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Book reviews

Organometallic Ion Chemistry
Ben S. Freiser (Ed.)
Kluwer Academic Publishers, Dordrecht, 1996
352 pages. £128.00
ISBN 0-7923-3478-7

Gas-phase metal ion chemistry has been the subject of intense research activity over the past two decades. Following the early experiments of Allison and Ridge on metal ion insertion, and Beauchamp and co-workers on the ion/dipole mechanism, the field has matured to a point where experimentalists now have control over the kinetic and potential (electronic-state) energy of an ion. These important developments have been matched by the ability of theorists to treat many-electron systems, and provide a quantitative understanding of the role low-lying electronic states play in structure and reactivity.

The review articles brought together in this book embrace all the most recent developments in theory and experiment. Articles by Armentrout and Kickel, van Koppen *et al.* and Russell *et al.* discuss the current state of transition-metal ion reactivity, and provide numerous case studies of the influence that changes in metallic electronic state have on chemistry. The power of recent advances in instrumentation is demonstrated through three examples: Armentrout and Kickel show how guided ion-beam techniques can be used to control reaction kinetic energy, van Koppen *et al.* discuss the use of ion chromatography to identify and select specific transition-metal atomic electronic states, and Russell *et al.* show how FTICR (Fourier Transform Ion Cyclotron Resonance) can be used to store ions and study their reactivity over extended periods of time. These three chapters are well complemented by reviews from Bauschlicher *et al.*, and Harrison and Kunze. Their articles cover recent theoretical studies of structure and bonding in small metal ion–molecule and radical complexes. *Ab initio* methods for the treatment of metallic systems have now reached a stage where they can be used with confidence both to verify and to predict the outcome of an experiment.

The range of reaction mechanisms afforded by metal ion–large molecule complexes is surveyed in an article by Eller. The work provides a good demonstration of how early ideas behind the interpretation of some of the very first experiments in the field can be verified and developed using modern experimental techniques. Photochemical studies of metal ion–molecule complexes are given comprehensive coverage in a chapter by Ranasinghe *et al.* Once again the power of FTICR is demonstrated as a technique for trapping and interrogating ions. However, in many respects photochemistry is one of the least developed of the research topics, in that systematic studies are hampered by the need in every case for a suitable chromophore. Recent advances in tunable laser sources will most certainly open new opportunities for research in this area. In the final chapter, Richardson provides a detailed summary of our current understanding of electron-transfer equilibria in organometallic systems. This work seeks to find a link between the ionization energies and electron affinities of isolated systems, and redox potentials of bulk analogues. One of the most exciting extensions of this topic, and many of the others discussed in the book, has to be the application of experiment and theory to the study of multiply charged metallic complexes.

A final bonus to the book is the presence of a very comprehensive listing of metal–ligand bond dissociation energies. The editor, Ben Freiser, is to be congratulated for bringing together an excellent series of reviews written by acknowledged experts in their field.

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Organic Reactions in Aqueous Media
Chao-Jun Li and Tak-Hang Chan
Wiley-Interscience, New York, 1997
199 pages. £50
ISBN 0-471-16395-3

This book has been jointly written by C.-J. Li, an Assistant Professor of Chemistry at Tulane University, and T.-H. Chan, a Professor of Chemistry and Vice-Principal at McGill University. With the current attitudes to cost, safety and the environment, and the potential advantages of performing organic reactions in water, it is perhaps surprising that such a book has not appeared before now. It is certainly a welcome addition.

The text is presented in seven chapters, starting with a brief introduction to the important issues that should be considered when using water as a reaction solvent, such as the fundamental properties of water, the hydrophobic effect and salt effects. The remaining chapters cover pericyclic reactions, nucleophilic additions and substitutions, metal-mediated and transition-metal-catalysed

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reactions, oxidation and reduction reactions and, finally, industrial applications. Reactions such as hydrolysis which are routinely performed in water are not included, and enzyme reactions and phase-transfer-catalysed reactions are only mentioned briefly because of their specialist nature. Within each chapter several different reactions are discussed that have been performed in water; for example, in Chapter 2 on pericyclic reactions, Diels–Alder, Alder–ene, 1,3-dipolar cycloadditions, sigmatropic rearrangements and photochemical reactions are all mentioned. The authors have clearly had to be selective, which has resulted in some sections being fairly brief, but this does not necessarily detract from the overall usefulness of the work because it is well referenced. The final chapter on industrial applications is particularly short; it contains a few selected examples.

Overall the work is well presented and comprehensively referenced and gives the reader a taste for what reactions can be successfully carried out in water. The amount of published information on organic reactions in aqueous media is comparatively small, and bringing it together within this work is extremely useful. It highlights the fact that although many of these areas of research are still in their infancy there are many potential applications. This book should appeal to anyone considering water-based reactions, and it extends Li's earlier review which focused on carbon–carbon bond-forming reactions in water.

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Progress in Organosilicon Chemistry
B. Marciniec and J. Chojnowski (Eds)
Gordon and Breach, Basel, 1995
xi + 592 pages. £72
ISBN 2-88449-122-8

This volume was only recently received for review although it appeared in 1995. It presents most of the plenary and invited lectures delivered at the very successful Tenth Jubilee International Symposium on Organosilicon Chemistry held in Poznan, Poland, in August 1993. After a most interesting personal account by Eugene Rochow of his very important invention of the direct process bearing his name and some other fundamental aspects of silicon chemistry in Section I, the book is divided into three main sections, namely: Section II, Synthesis, Structure and Properties of Molecular Organosilicon Compounds; Section III, Reactions and Intermediates in Organosilicon Chemistry; and Section IV, Silicon Polymers and Other Silicon-based Materials.

It is not practicable to attempt to present here assessments of the 33 individual contributions, and in picking out possible highlights a reviewer is inevitably attracted to the articles falling in his own areas of special interest. Thus in Section II, I was struck particularly by J. Schraml's account of 'Steric factors in ^{29}Si chemical shifts', a phenomenon of which I had been previously unaware, and one that that should be drawn particularly to the attention of organic chemists since, for example, the effects can be utilized for determination of the structures of trimethylsilylated steroids. It is of interest that the first two articles in this section both deal with compounds containing so-called 'supersilyl' groups; however, it is unfortunate that in the first, by N. Wiberg, this term denotes a tri-t-butylsilyl group whereas in the second, by H. Bock and his colleagues, it denotes the tri(trimethylsilyl)silyl group! If I had to suggest which of these usages should be abandoned it would be the former, since it seems to have little advantage over the correct chemical name that has been used without ambiguity for 50 years. However, for the $(Me_3Si)_3Si$ group my preference would be for the shorter and simpler 'sisyl' in view of the wide acceptance of the term 'trisyl' for the corresponding carbon-centred group $(Me_3Si)_3C$.

In Section III, I liked particularly A. R. Bassindale's article entitled 'Coordination and Reactivity in Organosilicon Chemistry', which brings out clearly the great complexity of the mechanisms of nucleophilic substitution at silicon, and concludes with the words, ''All observations on mechanisms in silicon chemistry should be tempered by the knowledge that silicon exhibits, in one situation or another, almost all known mechanistic pathways. The major rule in mechanistic organosilicon chemistry is 'seek and you will find'.''

In Section IV, I was attracted by J. W. White's survey of 'Recent Achievements in Industrial Silicon Polymer Science', which provides a well-written outline of the state of knowledge of silicon-based polymers with actual or potential industrial uses; it would provide an excellent brief introduction for newcomers to the field. Since in his article Professor Rochow expresses scepticism about the possibility of obtaining useful organosilicon nitrogen polymers (a view I advanced myself in my 1960 book), it is noteworthy that Dr White's account includes one such species, although it is not used directly as such but for production of stable silicon carbide–carbon composites suitable for a variety of fabrication techniques and moulding applications.

As with most compilations of papers given at symposia, the value of this one is limited by the fact that all or almost all the new material will have since been published elsewhere. The book will not be attractive to individual purchasers, but in libraries it could serve as a useful introduction to the main areas of activity in organosilicon chemistry in the mid-1990s, with the important exception that the vast field of the use of organosilicon compounds in organic synthesis is hardly touched upon.

The book has a rather better subject index than is usually found these days in such compilations.

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