Book Review

Molecular Clusters of the Main Group Elements Edited by Matthias Driess (Ruhr-Universität Bochum) and Heinrich Nöth (Ludwig-Maximilians Universität-München). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2004. xvi + 444 pp. $150.00. ISBN 3-527-30654-4.

Russell N. Grimes

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BOOK REVIEWS

Molecular Clusters of the Main Group Elements. Edited by Matthias Driess (Ruhr-Universität Bochum) and Heinrich Nöth (Ludwig-Maximilians Universität-München). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2004. xvi + 444 pp. $150.00. ISBN 3-527-30654-4.

Does the chemistry of main-group clusters exist as a well-defined area with underlying principles of structure, bonding, and reactivity that connect species as seemingly disparate as carboranes, Zintl ions, mercury clusters, and P_4? This book is an ambitious effort to explore this question, and it succeeds fairly well insofar as structure and bonding are concerned. Chemical reactivity is another matter: in truth, it is difficult to find much common ground linking preparative methods of different classes of clusters, even in those involving elements of the same group in the periodic table, such as boron and aluminum. The virtue of this well-designed volume is that it facilitates comparison of the bonding and chemical properties of a wide range of cluster types in a series of generally excellent chapters. There is much to like here, although one wonders, Where are the carbon clusters?—a seemingly major omission given the title of this book. Aside from a brief discussion of C_{60} in a theoretical context, neither the chemistry of the classically bonded fullerenes nor that of the nonclassical species, such as $C_5H_5^+$, is covered. Granted that this represents a vast area in itself, a chapter on the homonuclear clusters of carbon, which is, after all, a charter member of the main group club, would have been useful.

The book is well organized, and the authors include an impressive array of experts in the chemistry of clusters. In Chapter 1, King and Schleyer present a clear exposition of the theory of bonding in clusters, dating back to Lipscomb's nearly half-century-old equations of balance for the boranes (which could have been omitted since they have been iterated in countless reviews over the years and are primarily of historical value today). Their beautifully concise treatment of the aromaticity of clusters is particularly valuable, as is their discussion of the relationship of boranes to Zintl phases and other main-group clusters.

In Chapter 2, Nöth presents a highly selective summary of the chemistry of clusters having only boron atoms in the skeletal framework, including, for example, information on B_4H_{10} and B_5H_9 but omitting B_6H_{10} entirely and giving rather short shrift to $B_{10}H_{14}$, a compound at the center of an enormous area of research. A peculiar feature of the artwork is that the figures are drawn showing B−H−B bonds as linear rather than bent, as they almost always are in reality. This chapter is useful as a broad introduction to the boranes, but could have been shortened by the omission of the section on structure and bonding, which overlaps heavily, in text as well as figures, with Chapter 1.

Gabel and Endo present a nicely written overview of boron clusters in medical applications that is almost entirely limited to boron neutron capture therapy (BNCT). Other applications, such as radionuclide therapy using metallacarboranes or boron clusters that exhibit strong antitumor activity, are not discussed, although estrogen antagonists are mentioned. Overall, the review is a concise and reasonably up-to-date summary of the rapidly changing BNCT field.

The chapter on the heavier group 13 elements by Lintl, Schnöckel, Uhl, and Wiberg is outstanding: concise, informative, and nicely illustrated with an especially effective use of color figures. Dieseroth similarly does an excellent job with mercury clusters in the next chapter, as do Wiberg and Power in the area of group 14 clusters (again, why only the *heavier* group 14 elements?). This is a very informative treatment of Si, Ge, Sn, and Pb cluster chemistry, although one might question the value of numerous diagrams of large crystal structures in which bulky ligand groups occupy most of the space. The high level of quality is maintained in the succeeding chapters on group 15 and chalcogen clusters by Krossing and Sheldrick, respectively.

In the next chapter, Simon covers alkali and alkaline earth metal suboxides, which, in contrast to most compounds in this volume, exist mainly in the solid state rather than as discrete covalently bonded clusters. Nevertheless they *are* clusters, and it is useful to compare and contrast their structures and chemistry with the molecular species that inhabit the remainder of the book.

A chapter by Bernt, Hofmann, Siebert, and Wrackmeyer follows, offering a well-written discourse on certain aspects of carboranes, especially their relation to classical organoboranes and hydrocarbons, which is centered largely around the authors' own considerable past contributions. The treatment is highly selective, e.g., there is discussion of C_4B_2, C_4B_4, and C_4B_6 clusters but no mention of C_4B_8 systems, on which there is extensive literature. Dicarbon carboranes, whose chemistry dominates the field, are covered in just seven pages (a sixth of the review), and there is a statement that incorrectly (and no doubt unintentionally) gives the impression that no work has been done on the lower carboranes $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$ since their original synthesis a half century ago. Despite its limited scope, the chapter is a useful and highly readable contribution.

The chapter on heteropolyboranes of Si, Ge, and Sn by Wesemann and Hosmane is concise and clear. This is followed by a thorough and excellent survey of boron clusters that contain N, P, As, O, S, or Se heteroatoms by Paetzold. In the next chapter, Uhl and Roesky summarize the chemistry of heteropoly cage and cluster compounds of Al, Ga, In, and Tl that incorporate skeletal heteroatoms such as C and Si, a fascinating and fast-growing area. Finally, Driess, Mulvey, and Westerhausen survey the synthesis of clusters via aggregation of ionic fragments. This chapter has the distinction of being the only one that is focused on a general synthetic approach to the construction of clusters. For this reason, and also because it relates strongly to organometallic chemistry, it is likely to elicit broad interest. As with most of the other chapters, the illustrations have been prepared with great care and attention to detail.

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The book as a whole is attractively produced with very readable type, outstanding artwork, and generally up-to-date references, many dating from 2000 or later. The density of information is impressively high, and by current standards the price is not unreasonable; there is a lot of value here.

To return to the question raised at the start of this review, it will probably require a monograph, rather than a multi-chapter edited volume, to draw out the common features across the enormous range of chemistry of main-group clusters most effectively. Until then, having expertly written individual chapters bound together in the same work is the next best thing. This book is by far the best such compilation produced to date.

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Organometallics in Process Chemistry. Topics in Organometallic Chemistry, 6. Edited by Robert D. Larsen. Merck and Co., Inc.: Rahway, NJ. Springer-Verlag: Berlin, Heidelberg, New York. 2004. x + 296 pp. $229.00. ISBN 3-540-01603-1.

This book is the sixth volume in the *Topics in Organometallic Chemistry* series, which originated in 1998. It consists of 10 chapters, each of which is an independent, 15−40 page review of work in a given area. The book is not meant to be comprehensive and is far from it. The current volume examines the literature roughly through 2002.

The use of organometallic compounds in chemical process development in the pharmaceutical, agricultural, and fine chemical industries is the focus of this volume. As such, most of the chemistry described in the book arose from process chemistry/chemical development groups in those arenas. Most of the chapters deal with a specific metal or reaction type, some of which bear comment. The chapter on organolithiums, for example, is somewhat of a disappointment because a large percentage of it deals with organolithium-derived bases such as lithium diisopropylamide. Although interesting, this chapter is really more of a discussion of enolate chemistry than anything else. In contrast, the chapter on organotitanium reagents is well-written and contains a much larger variety of reaction types. In it, one can really get a feel for the extent of usage of this important family of metals in process development. The chapter on applications of rhodium and ruthenium concentrates mostly on reductions, as might be expected, whereas the chapter on non-salen metal-catalyzed asymmetric dihydroxylation and aminohydroxylation of alkenes focuses solely on the osmium-based methodology originated by Sharpless and developed further by many others. This chapter makes it clear that industrial use of this methodology in large scale chemical manufacturing is still a ways off. The two successive chapters covering the chemistry of organopalladium coupling have short introductory sections followed by numerous examples of Heck arylations and related cross-coupling reactions that have been developed by research groups in chemical processing. These latter two chapters are particularly well-written and show a broad range of industrial practice in organopalladium chemistry. Perhaps the most interesting and informative chapter in the book deals with the removal of metals from process streams. This is a brief but excellent overview of a general and pervasive problem in the chemical industrial setting that is not fully appreciated by the academic community.

Overall, the quality and layout of the drawings are quite good, which gives the book high readability. There is also a cumulative author index (through all six volumes) and a subject index. Although the book covers a fairly specialized area, it is one of growing importance and visibility in the organic chemistry community. Unfortunately, because of its title, the book will appeal most strongly to industrial organic chemists. However, the information and underlying message would be quite beneficial for academicians to experience and appreciate.

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Fundamental Electron Interactions with Plasma Processing Gases. By Loucas G. Christophorou (National Institute of Standards and Technology, Gaithersburg and Academy of Athens, Greece) and James K. Olthoff (National Institute of Standards and Technology, Gaithersburg). Kluwer Academic/Plenum Publishers: New York. 2004. xvi + 783 pp. $199.00. ISBN 0-306-48037-9.

The publication of this book is particularly timely because the area of "electron-driven chemistry" is currently undergoing a renaissance as a result of recent demonstrations showing that collisions with low-energy electrons, i.e., electrons with energies less than 20 eV, can play an important and direct role in defining the chemistry of radiation damage to materials and biological systems, including the breaking of DNA strands. The origins of modern experimental and theoretical methods for studying fundamental electron-driven processes in molecules lie principally in decades of efforts to understand the essential physics and chemistry of lighting and plasma processing technologies. Collisions with low-energy electrons are uniquely effective in transferring energy to the electronic degrees of freedom of atoms and molecules by directly exciting both singlet and triplet states, and thus they play a central role in all forms of modern fluorescent and plasma lighting technologies as well as in the broad arena of plasma processing of materials.

The principal objective of this book is to provide an exhaustive summary and evaluation of the existing body of experimental data on fundamental electron-impact processes in particular gases that are important in plasma processing. Given this formidable task, the book succeeds admirably. In the semiconductor industry, the fabrication of microelectronics depends on plasma reactors in which a low-temperature plasma is created by applying radio frequency power to a reaction chamber filled with a low pressure gas. As the authors explain in the early chapters, these reactors are used for both plasma etching and deposition, and generally several members of a long list of gas-phase echant and depositing molecules are employed in the reactor at the same time, although these gases do not generally react with silicon or silicon dioxide surfaces in the absence of low-energy electrons. However, when the plasma is created, the fragments of these molecules perform the chemistry of controlled etching and deposition. The modeling and

optimization of these plasmas requires controlling which fragments and ions are produced and therefore requires a detailed knowledge of the dynamics that produce those species. It is to that modeling community that this book is largely targeted.

The opening chapters provide an introduction to the fundamentals of this subject, cataloging the many kinds of fundamental processes initiated by electron interactions with molecules, including various types of excitation and many classes of fragmentation reactions. Particular attention is paid to the crucial distinction between "direct" (short-lived) and "indirect" (resonant and therefore long-lived) collisions, because the latter selectively enhance the rates of these fundamental processes. The applications of plasma processing are briefly explained, and a detailed explanation is given of contemporary experimental techniques involving both electron beams and swarms. These opening chapters provide a compact introduction to the subject that reveals the diversity of the physics and chemistry involved.

The authors establish a careful protocol for critically assessing and synthesizing the large body of experimental data that they have studied in an eight-year project on 10 important plasma processing gases at the National Institute of Standards and Technology. The remainder of the book focuses on experiments on those 10 gases: CF_4, SF_6, CCl_2F_2, Cl_2, BCl_3, CHF_3, CF_3I, C_2F_6, C_3F_8, and *c*-C_4F_8. The work is exhaustive, and each chapter contains hundreds of references. It establishes a critical baseline, including recommended values for the cross sections for a wide variety of important processes involving these gases. Some of the data are available electronically from NIST (http://www.eeel.nist.gov/811/refdata/), but this book provides vastly more data, with a detailed discussion of nearly all of it.

Because its focus is limited to these molecules and because it contains very little discussion of the large literature on theory and calculations on electron−molecule collisions, the authors analyze only a single segment of the broad and rich literature on this subject. The general reader can supplement it with recent reviews on other aspects of this subject, for example that of Hotop et al. (*Adv. At., Mol., Opt. Phys.* **2003**, *49*, 85−216). Nonetheless, this work will be an indispensable reference for the community because it provides an entry point and critical summary of a stunningly extensive literature on these measurements, and therefore it makes a major contribution to this field.

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Ruthenium Catalysts and Fine Chemistry. Topics in Organometallic Chemistry, 11. Edited by Christian Bruneau and Pierre H. Dixneuf (Université de Rennes 1). Springer-Verlag: Berlin, Heidelberg, New York. 2004. x + 347 pp. $329.00. ISBN 3-540-20543-8.

This reasonably concise overview of the modern use and development of reactions based upon ruthenium catalysts consists of 11 chapters written by 21 authors. It is because of this that there is considerable redundancy, which effectively increases the price of this book from close to $1.00/page to a somewhat higher amount. Although the title and preface refer to fine chemicals, the text does not in any meaningful way indicate which of the numerous transformations facilitated by ruthenium catalysts are in fact used to make so-called fine chemicals. There is no doubt that many of the reactions presented in the text are extremely useful and are a testament to modern transition metal-based catalysis, but a more systematic and critical presentation would have greatly enhanced both the readability and educational value of the book. As is stands, it is merely a catalog without a story. If that is all the reader requires then it is adequate. But, if insight, explanation, and logical historical development of the area are priorities, the reader should look elsewhere. Finally, there is no reason for the structures to be inconsistently formatted from chapter to chapter.

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Organic Chemistry in Photography. By Shinsaku Fujita (Kyoto Institute of Technology). Springer-Verlag: Berlin, Heidelberg, New York. 2004. xx + 588 pp. $249.00. ISBN 3-540-20988-3.

In the words of the author, "this book is devoted to comprehensive discussions on organic compounds used in color photography, especially, on their structures, functions, dynamic processes, R&D, syntheses, and related items." His purpose in writing this book was to present "a viewpoint based on organic chemistry [that] has been missing in the conventional descriptions on photography", a perspective that is developed in the following five parts: Fundamentals of Photography, Principles of Color Photography, Chromogenic Photography, Diffusion Transfer Photography, and Dye Bleach Photography.

The first part, Fundamentals of Photography (100 pages), is similar to many other works that have covered this subject, with a few notable exceptions. One of these is the section on the multilayer structure of photographic materials, which is a very welcome addition. The structure of photographic materials is extremely complex. Although many people know that photographic products are composed of a number of different layers, few truly appreciate the reasoning behind their detailed ordering and the interrelations between them. To address this subject, the author provides an example of one structure of a typical color paper (7 layers) and two structures of color negative films (13 and 16 layers) and then discusses the composition of each layer, providing structures of many of the organic compounds contained therein. There is also a section on tabular grains that even includes an example of how they can be prepared.

The second part (30 pages) concerns the principles of color photography. Although its contents are also similar to other books on the photographic process, this part gives substantially more detail on the syntheses of sensitizing dyes. It also includes a discussion of residual color due to sensitizing dyes, an additional sensitizing layer (four color records instead of three), infrared sensitizing dyes for digital printing, and sensitizing dyes applied to CD-R (compact disk recordable).

The real meat of this book lies in Parts III (Chromogenic Photography) and IV (Diffusion Transfer Photography). These are approximately 200 pages each. Chromogenic refers to the

conventional color photographic process practiced today, wherein image dyes are generated by the reaction of color couplers with oxidized developing agents. This part is dominated by a discussion of various types of color couplers. Particularly helpful are the sections on inhibitor- or accelerator-releasing couplers (development-inhibitor releasing, development accelerator releasing, bleach accelerator releasing, etc.), which have not been covered in other books on this subject.

Diffusion transfer photography is a type of instant photography that has largely been replaced by digital photography. This part is presented in great depth and detail, reflecting the author's long career in this area. The last part of this book is a short chapter (15 pages) covering dye bleach photography, which is most commonly used in the Ilfochrome process. Although there is a lot of interesting chemistry involved in these two processes, there is little commercial viability to these technologies, which is apparent by the age of most of the references.

The author worked at Fuji Photo Film for 25 years. Not surprisingly, most of the examples used in this book are from work published or patented by Fuji. For the convenience of the reader, however, corresponding U.S. patents are given for patents that were originally applied for in Japan. This is a nice touch, which should make it easier for English speakers to follow up the references. I would have liked to have seen more references included in this book, however.

To conclude, *Organic Chemistry of Photography* does a good job covering the topics that it chooses to cover. Although dated, I think that *The Theory of the Photographic Process* published in 1977 gives a more balanced overview of many of the important aspects of the photographic process. I question the wisdom or marketability of this book at the present time. Conventional photographic processes are rapidly being replaced by digital ones, and major photographic companies are rapidly downsizing or going out of business. There are few college courses that cover this material. I suspect that this book may be more important as a historical account of these technologies rather than the resource for active researchers or students in the field that it was intended to be.

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New Synthetic Methods. Advances in Polymer Science, 167. With contributions by Owen W. Webster (Chadds Ford, PA), Jean Jacques Robin (Ecole Nationale Supérieure de Chimie Montpellier), Takashi Uemura, Kensuke Naka, Yoshiki Chujo (Kyoto University), Younghwan Kwon (Daegu University), and Rudolf Faust (University of Massachusetts, Lowell). Springer-Verlag: Berlin, Heidelberg, New York. 2004. x + 156 pp. $179.00. ISBN 3-540-00544-7.

This latest volume of the venerable *Advances in Polymer Science* series includes four contributions related to preparative techniques and synthetic methodologies used in polymer chemistry. Two chapters focus on polymerization reactions and reagents, specifically group transfer polymerization (customarily known as GTP) in the first chapter, followed by a second chapter on ozone as a polymer-modifying reagent. The last two contributions concentrate on polymeric targets, i.e., dithiafulvalene-containing polymers and polyisobutylene-based block copolymers, respectively. All four reviews are solidly written and well-organized, extensive in their coverage, and composed by authors who have made significant contributions of their own.

Whether the substance of this monograph is adequately captured by the title (*New Synthetic Methods*) is debatable, as many of the methodologies and improvements reviewed in the individual chapters, although still in use today, were designed some time ago. A rapid statistical analysis of the contents shows that the average years of publication for the references in each section are 1991, 1977, 1991, and 1996, respectively, with very few recent contributions. Out of the 535 references in the entire monograph, only five correspond to manuscripts published in 2002 and 2003.

Despite this minor disparity between the book's title and its content, all four reviews provide high-quality reading for novices and experts alike. Although there is no real central theme, each chapter fulfills its objective of providing in-depth, up-to-date, and critical coverage of previous scientific contributions. In addition, useful data for comparison are provided that might be significant for polymer scientists interested in closely related topics and/or in polymerization techniques, in general. In particular, the critical assessment of techniques for polymerization of methyl methacrylate included by Webster at the end of his first chapter on GTP is worth reading by anyone interested in polymerization methodologies.

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Electrogenerated Chemiluminescence. Edited by Allen J. Bard (University of Texas at Austin). Marcel Dekker, Inc.: New York. 2004. viii + 540 pp. $165.00. ISBN 0-8247-5347-X.

This is the first book ever on electrogenerated chemiluminescence (ECL), a phenomenon discovered exactly 40 years ago that relates to light emission from energetic electron-transfer reactions among species generated electrochemically. Admittedly, I am quite surprised that this undertaking was not attempted before, given the impact of ECL in the last four decades, including its role as the first piece of evidence for the so-called Marcus inverted region and its role as the underlying operating principle for an important segment of clinical diagnostics that generated more than $400 million in sales in 2002.

The book consists of 11 contributed chapters, and the editor, who is also the author of Chapters 1 and 11, is credited as one of the three pioneers in the field. Overall, if I were to use only one word to describe this monograph, it would be "thorough". The editor has done an excellent job in selecting the contributing authors, and they, in turn, have captured and presented in an admirable fashion a balanced view of all the theoretical and practical aspects of ECL from the point of scientific discovery to the current level of understanding.

Chapter 1 serves as an overview and positions ECL historically in the context of the intellectual climate that led to its discovery. I found this historical account most interesting, and

in my opinion, it will outlive all other information in this book, remaining a lasting testimony to the power of combinatorial thinking. Chapter 2 is a unique source for how-to-do ECL experimentally, covering everything from electrodes, cells, and light detection, to ECL in the magnetic field. Chapters 3 and 4 concern the theoretical foundation of ECL, Chapters 5−7 its chemical aspects, and Chapters 8−10 its applications.

More specifically, Chapter 3 covers the mechanism of ECL from a global mass-transfer/homogeneous kinetics perspective, whereas Chapter 4 focuses on the electron-transfer step in relation to the energy available for excitation, as well as the implications of using ECL to study general kinetics and the mechanisms of electron-transfer reactions. Chapter 5 is a comprehensive review of the mechanistically interesting subject of co-reactants (agents that allow ECL from a unidirectional potential step or scan), and the next two chapters are reviews of organic and metal chelate ECL-active systems, respectively. Chapter 8 is a description of the applications of ECL in clinical diagnostics, life sciences research, water and food testing, and the detection of biological warfare agents. Other analytical uses of ECL, as for example in chromatography, are the topic of Chapter 9, and the following chapter is a review of ECL polymers for active displays that emphasizes the almost completely overlooked connection between light-emitting electrochemical cells and organic light-emitting diodes. In the final chapter, some miscellaneous topics related to ECL are discussed, but most importantly, the question "Is there anything else left to be discovered?" is addressed. The ensuing discussion delivers a clear message: not only is there much to be learned about organic intermediates and processes by adopting ECL as a basic mechanistic tool, but also new applications may emerge based on what is already known. I personally found the concept of using ECL with semiconductor electrodes in night-vision equipment (through the process known as up-conversion) particularly intriguing.

The book does not suffer from many of the problems of multi-author books, i.e., there is no unnecessary overlap, quality and style are uniform throughout, and referencing is up-to-date (2003). If I were to change something, I would probably reverse the order of Chapters 5 (on co-reactants) and 6 (on organic ECL systems). The book is still reasonably priced, although at $165.00, it is out of the reach of the graduate student. I would insist that it be in the must-read list for a wide range of professionals, from physicists to organic chemists to biologists, who work in such diverse areas as light-emitting diodes, combinatorial synthesis, wastewater management, or DNA sequencing.

Nicholas Leventis, *NASA Glenn Research Center*

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