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
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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

by ionic and π-bond interactions mainly in organometallic compounds of elements of Groups 1–3, e.g. in oligomeric organoalkali-metal derivatives and cyclopentadienyl compounds. Again this is a good introduction to the area but the extent of the literature means that much of the detail has had to be left out.

The authors have performed the valuable service of encouraging chemists to look at interactions between as well as within molecules. However, much of the 'self-assembly' discussed here is that of crystallization. There is little about self-assembly in solution, little about applications, and little sense of the way in which organometallic compounds might be synthesized to give sites specifically designed for recognition of particular molecules. These are topics for the future research which this book is likely to stimulate.

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Grignard Reagents—New Developments

H. G. Richey (ed),
Wiley, Chichester, 2000
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In 1900 the landmark paper by Victor Grignard, 'Sur quelques nouvelles combinaisons organométalliques du magnésium et leur application à des synthèses d'alcools et d'hydrocarbures' was published.[1] 'At the close of its first century, the Grignard reagent has achieved maturity but exhibits no signs of senescence'—so writes Herman Richey in his Preface. Indeed, on the evidence of this and other books, there are even signs of rejuvenation.

Grignard Reagents—New Developments is a collection of 12 detailed reviews of selected aspects of organomagnesium chemistry, in which important developments have taken place towards the end of the 20th century. Some of them review the new light that has been shed on old topics. For example, Holm and Crossland discuss the mechanism of reactions of Grignard reagents with carbonyl compounds and show that, in contrast to the simplistic picture presented in undergraduate textbooks, of nucleophilic attack by carbanionic carbon at the carbonyl carbon, in many cases an important reaction pathway involves initial electron transfer. Other chapters in this category are on nucleophilic displacements at carbon by Grignard reagents (Hill), and stereoselective additions of Grignard reagents to aldehydes (Gawley; a review of the general principles, but with the examples drawn from the specialized area of the author's own work, i.e. reactions of α-amino Grignard reagents). A heavyweight contribution in this category is by Garst and Ungváry, who present a comprehensive account of their side of the long-running argument concerning the mechanisms of Grignard reagent formation. Will this be the knock-out, or will Walborsky and others return for another round?

Several chapters are reviews of new topics, or topics which have shown major new developments: hydromagnesiation of alkenes and alkynes (Sato and Urabe), stereoselective addition of Grignard reagents to alkenes (Hoveyda, Heron and Adams), applications of magnesium anthracene in forming Grignard reagents (Raston), structures of organomagnesium compounds as revealed by X-ray studies (Bickelhaupt), X-ray absorption spectroscopy and large-angle X-ray scattering of Grignard compounds (Ertel and Bertagnolli; this chapter includes an account of the principles and practice of EXAFS and LAXS, which provide a good introduction to these techniques), di- and poly-functional organomagnesium compounds (Bickelhaupt), and the uninformatively titled 'Unusual Organomagnesium Compounds' (Smirnov, Tjurina and Beletskaya). This last chapter is an account of the authors' work on the intriguing, though still ill-defined, substances obtained by co-deposition of magnesium vapour and organic compounds, and formulated by them as RMg_nX or RMg_nH.

At first sight the remaining chapter, entitled 'Grignard Reagents—Industrial Applications and Strategy', by Busch and de Antonis, appears out of place, though it could be argued that the large-scale industrial use of Grignard reagents is a fairly recent development. I have some criticism of this chapter. Some of the statements made are questionable: for example, the reaction of a Grignard reagent with a ketone does not give 'a complex of the product alcohol with the residual magnesium salts', and to describe the role of ethereal solvents as 'stabilizing the Grignard reagent' begs some questions. It should also have been noted that carbon dioxide, as well as water, should not be used on burning magnesium. Nevertheless, most readers of this book are likely to be from academic institutions, and this chapter will provide such readers with a salutary insight into the challenge faced by those needing to scale up laboratory syntheses for industrial use.

In 1954, just over half-way through the Grignard reagent's first century, Kharasch and Reinmuth's monumental *Grignard Reactions of Nonmetallic Substances* was published. It has been clear to authors of recent books (including myself) that the subject was now so large that they could not hope to emulate Kharasch and Reinmuth's achievement. In editing this book, Herman Richey has opted to cover selected topics in depth, and the result will be invaluable to those working in the chosen areas. The book as a whole should also find a place in libraries, though its price will put it beyond the reach of most individuals.

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