APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 394–399 (2000)

Book reviews

Solid State Organometallic Chemistry: Methods and Applications
M. Gielen, R. Willem and B. Wrackmeyer (eds)
John Wiley and Sons, Chichester, 1999
xviii + 529 pages. £165
ISBN 0-471-97920-1

This book is the second volume of a series dedicated to *Physical Organometallic Chemistry*, the aim of which is to offer reviews of 'hot topics' in the area of organometallic chemistry to postgraduates and established researchers alike. Volume 1 in the series, which was devoted solely to advanced applications of NMR to organometallic chemistry, is now complemented in Volume 2 by aspects of organometallic chemistry in the solid state, under the dual headings of methods and applications.

The majority of the book (seven chapters) addresses the application of physical methods to the understanding of the molecular and electronic structures of organometallic compounds and materials. The final three chapters are devoted to applications, and cover aspects of polymer chemistry in the form of either silicon-containing materials or polymer-supported organometallics. The attitude of most authors in preparing their contributions is best summarized by the comments of Melinda Duer in her chapter on solid-state NMR: 'The work is not intended to be an exhaustive compilation … but rather a selective review intended to highlight the scope and potential for future applications'. Despite the subjective nature such an approach entails, the contributors should be congratulated for their selections.

The chapters devoted to physical methods all refer the reader to fuller texts dealing with the background theory of a given technique and, as such, none of the chapters makes easy reading for the totally uninitiated. Chapters 1–3 all relate to X-ray crystallography, with Chapters 1 and 2 covering aspects of data collection and refinement. Tiekink's opening chapter on current practice in the area is a very readable summary of the steps involved in small-molecule crystal structure determination, and should be required reading for all new postgraduates hoping to fill their theses with ORTEP diagrams. This is complemented by a more specialist review by Flavello of analysing less-than-optimum data sets and is a lesson (again for all new postgraduates!) that crystallography is not infallible. It is additionally worth noting that, despite the current level of sophistication surrounding contemporary crystallographic instrumentation and methodology, there is still room for debate and conjecture, typified by the comments on absorption corrections which pepper the two contributions. The final contribution to the X-ray triad is a more specialist article by Braga *et al.* on hydrogen bonding in organometallic systems and, although short, will be of interest to anyone interested in the more general field of crystal engineering.

Three chapters are devoted to structure determination methods which apply to both ordered and disordered systems: XAFS, solid-state NMR and Mössbauer. The latter two techniques are very closely related, in that much of the ground formerly occupied by Mössbauer is now being supplanted by practitioners of solid-state NMR. The two chapters are disproportionate in size, with the Mössbauer contribution (*ca* 100 pages, 690 references) by far the largest in the book and almost twice the size allotted to solid-state NMR (47 pages 118 references). A non-scientific survey of the Mössbauer reference list suggests that the majority pre-date the 1990s and thus Silver's chapter constitutes more of a backward-looking survey, albeit a comprehensive one, covering the major Mössbauer nuclei (Sn, Te, Sb, Fe, Au), than a pointer to the future. Surely an update in five years' time, based objectively on only new data, will reverse these weightings. Both chapters suffer somewhat in having to limit themselves to examples from organometallic chemistry, with carbonyl and cyclopentadiene derivatives figuring strongly in both contributions. The chapter on XAFS by Slovokhotov begins with an overview of the technique followed first by examples of studies of simple mononuclear species, then by application to more complex problems, e.g. structure in solution, metal colloids and supported metal clusters. The general tone of this chapter is the caution with which XFAS results must be treated, particularly in comparison with X-ray diffraction results.

The final 'methods' chapter by Fröhlich and Frenking is devoted to the power of *ab initio* calculations in explaining the electronic structure of (primarily) organotransition metal compounds. As with the earlier chapters, newcomers will not make much of the array of acronyms which accompany the methodology, but the applications are well chosen and will convince any sceptic of the value of such techniques to understanding, not just mimicry, of molecular and electronic properties. Two examples—Bent's rules and the Dewar–Chatt–Duncanson model of bonding in metal carbonyls—are presented and in both cases the accepted theory is

reviewed and refined. For example, an apparent anomaly—why main group R_2MCl_2 species have bond angles which obey Bent's rule while transition metal examples appear not to—is shown simply to require a more sophisticated statement of the rule! A very sophisticated and convincing analysis of the bonding in transition metal–CO, –carbene and –carbyne complexes is also presented. As the authors clearly demonstrate, quantum chemistry can give insight as well as just numbers.

The three 'applications' chapters are linked by the common theme of polymer chemistry. Uhlig highlights the elegant use of silyl triflates in the synthesis of a wide range of silicon-containing polymers, while the final two contributions by Delmond/Dumartin and Cameron deal with polymer-supported organometallics. The former concentrates largely on the applications of supported organotin hydrides, while the latter is a wider review of polymer-bound metal complexes. These include, *inter alia*, supported catalysts, polymer electrodes, conducting films and photochromic systems. Such is the breadth of material available that this is the most selective of all the chapters written and includes examples from only the last two years. It is very much as 'taster' of what is currently going on in the field and is a good overview for those unfamiliar with the area, although the restriction to mainly organic polymer supports has eliminated much of the current work involving polysiloxane materials.

The book is generally well balanced, with most chapters averaging around 40–50 pages. The short chapters on crystal engineering and supported organotin reagents (about 20 pages each) reflect their specialist nature, and only the Mössbauer chapter is disproportionately large. At £165 a copy this book will, however, grace few personal collections. It will be a valuable addition to library stocks and will particularly benefit new postgraduates who, with an initial knowledge of their research topic, will wish to expand the depth and breadth of their understanding. The authoritative nature of the contributions the editors have collected together makes this an excellent starting point.

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Supramolecular Organometallic Chemistry

Ionel Haiduc and Frank T. Edelmann
Wiley–VCH, Weinheim, 1999
viii + 471 pages. £95
ISBN 3-527-29533-X

One of the interesting features of chemistry as an academic subject is that it is constantly recast like the images in a kaleidoscope to reveal new connections between its component parts. Lines of research which have been developed separately are brought together to show new insights and give new applications. In this book by two writers with very strong track records and high reputations, an attempt is made to define a new branch of chemistry, 'supramolecular organometallic chemistry', by drawing on the vast literature of organometallic chemistry to describe the variety of intermolecular interactions that have been found. The resulting monograph will be of immense value to researchers in organometallic chemistry, but at the same time it is unsatisfying. There is a real feeling, which the authors acknowledge in their introduction, that the story is incomplete, that in spite of their scholarship (more than 2100 references, some as late as 1999) the coverage is somewhat arbitrary and that the outlines of the new subject are only just beginning to emerge.

Chapter 1 covers basic concepts and principles. The widely used terms 'supramolecular chemistry', 'molecular recognition', 'self-assembly' and 'self-organization' are defined and illustrated with examples from organometallic chemistry. The various types of intermolecular bond are discussed in subsequent chapters.

Chapter 2 covers molecular recognition and host–guest interactions e.g. in organomercury and organotin macrocycles as receptors for anions, in organocyclosiloxanes as sequestering agents for metals, in ferrocene-containing crown ethers and cryptands (and related nitrogen, phosphorus and sulfur derivatives), in calixarenes modified by organic groups and in crown ethers, cryptands and zeolites with organometallic guests. The topics covered range widely and, although there are many clear line diagrams to assist the reader to see the trees within the wood, the sheer vastness of the subject means that some pages contain little more than lists.

Chapter 3 deals with supramolecular self-assembly by electron pair donor–acceptor interactions. The molecular organometal halides, alkoxides, amides and related compounds of elements of Groups 12 and 13, tin and lead are coordinatively unsaturated so that they are almost invariably (i.e. except when they contain very bulky organic groups) associated in the solid state. The chapter gives a good description of this association and is certainly a valuable entrée into the literature but readers seeking detailed knowledge of particular areas will have to turn to more specialized reviews. Chapter 4 discusses supramolecular self-assembly by formation of secondary bonds, i.e. those with lengths greater that the sum of the covalent radii but less than the sum of the Van de Waals radii. There is a brief section on homoatomic bonds between elements of Groups 15 and 16, but most of the chapter covers interactions between the heavier elements of Groups 12–16 and halogen, alkoxo, thiolato or nitrile substituents in organic groups. Judgements about whether the 'secondary' bonds are 'true' bonds are necessarily arbitrary and sometimes controversial.

Chapter 5 covers supramolecular assembly by hydrogen-bond interactions. This is a common form of self-assembly in organic chemistry but it is also important for organosilanols and for the less moisture-sensitive compounds of the transition metals in which hydroxy or carboxy substituents can be attached to the organic group. The two final chapters cover self-assembly caused

