Additions and Corrections

Mechanistic Variations and Rate Effects of Alkoxy and Thioalkoxy Substitutents on Anionic Oxy-Cope Rearrangements [*J. Am. Chem. Soc.* **1999**, *121*, 11880−11884]. FREDRIK HAEFFNER, K. N. HOUK,* Y. RAVINDRA REDDY, AND LEO A. PAQUETTE*

Page 11883: Figure 10 was a duplicate of Figure 8. The correct figure and caption appear below.

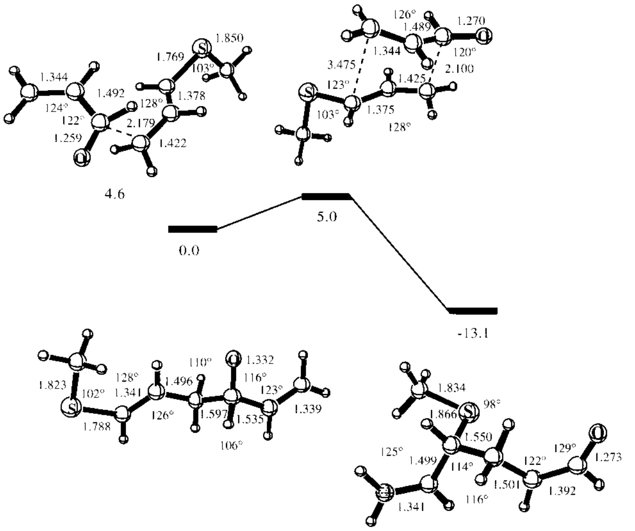

Figure 10. Stationary points located for the anionic oxy-Cope rearrangement with a thiomethoxy substituent at C6 and geometry optimized with B3LYP/6-31+G*. Zero-point energies are included.

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Will an η^3-Si_3H_3 Ligand Form Sandwich Compounds with Main Group Elements? [*J. Am. Chem. Soc.* **2000**, *122*, 1725−1728]. GANTASALA N. SRINIVAS, TRACY P. HAMILTON, ELUVATHINGAL D. JEMMIS, MICHAEL L. MCKEE, AND KOOP LAMMERTSMA*

Page 1727, Table 1: The last column of this table, the relative energies for structures **7**-B$^+$ through **10**, was omitted in printing. This portion of the table is reprinted below.

Table 1. Total (in au), Zero Point (ZPE, in kcal/mol), and Relative Energies (in kcal/mol).[a]

structure	level	total energy	ZPE	NIF	rel energy
7-B$^+$, C_s	HF/A	−1761.24106	39.09	0	−8.2
	B3LYP/A	−1765.02060	35.68	0	−7.8
	B3LYP/B	−1765.18445			−8.5
	MP2/B	−1762.10633			−2.6
8-B$^+$, C_2	HF/A	−1761.28670	39.35	0	−36.6
	B3LYP/A	−1765.05637	36.21	0	−29.7
	B3LYP/B	−1765.22032			−30.5
	MP2/B	−1762.13449			−20.0
5-Be, D_{3h}	HF/A	−1751.38578	37.05	4	87.8
	B3LYP/A	−1755.15389	33.45	2	59.0
7-Be, C_s	HF/A	−1751.41728	36.46	0	67.5
	B3LYP/A	−1755.16760	33.62	0	50.6
	B3LYP/B	−1755.32762			47.5
	MP2/B	−1752.24745			47.3
8-Be, C_2	HF/A	−1751.45253	36.72	0	45.7
	B3LYP/A	−1755.19557	34.02	0	33.4
	B3LYP/B	−1755.35525			30.5
	MP2/B	−1752.26880			34.1
9, C_{2v}	HF/A	−1751.52868	39.05	0	0.0
	B3LYP/A	−1755.25142	35.69	0	0.0
	B3LYP/B	−1755.40648			0.0
	MP2/B	−1752.32655			0.0
10, C_1	HF/A	−1751.35420	35.98	0	106.7
	B3LYP/A	−1755.17066	33.83	0	48.9
	B3LYP/B	−1755.34404			37.4

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Book Reviews

A to Z of Thermodynamics. By Pierre Perrot (Université des sciences et technologies de Lille). Oxford University Press: Oxford, New York, and Tokyo. 1998. vi + 329 pp. $65.00. ISBN 0-19-856556-9 (Hardback).

Thermodynamics is a fascinating subject with a logical and mathematical structure that sometimes presents difficulties in teaching. Precise statements of the thermodynamic laws can be abstract, and translating these laws into application requires the definition of many secondary quantities such as the fugacity. Thus, there is a large specialized vocabulary associated with this subject. *A to Z of Thermodynamics* is an interesting and novel contribution to the teaching literature in the field of thermodynamics. This little book is presented as a dictionary of thermodynamic terms. In many cases the author also presents brief histories, etymological developments, and biographical sketches. Professor Perrot's stated goals are to produce a rigorous treatment of thermodynamic principles that serves to "demythify" the topic. The author cites 20 years of experience in teaching thermodynamics and is not reluctant to share his personal perspective from time to time throughout the book. It appears that this book is intended as an alternate or a supplement to classical treatments of thermodynamics that the author regards as highly mathematical. It is intended to be accessible to first-year undergraduates, but it is not a conventional textbook in that there are no numerical examples, homework problems, or references to the recent literature.

The scope of this volume is quite broad. Entries range from the essential (first law, second law, equilibrium, etc.) to the obscure (e.g., entropology, renversable) to the outdated and discredited (phlogiston). The book covers concepts from both classical and statistical thermodynamics. In addition, there are numerous entries from related fields such as mathematics, chemical kinetics, and materials science. Thus, for example, the reader may obtain a short perspective on the Kronecker delta, integrating factors, activation energy, catalysis, the Young's modulus, and magnetic susceptibility. Thermodynamics has a very strong logical structure and many interesting philosophical consequences as a result of the second law. The author therefore provides selected entries dealing with logic and philosophy (e.g., paradox, paradigm, and mention of the philosophers Thomas Kuhn and Karl Popper).

The author notes that the number of applications of thermodynamics is so large that comprehensive treatment cannot be given in a single volume. Thus, educators will be interested in the limits of this book. The author discusses applications such as refrigeration, as well as the Brayton, Otto, and Rankine power cycles. There is a good, concise treatment of certain pure component and multicomponent phase diagrams and the definitions associated with those phase diagrams.

However, there is no discussion of the modeling of phase equilibrium, which is the subject of most of the current research in macroscopic thermodynamics. Thus, while the author defines the activity coefficient and the fugacity coefficient and introduces the equation of state concept, the discussion of models for solution phase behavior are limited to elementary models, such as Raoult's law, and the van der Waals equation. Well-accepted engineering models such as the Wilson equation, the UNIFAC model, and cubic equations of state such as the Peng−Robinson are not discussed in this book. Likewise, current topics in implementation of statistical thermodynamics are not covered.

This book is valuable, informative, and even entertaining as a reference book for educators and researchers and as a supplemental reference for advanced undergraduate and graduate students. Just as one would not endeavor to teach something as intricate as an entire language solely through the use of a dictionary, it is not recommended that any educator attempt to teach the intricacies of thermodynamics solely through the use of this volume. However, teachers and learners should profit by combining the novel approach of this book with a more standard textbook on thermodynamics.

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Advances in Metal−Organic Chemistry. Volume 6. Edited by Lanny S. Liebeskind (Emory University). JAI Press: Stamford, CT. 1998. 229 pp. $109.50. ISBN 0-7623-0206-2.

Volume 6 of this series is comprised of five monographs on varied topics in preparative organometallic chemistry. In the first, Echavarren and Castaño review the synthesis and reactivity of five- and six-membered oxa/azametallacycles of nickel. Several methods are detailed for their preparation, although the discussion focuses heavily on stoichiometric, decarbonylated complexes formed by treating cyclic anhydrides with a source of nickel(0). The reactions described for the resultant nickel(II) species (carbonylations, migratory insertions, carboxylations, eliminations) parallel those observed for related palladium(II) and platinum(II) complexes, although the beryllium chloride-mediated ring contraction of nickel-containing furanones and the manganese-promoted homologation of alkyl iodides with a bipyridyl-ligated nickelacycle are fascinating exceptions.

The second chapter deals with transition metal-catalyzed manipulations of the norbornadiene skeleton. Lautens and Tam do an excellent job presenting both their own results and those of others in the context of generating useful synthetic intermediates from a common structural prototype. Catalysis is separated into those processes that engage either an isolated olefin or both π-bonds of the strained ring system. When involving alkenes and alkynes, the latter are formally $[2\pi + 2\pi + 2\pi]$ cycloadditions and represent homologous Diels−Alder reactions. Nickel and cobalt complexes catalyze both inter- and intramolecular variants. An extensive evaluation of substituent effects, regioselection, and norbornadienes that participate in formal $[2\pi + 2\pi]$ cycloadditions underlies the mechanistic scenarios proposed. A section on asymmetric catalysis is also included.

Chapter 3 returns to a discussion of stoichiometric metallacycle chemistry, in particular, cyclometalated complexes of palladium in which the metal is σ-bonded to an sp^2 carbon and stabilized by a dative bond emanating from an internal Lewis base. Spencer and Pfeffer concentrate on work published from their laboratory over the past decade in which various substituted alkynes (and certain dienes/allenes) insert into the metal−carbon bond to afford ring-expanded complexes. Induced reductive elimination of a metal fragment subsequently generates substituted carbocycles and heterocyclic salts. The discussion is well-written and guides the reader through sections on scope, mechanism, and separate treatments of mono- and di-insertion complexes as well as their demetalated products. Plausible, although often speculative, mechanistic schemes are offered throughout, as are selected experimental details.

The chemistry of π-allyl and dienyl complexes of molybdenum (and to a lesser extent tungsten) are reviewed by Liu in Chapter 4. The account is an expanded version of a 1990 review by Pearson, although it is difficult to regard it as timely because no reference is more recent than 1993. Methods of reagent preparation and manipulation are reiterated, while the remainder of the article describes their utility in multistep, stereoselective synthesis. The dense and overly intricate reaction schemes make for slow reading, perhaps too slow to capture the attention of a general audience.

Suzuki biaryl syntheses are reviewed by Miyaura in the final chapter. Methods to prepare, analyze, and purify aryl boronic acids/boronates are covered, as is a clear and informative description of mechanistic work aimed at identifying species competent to participate in catalyzed cross-couplings with organic electrophiles. Individual sections on the effects of catalyst, base, and the scope of cross-coupling partners are followed by a particularly valuable discussion of common byproducts and competing side-reactions. The review concludes with a tabular survey of unsymmetrical biaryls synthesized using Suzuki protocols.

Overall, this book is a must for library archives and, while certain sections are quite specialized, those that are not make it a great addition to a personal collection.

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Molecular and Supramolecular Photochemistry. Volume 3. Organic Molecular Photochemistry. Edited by V. Ramamurthy (Tulane University) and Kirk S. Schanze (University of Florida). Marcel Dekker: New York and Basel. 1999. ix + 344 pp. $175. ISBN 0-8247-6606-7.

This book is devoted to supramolecular (Chapters 1 and 6) and molecular (Chapters 2−5) aspects of photochemistry. It will be useful as a reference guide for the initiated or as an introduction for those entering the field. Each chapter provides a historical, critical review with extensive references through 1997 and a few references to mid-1998. The index is adequate to find general topics.

Chapter 1, by Y. Ito, presents examples of, as well as the terminology and methodology associated with, the photochemistry of mixed molecular crystals. A distinction is made between mixed crystals and either crystalline molecular compounds or mechanical mixtures, and interesting designs for solid state irradiations are provided. Chapter 2, by S. R. L. Everitt and Y. Inoue, is devoted to asymmetric photochemical reactions in solution. It discusses enantiomeric and diasteromeric selectivity in unimolecular and bimolecular reactions, including those induced by circularly polarized radiation. Cis−trans isomerizations in triplet (Chapter 3, by T. Arai) and singlet states (Chapter 4 by V. J. Rao) are relatively mature subjects that have been reviewed extensively. The approaches in these chapters are more physical than in the others. Direct and sensitized processes and the basis for "one- and two-way" isomerizations are covered. Cleavage reactions of benzyl−heteroatom bonds are discussed in detail in Chapter 5, by S. A. Fleming and J. A. Pincock. Experimental variables (the chromophore, solvent, excited state multiplicity, energy of the radical and ion pair intermediates, substituents, and leaving groups), as well as theoretical aspects of the bond cleavage process, are covered in individual sections. Photophysical probes and the organized assemblies in which they have been studied are reviewed in Chapter 6, by K. Bhattacharyya. They are discussed separately first and then together. The emphasis is largely on lyotropic assemblies (i.e., those containing surfactants) and probes that respond to polarity changes.

Overall, this is a very useful and relatively up-to-date book. The chapters are well-written and there are extensive illustrations. My one complaint is that $175 is ridiculous for a book with 344 pages and no color illustrations or photographs. I will not recommend it to my library at that price.

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