H. Hirai and N. Toshima have contributed a well-organized chapter covering the literature of polymer-attached transition-metal complex catalysts, illustrating, for example, the role of the physical properties of the support in influencing the catalyst structure and performance: properly chosen supports can stabilize coordinative unsaturation of metal centers, allow chelation of metal centers with ligands such as phosphines to facilitate control of catalyst selectivity, and allow positioning of catalyst and promoter functions to facilitate their cooperative action. The chapter by Y. Iwasawa concerns transition-metal complexes bonded to metal oxides. The surface chemistry of some of these catalysts is remarkably well-known; the role of silica, for example, as a ligand for supported molybdenum complexes is illustrated with precisely defined structures, with even the Mo–O bond lengths determined by extended X-ray absorption fine structure spectroscopy. R. F. Howe has compiled the literature of catalysts prepared from mononuclear metal carbonyls supported on inorganic solids. Some structurally well-defined species are known, but typically the catalytically active species formed from these precursors are unknown and structurally complex. M. Ichikawa's chapter on supported catalysts derived from metal clusters has some tantalizing information about well-defined surface species, but most of the catalysts are ill-defined and consist of metal aggregates on the supports. Much of this chapter is focused on CO hydrogenation catalysis; the influence of organometallic chemistry on the interpretation of reaction mechanism, even with the supported metal aggregates, is strongly in evidence. The literature of asymmetrically modified nickel catalysts is reviewed by A. Tai and T. Harada. These hydrogenation catalysts consist of optically active compounds implanted on the nickel surface; the nickel activates hydrogen, and the optically active component acts as a stereochemical regulator of the organic reactant.

This book covers the literature through 1982, with a few references to later work. It is an important source of ideas and a stimulating account that justifies the use of the term "tailored catalysts". There are still only a few supported transition-metal catalysts that have truly been designed, and most of these are simple analogues of soluble molecular catalysts. Nonetheless, the knowledge of these is developing rapidly, and there are compelling prospects for "tailored" surface species with new structures and unique catalytic properties (such as multinuclear metal assemblies and uniquely sized metal aggregates). Wider recognition of these prospects will strengthen the role of organometallic chemistry in surface catalysis.

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Metal Clusters in Catalysis (Studies in Surface Science and Catalysis. 29.). Edited by B. C. Gates, L. Guczi, and H. Knözinger. Elsevier, Amsterdam. 1986. xxvii + 648 pp. $84.75.

Metal cluster chemistry has been developed at least in part because of the potential offered for improved catalysts, either homogeneous or heterogeneous. The stated purpose of this monograph is "to give a thorough and critical evaluation of the literature and prospects of metal clusters in catalysis". In large part that goal has been achieved.

Part I concerns molecular cluster chemistry. Short chapters by G. L. Geoffroy review syntheses (18 pages, 60 references) and structures (11 pages, 8 references). Missing is any discussion of the theories of bonding and structure in larger clusters, but references to comprehensive reviews are given. Thermochemistry and energies of metal–metal and metal–ligand bonds are tabulated by J. A. Connor (8 pages, 26 references). A chapter on reactivities of metal clusters (G. Lavigne and H. D. Kaesz, 40 pages, 168 references) emphasizes reactions of molecular clusters which have some relevance to catalysis. Concluding this part is a chapter on homogeneous catalysis (28 pages, 116 references) by L. Markô and A. Vizi-Orosz; although many examples of cluster catalysis are reviewed, the authors note that in most cases it is difficult to prove that the catalyst is actually a cluster. Part I will be of value to readers who are not active in molecular cluster chemistry, but the brevity of the chapters and the fact that most references are pre-1984 makes the section less valuable to researchers in the area.

Part II addresses the primary topic of the volume, supported metal clusters. This section begins with general chapters on methods of characterization of supported clusters: vibrational (38 pages, 155 references), optical (12 pages, 36 references), and magnetic resonance spectroscopy (18 pages, 82 references) and thermoanalytical methods (4 pages, 12 references) by H. Knözinger, photoelectron (9 pages, 40 references) and Mössbauer specroscopy (9 pages, 17 references) by L. Guczi, and X-ray absorption spectroscopy (27 pages, 29 references) by R. F. Pettifer. Next the preparation and characterization of supported metal clusters are presented: a thorough review of deposition of metal clusters in matrices by metal atom vaporization (G. A. Ozin and M. P. Andrews, 86 pages, 151 references), clusters supported in zeolites (P. A. Jacobs, 51 pages, 198 references), molecular metal clusters supported on polymers or chemically modified oxides (B. C. Gates, 9 pages, 42 references), and clusters on unfunctionalized oxides (R. Psaro and R. Ugo, 59 pages, 277 references). This part concludes with chapters on the use of supported clusters for alkene conversions (Gates, 10 pages, 20 references), hydrogenolysis and skeletal isomerization of hydrocarbons (G. Maire, 19 pages, 56 references), CO reduction (Knözinger and Gates, 13 pages, 52 references), and bimetallic catalysts derived from clusters (Guczi, 24 pages, 98 references). This part should be of great usefulness both to workers in the area of supported metal clusters and to molecular cluster chemists who wish to understand the frequently contradictory results obtained by using surface-supported molecular clusters.

Part III is a succinct but well-written analysis of the analogy between metal cluster chemistry and metal surface chemistry by G. Ertl (25 pages, 67 references).

Gates, Guczi, and Knözinger conclude in a short summary and evaluation that, although predictions of new catalytic processes related to the unusual bonding patterns of metal clusters have not come to pass, clusters do provide good models for metal surfaces. The metal cluster–surface analogy is valid in terms of structure and bonding but not catalytic activity. Supported metal clusters provide an opportunity for the investigation of molecular catalysis on surfaces.

This book provides a much needed bridge between molecular metal cluster chemistry and metal surface chemistry. Although the treatment in most chapters is far from being comprehensive, the broad overview nicely ties together results in very divergent areas. The value of the book is further enhanced by the inclusion of indices by subject and by molecular formula for clusters mentioned in the text. The book is a valuable addition to any institutional library, and it should find its way into many personal libraries, as well.

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Organotitanium Reagents in Organic Synthesis. By Manfred T. Reetz. (Volume 24 of the series "Reactivity and Structure Concepts in Organic Chemistry"). Springer-Verlag, Berlin, Heidelberg. 1986. x + 236 pages. $76.50

Titanium complexes have been shown to be broadly useful in new synthetic organic methodology, and the author of this monograph is one of the leading figures in this endeavor. The book which he has written, however, is far more comprehensive with regard to the "organic chemistry" of titanium than that which one might estimate from the title. Chapter 1 (Introduction) provides an overview of the use of titanium species in organic synthesis, and chapters 3 (Chemoselectivity in Reactions of Organotitanium Reagents with Carbonyl Compounds), 5 (Stereoselectivity in the Addition of Organotitanium Reagents to Carbonyl Compounds), 6 (Michael Additions) and 7 (Substitution Reactions) elaborate on these concepts. Reetz' treatment is not only comprehensive (and, as one might expect, thoroughly up-to-date), but he also explains *how* systems are believed to operate and *why* systems are chosen as they are to impart desired selectivities of transformations. In this way, he elaborates for us the chemistry of *C*-, *N*-, and *O*-titanium-bound reagents for organic synthesis. Chapter 8 (Wittig-type Methylenation of Carbonyl Compounds) describes some new chemistry of titanium alkylidene transfer reagents.

What really distinguishes this monograph from other similar ventures is the correlary information which Reetz provides for the synthesis-minded chemist. For example, Chapter 2 (Synthesis and Properties of Some Simple Organotitanium Compounds), which appears under this "simple" heading, is really an in-depth analysis not only of synthesis but also, more importantly, of structure and bonding in organotitanium compounds. This chapter is replete with important physical information, thermochemical data (including bond energy information), photoelectron spectroscopic analysis, crystal structure determinations, and theoretical considerations for bonding in these important organometallic species. Thus, in one chapter, essential features of structure, bonding, and relationships to synthetic problems are neatly and elegantly tied together. Chapter 4 (Rates of Reactions) is also very useful and, again, unusual for a synthesis-oriented book. In this chapter, the chemistry of organotitanium species is treated from the "physical organic" perspective, and the reactivity trends described in this chapter will prove to be very useful to the practicing synthesis chemist in the same way that analogous material in classical mechanistic organic chemistry is to him.

"Organotitanium Reagents in Organic Synthesis" is an exciting addition to Springer-Verlag's series "Reactivity and Structure Concepts in Organic Chemistry" (of which it is Volume 24). It is a book that should be on the shelf of every modern synthetic organic chemist who intends to keep abreast of new developments, and also on the shelf of practicing organometallic chemists who aim to develop new methodologies of use for their "synthesis" colleagues.

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Inorganic Reactions and Methods. Volume 15. Electron-Transfer and Electrochemical Reactions; Photochemical and Other Energized Reactions. Edited by J. J. Zuckerman. VCH Publishers, Inc., Weinheim and Deerfield Beach, Florida. 1986. xxiii + 399 pages. $98.00.

This volume, part of an 18-volume series on inorganic reactions and methods, collects reviews of electron-transfer, electrochemical, photochemical, and pulse radiolysis reactions. Other energized processes such as sonochemical and ion molecule reactions are not covered. The chapters (pages 1–16) on electron-transfer reactions by R. G. Linck briefly survey reactions of simple coordination complexes. The next 52 pages that discuss theoretical models and kinetic behavior for electron-transfer reactions were written by N. Sutin or by C. Creutz and N. Sutin. The discussion of classical, semiclassical, and quantum mechanical theories is complete with examples that nicely illustrate the principles. A 19-page section of specific reactions by R. G. Linck provides a somewhat dated overview of examples of electron-transfer reaction patterns from coordination chemistry. Examples of electron-transfer reactions of organometallics and metalloproteins are either absent or receive cusory treatment in this volume.

The section on electrochemistry is divided into two parts. The first (60 pages) by W. E. Geiger provides a good introduction to techniques such as DC, AC, and pulse polarography, cyclic voltammetry, rotating electrodes, and electrochemical synthesis. This includes a good selection of examples from coordination and organometallic chemistry. Kinetic effects on electrochemical systems are also discussed. Equations used in data analysis are presented and defined clearly. A rigorous discussion by M. J. Weaver of the thermodynamics and theory for heterogeneous electron transfer (28 pages) concludes this section. Notably absent from the discussions on electrochemistry are some current research areas such as microelectrode techniques, semiconductor electrodes, modified electrode surfaces, and other areas of interest to inorganic chemists.

In the photochemistry section P. C. Ford provides a concise overview (28 pages) of the photochemistry of coordination complexes, followed by a 17-page discussion of metal carbonyl photochemistry by H. B. Abrahamson and a 30-page section on other organometallic complexes by G. L. Geoffroy and H. B. Abrahamson. A summary (12 pages) of photoinduced electron-transfer reactions by N. Sutin concludes the photochemistry discussion. A 26-page discussion by M. Z. Hoffman of pulse radiolysis provides an excellent introduction to a less routine technique. Studies of coordination complexes and of a few metal carbonyl systems are summarized in an element by element approach.

The book is well-edited with few apparent errors; however, the reproduction of some figures in the electrochemistry section was faint. This is not a volume that a researcher familiar with the topics covered will find valuable enough to purchase. The lag time between publishing and editing a multiauthor work makes this volume 4 years out of date. It contains few references from 1982 or 1983. Extensive author (29 pages) and compound (60 pages) indices should prove useful to someone interested in a specific compound. By comparison the 5-page subject index is incomplete. Most research experts will find more current reviews, often from the same authors in this volume, in the literature. The chief value of this book will be as a concise introduction to nonspecialists and to students who may want to become familiar with a topic covered in this volume. As such it should be included in library collections.

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