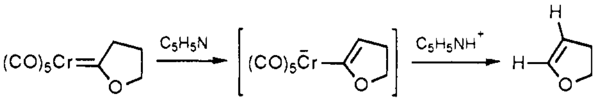
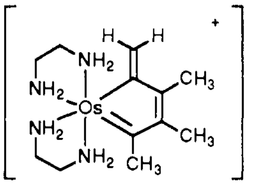
between the planes of Os–C(5)–C(6) and Os–N(1)–N(2)–N(3) (mean deviation is 0.0098 Å). The remaining carbene double bond [Os–C(9)] distance of 1.895 (11) Å is slightly shorter than those observed in **1** [1.940 (8) and 1.931 (8) Å] and a previously reported osmium carbene complex [Os(=CHPh), 1.94 (1) Å].[11]

In an earlier study of the reaction scheme represented by A, a mechanism involving initial deprotonation of the carbene ligand followed by protonation of the metal–carbon bond was proposed.[12]



(A)

A similar mechanism, i.e., the formation of an α-substituent-deprotonated metallacycle intermediate **4**, can also account for the osmacyclopentatriene isomerization we have observed. Protonation of the Os–C single bond of intermediate **4**, followed by the coordination of the resulting double bond to the metal center, will generate **2**. Only recently has any work on the chemistry of substituents on metallacycles been reported.[13] The isomerization described here, involving activation of an α-substituent by a carbene, is a new reaction mode of a metallacycle.



4

The 1,2-hydrogen shift of alkyl carbene ligands can also occur in the absence of base. For example, Fischer observed a transient aryl–alkyl chromium carbene species formed at −40 °C which undergoes a 1,2-hydrogen shift to generate a stable alkene complex.[14] When a crystal of **1** under dynamic vacuum is heated at ~165 °C for 1.2 h, only very small amount of it decomposes. Among the products is that resulting from the 1,2-hydrogen shift, **2**, which is detected by ^1H NMR spectroscopy. The synthesis and isomerization of the osmacyclopentatriene complex represent an overall conversion of two dialkyl-substituted alkynes to a metal vinyl carbene species. This transformation may serve as a model

$$M + 2\,{-}{\equiv}{-} \rightarrow M{=}{-}{=}{-}{=}$$

for the generation of a metal carbene catalyst in the polymerization of internal alkynes catalyzed by certain transition metal complexes.[15] A conjugated metallacyclohexatriene has also been proposed as an intermediate in carbene alkyne coupling reactions to form cyclic organic compounds.[3a] Research on the reactivity of the metallahexatriene complexes through introduction of alkene or alkyne molecules onto the metal center is in progress.

Acknowledgment. Financial support from the National Institutes of Health (GM-13638-25) is gratefully acknowledged. We also thank Prof. H. Hope at the University of California—Davis for providing the X-ray facility.

Supplementary Material Available: Listings of analytical and spectroscopic data for compounds **2** and **3** and tables of atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, hydrogen atom coordinates, and isotropic displacement coefficients (7 pages); table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

(10) Crystal data for **3** (120 K): $C_{12}H_{29}N_4Cl_3Os\cdot0.5C_2H_5OH$, triclinic, $P\bar{1}$; a = 7.388 (1) Å, b = 8.756 (1) Å, c = 16.149 (2) Å, α = 95.54 (1)°, β = 102.93 (1)°, γ = 90.31 (1)°, V = 1013.0 (2) Å^3, Z = 2, D_{calcd} = 1.805 g cm^{-3}, μ = 15.643 mm^{-1}. A green tabular plate (0.14 × 0.10 × 0.04 mm) was used for data collection (Siemens P4RA, 0.0° < 2θ < 108.5°, Cu Kα). Of 2702 reflections collected, 2473 were independent, and 2316 with $F_o > 6.0\sigma(F)$ were considered observed and were empirically corrected for absorption by using the XABS program (this program generates an absorption correction tensor based on F_o and F_c differences. Hope, H.; Moezzi, B. Chemistry Department, University of California at Davis). The atoms were located by Patterson methods and refined by full-matrix least-squares. Hydrogen atoms were calculated and refined by a riding model with fixed isotropic U: R = 5.83%, R_w = 6.62% ($R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$), all data R = 6.03%, GOF = 1.04. All computer programs and sources of scattering factors are contained in SHELXTL PLUS (G. M. Sheldrick, A program for crystal-structure determination, version 4.0, 1989, Siemans Analytical X-ray Instruments, Madison, WI).

(11) Roper, W. R. in ref 3b.

(12) (a) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. (b) Casey, C. P. In *New Applications of Organometallic Reagents in Organic Synthesis, Journal of Organometallic Chemistry Library*; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; Vol. 1.

(13) A metallacycle α-substituent is involved in an alkyne cleavage reaction: O'Connor, J. M.; Pu, L. *J. Am. Chem. Soc.* **1990**, *112*, 9013.

(14) Fischer, E. O.; Held, W. *J. Organomet. Chem.* **1976**, *112*, C59.

(15) (a) Costa, G. In *Comprehensive Polymer Science*; Allen, S. G., Bevington, J. C., Eds.; Pergamon Press: New York, 1989; Vol. 4. (b) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1987**, *81*, 121. (c) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

---

*Book Reviews**

Ions, Electrodes and Membranes. Second Edition. By J. Koryta (Czechoslovak Academy of Sciences). J. Wiley & Sons: New York. 1991. xiv + 198 pp. $74.95. ISBN 0-471-93079-2.

This little book introduces concepts about ionic solutions, electrochemistry, and membranes in a nonmathematical way to scientists from other disciplines, especially, from its content and approach, to those in biology. Crammed into 198 pages is a rather superficial treatment of many topics. For example, within the space of 4 pages, one can find a discussion of ionically and electronically conductive polymers, alkali metals in liquid ammonia, and high-temperature superconductors. Even cold fusion gets a paragraph. Reading this book reminds me very much of those tours that take you through eight countries in five days: there are lots of interesting things to see, but you never feel like you have seen enough. Nevertheless, this is a useful little book. It is full of interesting facts and information, and the personal and informal approach of the author makes it rather easy reading. I found a few small errors, e.g., Nafion is not "a perfluorostyrene sulphonate" (p 142) and the equation on p 150 and the current axis and caption for Figure 94 on p 174 cannot be correct. It is hard to justify the high price of the hardback version, but a cheaper paperback version, if one were available, would be a nice way to introduce ionic solutions, electrochemistry, and membranes to a neophyte.

Allen J. Bard, *University of Texas at Austin*

Strategies and Tactics in Organic Synthesis. Volume 3. Edited by Thomas Lindberg (The Upjohn Company). Academic Press: San Diego. 1991. xx + 544 pp. $125.00. ISBN 0-12-450282-2.

Volume 3 of the well-known series *Strategies and Tactics in Organic Synthesis* maintains the same high standards of presentation and content that were set by the preceding volumes. Each of the thirteen chapters is written either by leading industrial or academic practitioners and focuses on material of current interest. The contributions are full of insights concerning the tribulations and triumphs associated with the research endeavor.

The book is very enjoyable to read, being both entertaining and highly educational. The style differs from that of the original literature in a

---

*Unsigned book reviews are by the Book Review Editor.

manner that provides the reader with a far greater sense of the thought processes and strategies that go into the planning and execution of a total synthesis. Both the seasoned professional and those just beginning to appreciate the beauty of organic synthesis are certain to find the present volume worthy of their purchase and reading.

R. Daniel Little, *University of California, Santa Barbara*

The Chemical Bond: Structure and Dynamics. Edited by Ahmed Zewail (California Institute of Technology). Academic Press, Inc.: San Diego. 1992. xviii + 314 pp. $49.95. ISBN 0-12-779620-7.

This elegant book, dedicated to Linus Pauling, contains articles written by Pauling, Max Perutz, Alexander Rich, Francis Crick, George Porter, John Polanyi, Dudley Herschbach, Ahmed Zewail, and Richard Bernstein. The book is organized into two sections, the first on Structure and the second on Dynamics. There is a brief biography of each of the authors and a short index. The book is replete with pictures and figures, many in color.

Direct Methods of Solving Crystal Structures. NATO ASI Series, Series B: Physics Volume 274. Edited by Henk Schenk (University of Amsterdam). Plenum Press: New York and London. 1992. x + 446 pp. $115.00. ISBN 0-306-44040-7.

This book contains the proceedings of the 1990 NATO Advanced Study Institute on "Direct Methods for Solving Crystal Structures" held in April in Erice, Sicily. The 47 chapters, in typescript form, are followed by a short subject index. Affiliations of the authors are given at the heading of each chapter/paper.

Supercritical Fluid Technology. Theoretical and Applied Approaches in Analytical Chemistry. ACS Symposium Series No. 488. Edited by Frank V. Bright (State University of New York at Buffalo) and Mary Ellen P. McNally (E. I. du Pont de Nemours and Company). American Chemical Society: Washington, DC. 1992. x + 374 pp. $86.95. ISBN 0-8412-2220-7.

This book was developed from a symposium sponsored by the Division of Analytical Chemistry at the 201st National Meeting of the ACS in Atlanta, GA, April 14–19, 1991. It consists of 22 chapters that are organized into two sections: Spectroscopic Investigations and Separation Science. There are indexes of authors, their affiliations, and subjects.

Viscoelasticity of Biomaterials. ACS Symposium Series No. 489. Edited by Wolfgang Glasser (Virginia Polytechnic Institute and State University) and Hyoe Hatakeyama (Industrial Products Research Institute, Japan). American Chemical Society: Washington, DC. 1992. x + 406 pp. $84.95. ISBN 0-8412-2221-5.

This book was developed from a symposium sponsored by the Division of Cellulose, Textile, and Paper Chemistry at the 199th National Meeting of the ACS held in Boston, MA, April 22–27, 1990. The 26 chapters are divided into three sections: (1) Structure–Property Relationships; (2) Biogels and Gelation; and (3) Relaxation Phenomena. There are indexes of authors, their affiliations, and subjects.

Biotransformations. Volume 4. A Survey of the Biotransformations of Drugs and Chemicals in Animals. Edited by D. R. Hawkins (Huntingdon Research Centre Ltd.). Royal Society of Chemistry: Cambridge. 1992. xxix + 491 pp. £99.50. ISBN 0-85186-187-3.

This volume continues the high standard established by the earlier members of this series. The objective of the editor for this volume, as with the others, is to provide a complete survey of the current literature on the biotransformations of pharmaceuticals, pesticides, food additives, and environmental and industrial chemicals. The entire series broadly covers the literature for the calendar years 1987 through 1990.

The format is consistent throughout the series with each volume divided into four sections. The first is a structural listing of the key functional groups used to categorize the entries; these can be rapidly scanned for relevance to any particular search and the biotransformations for that specific functional group can easily be found by turning to the index. The second section is an overview of recent metabolic conversions and provides a state-of-the-art review on novel biotransformations, mechanisms of toxicity, and stereoselective and stereospecific processes. The third and largest subdivision is composed of nearly 300 brief abstracts with flow sheets each describing the bioconversion of specific compounds. The heading for each abstract lists the chemical or generic name, its use, the key functional groups present, and the test system including species, dose, and route of administration. The structural changes occurring in each step of the biotransformation are clearly indicated in the flow sheet format and described concisely in the text. The location of radiolabeled atoms is indicated when appropriate. A complete literature reference is conveniently provided after the description of the metabolites.

The final section is a very usable index, which is cumulative over the four volumes. The index itself is divided into three searchable sets. One can query by specific compound, by the key functional groups described in section 1, and by bioreaction type. This structure makes the index very usable and most questions regarding actual or possible bioconversions can be readily addressed. The functional group classification is especially useful and provides an index-related procedure for retrieving information on structurally related compounds. As recognized by the editor, this indexing method has the potential for the development of a computerized database.

Because of the completeness and excellent search capabilities of this series, *Biotransformations* is likely to become one of the most frequently used reference sources in its field. The addition of abstracts on in vitro metabolism would significantly broaden the information base; hopefully we can look forward to such an extension in future volumes.

J. J. Baldwin, *Merck Research Laboratories*

^{13}C-NMR of Natural Products. Volume 1. Monoterpenes and Sesquiterpenes. By Atta-ur-Rahman and Viqar Uddin Ahmad (University of Karachi). Plenum Press: New York. 1992. x + 968 pp. $135.00. ISBN 0-306-43897-6.

This is an excellent compilation of carbon-13 spectral data for a large number of mono- and sesquiterpenes. One presumes that there will be additional volumes following about other terpenes and perhaps other natural products groups. The data are supplied on structural representations of the compounds with the numbers associated with the appropriate carbons. The figures are large and easy to read. Given the complexity and variety of terpene structures, it might have been helpful to include an index by ring type so that, for example, data for ten-membered-ring systems could be found easily. Nonetheless, the structures are sufficiently large that such an operation can be managed manually. Overall, the shift assignments provided were taken from the original citations and were made available for the vast majority of entries. It would have been useful, however, to include some indication of the basis for shift assignments used by the original authors. Four separate indices are provided: name; source (i.e., plant); molecular formula; and molecular weight.

This volume will certainly serve as a ready source of carbon-13 spectral data for a large range of compounds. It should be useful to not only natural products chemists but also those looking for structural models to use analogously when assigning carbon-13 shifts.

Flavor Precursors. Thermal and Enzymatic Conversions. ACS Symposium Series No. 490. Edited by Roy Teranishi and Gary R. Takeoka (Department of Agriculture) and Matthias Güntert (Haarmann and Reimer GmbH). American Chemical Society: Washington, DC. 1992. x + 270 pp. $64.95. ISBN 0-8412-2222-3.

This book was developed from a symposium sponsored by the Division of Agricultural and Food Chemistry at the Fourth Chemical Congress of North America (202nd National Meeting of the ACS) held in New York, NY, August 25–30, 1991. After a 1-page preface by the editors and an introductory overview, it contains 18 chapters in typescript form organized under the following headings: Enzymatic Reactions; Glycosidic Precursors; and Thermal Generation. There are indexes of authors, their affiliations, and subjects.

Dynamics of Gas–Surface Interactions. Advances in Gas Phase Photochemistry and Kinetics. Edited by C. T. Rettner and M. N. R. Ashford. Royal Society of Chemistry: Cambridge. 1991. xvi + 366 pp. $97.50. ISBN 0-85186-853-3.

This volume is an ambitious attempt to bring together most of the important research in recent years on this topic. It succeeds admirably by taking a decidedly pedagogical approach to the subject. Although all of the contributors are experts at the forefront of their respective fields, the focus is on fundamentals and the understanding of the big picture rather than for a presentation of all the details for those in the field. For this reason, this volume should be of interest to the gas-phase dynamicist as well as to those in the condensed matter physics and materials science communities.

The chapters by J. Harris on mechanical energy transfer, A. Depristo on the dynamics of chemisorption, W. H. Weinberg on the kinetics of surface reactions, and H. J. Kreuzer and S. H. Payne on thermal desorption kinetics will provide those from other fields with a rich introduction to these areas. In order to apply these concepts to a particular system, B. E. Hayden has written a detailed summary on the dissociative adsorption of dihydrogen on copper surfaces. This model system has provided much for theoreticians to ponder and still has much to offer. This is also reflected in the chapter on quantum effects in gas–solid interactions, which discusses the hydrogen–copper case as well as more general issues. Whereas these articles focus on gas–surface collisions, the last two chapters deal with excitations within the adsorbed layer caused by electrons and photons. R. D. Ramsier and J. T. Yates, Jr., summarize both the underlying fundamentals and the recent developments in electron stimulated desorption. J. C. Polanyi and H. Rieley discuss photochemical processes in the adsorbed layer, including photodissociation and photoreaction.

This volume fills several needs. It provides a broad and expert overview for those in the field and those approaching it from their diverse disciplines. It also succeeds in focussing the attention of the reader on the basics and on the similarities between different systems rather than on more subtle differences. This is a needed attempt to take stock of what is known that applies to many diverse gas–surface systems. Finally, it provides an advanced textbook level overview of the field which will be invaluable (though not necessarily affordable) to workers in this area. Evolution in a field sometimes accelerates while a text is in the throes of publication, and this has happened in our understanding of the hydrogen–copper system. Recent work by Rettner and Auerbach are recommended as a supplement. These articles also make it abundantly clear how complex a field like this is and that experimentalists and theorists must work closely together to define model systems worthy of detailed study and to extract the essence from the experimental data. The editors are to be congratulated for their efforts in putting together this volume.

Thomas Engel, *University of Washington*

Electroorganic Synthesis. Festschrift for Manuel M. Baizer. Edited by R. Daniel Little (University of California, Santa Barbara) and Norman L. Weinberg (The Electrosynthesis Company, East Amherst, NY). Marcel Dekker, Inc.: New York. 1991. xxxvi + 434 pp. $150.00. ISBN 0-8247-8584-3.

This book is based on the Manuel M. Baizer Memorial Symposium held in Montreal, May 6–11, 1990 and is published in honor of Dr. Baizer. The introductory pages consist of a preface by the editors, a list of contributors, a list of Dr. Baizer's 104 publications and patents, two pages of limericks and haikus by the honoree, and a brief anecdote by Fritz Beck. The 48 chapters are organized under the following headings: Mechanism; Reduction; Oxidation; Mediated Reduction and Oxidation; Biochemical, Biomass, and Natural Products; Modified, Sacrificial/Consumable Electrodes; Electrogenerated Bases (EGB); Film-Forming Electropolymerization; and Ion Exchange. There is a good subject index.

Transport and Remediation of Subsurface Contaminants. Colloidal, Interfacial, and Surfactant Phenomena. ACS Symposium Series No. 491. Edited by David A. Sabatini and Robert C. Knox (University of Oklahoma). American Chemical Society: Washington, DC. 1992. xii + 252 pp. $69.95. ISBN 0-8412-2223-1.

This book was developed from a symposium sponsored by the Division of Colloid and Surface Chemistry of the ACS at the 65th Annual Colloid and Surface Science Symposium held in Norman, OK, June 17–19, 1991. After a 1-page preface by the editors and an overview introduction, it contains 18 chapters in typescript form organized under the following headings: Colloids; Inorganic Compounds; Surfactants; Organic Compounds; and Review and Future Directions. There are indexes of authors, their affiliations, and subjects.

Computer Modeling of Chemical Reactions in Enzymes and Solutions. By Arieh Warshel (University of Southern California). John Wiley and Sons, Inc.: New York, Chichester, Brisbane, Toronto, and Singapore. 1991. xiv + 236 pp. $90.00. ISBN 0-471-53395-5.

This book is a unique attempt to describe in one volume the basic concepts needed to characterize chemical reactions in solution and in enzymes and also how to apply them in a useful way. In it, the reader is led in a focused and hands-on fashion from fundamental principles to practical experience.

The first chapter deals with the fundamental descriptions of chemical bonding and the next two chapters with specific quantum chemical methods for calculating potential energy surfaces and rates of chemical reaction in gas phase and in solution. The fourth and fifth chapters present the basic concepts required to describe chemical reactions in proteins, including a discussion of the types of force fields, energy minimization schemes, and molecularly dynamic simulations to be used. The central electrostatic model used throughout this book for the effect of the protein environment on chemical reaction pathways, based on the Langvin dipole formalism, is also described. Chapters 6, 7, and 8 present three specific examples of studies of enzyme reactions: lysozyme (Chapter 6); serine proteases (Chapter 7); and two metalloenzymes, staphylococcal nuclease and carbonic anhydrase (Chapter 8). The book's final chapter (Chapter 9) presents the author's point of view of how "enzymes really work".

The book is written with a distinct and clearly stated point of view. In fact, the material presented is essentially a systematic and useful description of the methods of choice of the author and the specific applications made of them during his many years of research in the field of modeling chemical reactions in solution and in enzymes. This perspective limits the scope of the book in the following ways: (i) an empirical valence bond formalism is the quantum mechanical method of choice, and it is the main method described and elaborated; (ii) the types of reactions considered are limited to those in which charge transfer occurs; (iii) the environmental effects of solvent and protein are assumed to be mainly electrostatic, and the specific models developed to describe them are limited to these types of interactions; and (iv) the final chapter on how "Enzymes Really Work" is biased toward the author's firm conviction that electrostatic stabilization of charge separation is the key to the catalytic power of enzymes.

With these limitations in mind, the material presented in this book is described and taught in a very effective and useful fashion. Thus, it can serve, as the author intended, as a one-volume primer for a novice in this field.

The success of the author in achieving this main goal is the result of three unique features of the book: (i) it is self-contained and focused, presenting only the concepts that are necessary for describing the particular type of chemical reactions chosen and for evaluating the electrostatic effect of the protein and solvent on them; (ii) throughout each chapter are well-considered exercises together with their solutions that teach and reinforce the basic concepts and the use of them for specific applications; and (iii) at the end of each chapter computer programs are given, some to be used to solve the problems in the text and some to better understand the principles presented in it.

Dr. Warshel's extensive experience has allowed him to choose the most relevant concepts to present and to select the hands-on exercises and computer programs that will lead to rapid comprehension for the conscientious reader.

Gilda H. Loew, *Molecular Research Institute*

Polymer Monographs. Volume 10. Polyacetylene and Polyarylenes. By I. V. Krivoshei and V. M. Skorobogatov (Khar'kov State University, USSR). Gordon and Breach Science Publishers: Philadelphia. 1991. 402 pp. $96.00. ISBN 2-88124-756-3.

This monograph presents an overview of the field of electronically conducting polymers based on conjugated polymer systems. It will serve as an excellent informative resource for chemically oriented scientists as they enter into this highly interdisciplinary field and as a useful compendium of information for researchers actively investigating conducting polymers. The inclusion of 1394 references, with their titles, gives the reader direct access to many of the vast number of papers that are distributed throughout the primary literature up to about 1988. While the authors apologize for any citation oversights in their Introduction, they have done a highly commendable job.

After a general introduction to the field, Chapters 3 and 4 review the synthesis of the major conjugated polymer families that have been studied to date. These include Polyacetylenes, Polyphenylenes, Polypyrroles, Polythiophenes, Poly(arylene vinylenes), Poly(phenylene sulfide), and Polyanilines. Structure to property comparisons are given where possible along with the benefits and deficits of the various synthetic methods. Chapter 5 describes the chemistry of redox doping of conjugated polymers, including the generally accepted mechanisms of doping with iodine and other halogens, arsenic and antimony halides, metal halides, protonic acids, nitrosonium salts, reducing metals, and electrochemical doping. Chapter 6 gives a short overview of research into structure and morphology. Due to the distinct differences between each polymer, correlations are not (as they should not be) made. Chapter 7 describes the nature of the electronic states of the doped polymers in relatively simplistic terms. Chapters 8 and 9 center on the electrical properties of doped and undoped polyacetylene in both its as-made and oriented states and its substituted derivatives. This framework will serve as a useful introduction to concepts that can be extended to other polymers. Chapter 10 presents an overview of electronic properties and mechanisms of electrical transport correlating both theoretical and experimental results.

This is an easily readable book for those familiar with the field and will serve as an excellent text for bringing new graduate students and researchers up to speed.

John R. Reynolds, *University of Florida*