

the mechanism proceeds via a proton transfer rather than a hydride shift.

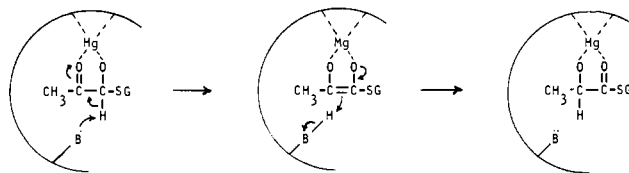
In a typical experiment a stock solution was prepared by dissolving a mixture of 48 mg (0.47 mmol) of methylglyoxal,⁸ 146 mg (0.47 mmol) of glutathione, and 12 mg of DSS (NMR internal chemical shift and integration reference, sodium 4,4-dimethyl-4-silapentanesulfonate) in 6 ml of ²H₂O (99.7%). The pH of this stock solution was immediately adjusted to 7.01 (p²H 7.41) by the addition of 203 mg of anhydrous K₂HPO₄ (buffer component) and equilibrated at 21 °C for 30 min before 0.68-ml aliquots were transferred to 5-mm NMR tubes. Then each tube was equilibrated at its designated experimental temperature (25 or 35 °C) for 5 min before 50 units of glyoxalase I (5 μl, ²H₂O solution)⁹ was added and the solution incubated for 5 min in its respective bath. All NMR tubes were then placed in the 25 °C bath and 4 units of glyoxalase II (20 μl, ²H₂O solution)¹⁰ was added to hydrolyze the thiol ester **3**. After 20 min, the NMR tubes were cooled to 0 °C. As soon as possible (within 5–20 min) the NMR spectrum of each sample was recorded (probe at 28 °C) at 100 MHz using a Jeol Model JNM-PS-FT-100 fast Fourier transform NMR spectrometer (25 transients using a 90° pulse, 8K data points, 625 Hz spectral width). The NMR chemical shifts are reproducible to ±0.003 ppm. In all cases identical control reactions were carried out side-by-side with the above reaction tubes except that glyoxalase I was omitted.

Figure 1 displays the NMR spectrum of each reaction (spectra A and B) along with its control (spectra A' and B'). To facilitate unequivocal assignments, after the above spectra were obtained various amounts of authentic lactic acid (1.315 ppm (3 H, d, *J* = 6.9 Hz, peaks at 1.279 and 1.348 ppm), 4.098 ppm (1 H, q, *J* = 6.9 Hz)) and [2-²H]lactic acid (1.306 ppm (3 H, apparent s)) were added to each NMR tube and the spectra (not shown) determined again.¹¹ By this procedure, it was clearly demonstrated that the spectra in Figure 1 contained mixtures of lactic acid and [2-²H]lactic acid (as well as glutathione). The percent incorporation (ca. 15% at 25 °C and 22% at 35 °C) was estimated by measuring (planimetry) the area of the methyl doublet and singlet due to the lactic acid mixture and correcting for any possible lactic acid formation in the control. Using the DSS in each spectrum as an integration reference, it is also clear that the relative area of the methyl singlet at 1.306 ppm due to [2-²H]lactic acid increased as the temperature of the enzyme reaction was raised, and the relative areas of the methyl doublet centered at 1.315 ppm and the tertiary hydrogen quartet centered at 4.098 ppm of lactic acid decreased. It should also be noted that sufficient enzyme was used since the methyl singlet at 2.317 ppm and the tertiary hydrogen singlet at 5.584 ppm from the α-ketohemithiol acetal **2** present in each control spectrum is absent in the corresponding reaction spectrum. Other important control experiments established that neither *S*-lactoylglutathione (**3**) nor lactic acid (**4**) incorporates deuterium when exposed to these reaction conditions.

In addition, the fast enediol-proton transfer mechanism for the mode of action of glyoxalase I was unequivocally confirmed by the following experiments. When either phenylglyoxal, also a substrate for this enzyme system, in ²H₂O or [1-²H]-phenylglyoxal¹² in H₂O was exposed to the experimental enzyme conditions previously discussed, mixtures of mandelic acid and [2-²H]mandelic acid (determined by NMR and MS) were obtained. Finally, all model systems that we have examined, as would be expected, result in nearly quantitative incorporation.¹³

Clearly, the mechanism of glyoxalase I proceeds via an enediol-proton transfer rather than a 1,2-hydride shift. The low incorporation of solvent protons indicates a fast shielded proton transfer that is occurring at a highly protected active site. Such a mechanism is depicted where a substrate is shown

chelated to a Mg²⁺ ion at the active site^{2,15} and the B group represents a basic amino acid residue that is part of the active site of glyoxalase I.¹⁶



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References and Notes

- (1) This investigation was supported primarily by PHS Research Grant No. CA 12984 from the National Cancer Institute.
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- (7) I. A. Rose and E. L. O'Connell, *J. Biol. Chem.*, **236**, 3086 (1961).
- (8) The methylglyoxal was prepared by diluting a 40% aqueous solution with saturated NaHCO₃-NaCl and extracting with Et₂O. The organic layer was dried (Na₂SO₄) and concentrated in vacuo, and the residue distilled at 55–63 °C (95 Torr). This fraction was lyophilized for 20 h, deuterium oxide added, and, after a few hours, lyophilized again for 20 h. The NMR (100 MHz, D₂O) spectrum of this sample (singlets at -2.478 and -3.406 ppm relative to HOD) suggests a 1:1 mixture of the mono- and dideuterate of methylglyoxal.
- (9) Glyoxalase I (grade X from yeast, lyophilized powder containing 95% protein and 5% citrate buffer salts) is available from Sigma Chemical Co. Just prior to the experiment, 0.244 mg (209 units) was dissolved in 21 μl of D₂O. One unit will convert 1.0 μmol of substrate to product per minute at pH 6.6 at 25 °C.
- (10) Glyoxalase II (from beef liver, lyophilized powder containing 80% protein and 20% phosphate-citrate buffer salts) is available from Sigma Chemical Co. Just prior to use, 2.41 mg (20 units) was dissolved in 100 μl of D₂O. One unit will hydrolyze 1.0 μmol of substrate to product per minute at pH 7.4 at 25 °C.
- (11) The authentic samples were prepared by the NaBH₄ and NaB²H₄ reduction of pyruvic acid, respectively.
- (12) Prepared by selenous acid oxidation of [2-³H]acetophenone by the method of (a) D. L. Vander Jagt and L.-P.B. Han, *Biochemistry*, **12**, 5161 (1973); (b) H. L. Riley, J. F. Morley, and N. A. C. Friend, *J. Chem. Soc.*, 1875 (1932).
- (13) Using these techniques we have found that all model catalysts, general bases^{2,14} as well as Franzen's (V. Franzen, *Chem. Ber.*, **88**, 1361 (1955)), that mimic this enzyme reaction result in the incorporation of deuterium into the α-positions of lactic and mandelic acid. In all of these reactions the extent of incorporation is ca. 100% (within the limits of detection, purity of ²H₂O, and possible isotope effects).
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- (17) Taken in part from the Ph.D. Thesis of A.M.D. that was submitted to the Graduate School, Rutgers University, Oct 1975.

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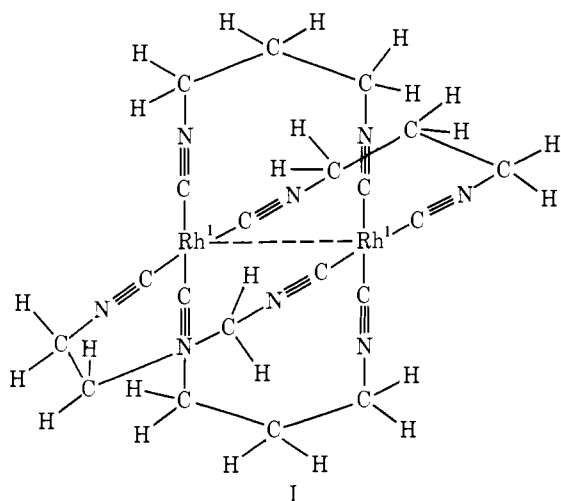
Oligomerization and Two-Center Oxidative Addition Reactions of a Dimeric Rhodium(I) Complex

Sir:

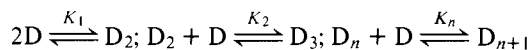
We have shown previously that cationic arylisocyanide complexes of rhodium(I) aggregate in solution through for-

mation of metal-metal bonds.¹ The chemical behavior of these oligomeric species should be quite interesting, as the opportunity for two-center oxidative addition exists. In order to explore this possibility in a simple case, we have synthesized and characterized a dimeric Rh(I) complex containing four 1,3-diisocyanopropane (bridge) ligands. We have found that this dimer aggregates still further in solution to form higher oligomers, and that it undergoes two-center oxidative addition reactions with several substrates.

The chloride salt of the dimer, $[\text{Rh}_2(\text{bridge})_4]\text{Cl}_2$, was obtained by addition of bridge to a stoichiometric amount of $[\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ in chloroform solution. A blue precipitate was isolated and converted to a purple tetraphenylborate salt by metathesis in methanol. The BPh_4^- salt was recrystallized from acetonitrile.³ The infrared spectrum of a KBr pellet of the dimer exhibits one $\text{C}\equiv\text{N}$ stretch at 2172 cm^{-1} . There are no bands in the IR attributable to bridging isocyanides. The ^1H NMR spectrum of the dimer in Me_2SO displays broad singlets at 3.7 (terminal CH_2) and 1.9 ppm (central CH_2). As steric considerations rule out bidentate coordination by bridge at a single Rh(I) center, we assume that the structure of $[\text{Rh}_2(\text{bridge})_4]^{2+}$ is as shown in I.



The concentration dependence of the absorption spectrum of $[\text{Rh}_2(\text{bridge})_4]\text{Cl}_2$ in methanol has been studied. Absorptions at 318, 342, and 555 nm are the only bands observed at low concentrations of $[\text{Rh}_2(\text{bridge})_4]\text{Cl}_2$, and are logically assigned to the dimer $[\text{Rh}_2(\text{bridge})_4]^{2+}$, or D, itself. This assignment is supported by the observation that absorptions owing to $[\text{Rh}(\text{CNPh})_4]_2^{2+}$ and $\text{Rh}(\text{CNPh})_4^+$ are reported, respectively, at 568 and 411 nm in acetonitrile solution.¹ As the solution becomes increasingly concentrated, principal low energy bands appear at 778, 990, 1140, and 1735 nm. The concentration dependence of the absorption spectrum may be interpreted in terms of the following equilibria:



A plot of A_{555} vs. $(A_{778})^{1/2}$ is a straight line, as is A_{555} vs. $(A_{990})^{1/3}$, indicating that the bands at 778 and 990 nm be assigned to tetrameric and hexameric Rh(I) species (analysis of these data yields: K_1 5×10^2 ; K_2 $3 \times 10^2\text{ M}^{-1}$). The bands at 1140 and 1735 nm are present only in the most concentrated solutions, and are logically attributable to higher oligomers ($n > 3$).

The observed spectroscopic behavior of the $[\text{Rh}_2(\text{bridge})_4]^{2+}$ oligomers accords with simple MO theory. The 555-nm absorption may be assigned to the fully allowed $1a_{2u} \rightarrow 2a_{1g}$ transition, by analogy to the 568-nm band observed¹ in $[\text{Rh}(\text{CNPh})_4]_2^{2+}$. Similar analysis of the tetrameric Rh(I)

units suggests that the 778 nm band be assigned to $2a_{2u} \rightarrow 3a_{1g}$, and the hexameric Rh(I) absorption at 990 nm be assigned to $3a_{2u} \rightarrow 4a_{1g}$. The band at 1140 nm is attributed to $4a_{2u} \rightarrow 5a_{1g}$ in an octameric species ($n = 4$).⁴

Upon addition of I_2 to dilute acetonitrile solutions of $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2$, oxidation to a diiodo adduct, $[\text{Rh}_2(\text{bridge})_4\text{I}_2]^{2+}$, takes place immediately.⁵ The product was isolated as a red triiodide salt.⁶ This oxidative addition product presumably contains two Rh(II)-I units connected by a single metal-metal bond. In terms of the MO formulation of the metal-metal interaction in $[\text{Rh}_2(\text{bridge})_4]^{2+}$, the two electrons in the $1a_{2u}$ orbital are transferred to the two I atoms to give two I^- groups and a Rh(II)-Rh(II) bond ($1a_{1g}$).² The infrared spectrum of a KBr pellet of $[\text{Rh}_2(\text{bridge})_4\text{I}_2](\text{I}_3)_2$ exhibits a single $\text{C}\equiv\text{N}$ stretching frequency at 2227 cm^{-1} , indicating trans I-Rh(II)-Rh(II)-I stereochemistry, as would be expected. The higher $\text{C}\equiv\text{N}$ frequency observed for $[\text{Rh}_2(\text{bridge})_4\text{I}_2]^{2+}$ as compared to that for $[\text{Rh}_2(\text{bridge})_4]^{2+}$ is consistent with the Rh(II) formulation of the diiodo adducts.

Similar chemistry was observed when Br_2 was used as the oxidizing agent, yielding $[\text{Rh}_2(\text{bridge})_4\text{Br}_2](\text{Br}_3)_2$.⁷ Interestingly, the Br_2 oxidative addition is thermally reversible in either acetonitrile or DMF-water solutions, and blue $[\text{Rh}_2(\text{bridge})_4]^{2+}$ may be recovered or may be reoxidized with the addition of further bromine. Methyl iodide also may be added to $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2$ in acetonitrile solution, yielding a yellow solution containing *trans*- $[\text{Rh}_2(\text{bridge})_4(\text{CH}_3)(\text{I})]^{2+}$. The CH_3I adduct was isolated as reddish brown crystals of a tetraphenylborate salt by slow addition of diethyl ether.⁸ The infrared spectrum of the *trans*- $[\text{Rh}_2(\text{bridge})_4(\text{CH}_3)(\text{I})]^{2+}$ exhibits $\text{C}\equiv\text{N}$ stretches at 2183 and 2212 cm^{-1} , which is consistent with the structural formulation. The ^1H NMR spectrum of the adduct exhibits broad singlets at 4.0, 2.1, and 1.3 ppm. As the resonance at 1.3 ppm does not correspond to any feature in unoxidized $[\text{Rh}_2(\text{bridge})_4]^{2+}$, it is therefore attributed to a methyl group bonded directly to rhodium. The observation of a 1-2 Hz splitting of the 1.3 ppm resonance owing to coupling to the ^{103}Rh nucleus confirms the assignment. Integration of the spectrum indicates that the compound contains only one methyl group per dimer, which is consistent with the proposed *trans*- $[\text{Rh}_2(\text{bridge})_4(\text{CH}_3)(\text{I})]^{2+}$ structure.

The electronic absorption spectrum of $[\text{Rh}_2(\text{bridge})_4\text{I}_2]^{2+}$ in acetonitrile solution exhibits intense bands at 465 (ϵ 23 200) and 397 nm (ϵ 62 000). The very intense 397-nm band is logically attributable to the $\sigma \rightarrow \sigma^*$ transition ($1a_{1g} \rightarrow 1a_{2u}$) in the Rh(II)-Rh(II) single-bonded species. Similarly intense $\sigma \rightarrow \sigma^*$ bands in this energy region have been observed for $\text{Mn}_2(\text{CO})_{10}$ as well as numerous other $d^7 - d^7$ metal-metal bonded complexes.⁹ The band at 465 nm could be due to one or more $d\pi \rightarrow \sigma^*(1a_{2u})$ transitions, again by analogy to $\text{Mn}_2(\text{CO})_{10}$. Intense bands at 438 and 373 nm in $[\text{Rh}_2(\text{bridge})_4\text{Br}_2]^{2+}$ and 470 and 397 nm in $[\text{Rh}_2(\text{bridge})_4(\text{CH}_3)(\text{I})]^{2+}$ (acetonitrile solution) presumably represent the $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions, respectively, in these adducts.¹⁰ It is reasonable to expect that the $1a_{1g}$ orbital will be delocalized to some extent over the X-Rh-Rh-X unit, and as a result the $1a_{1g} \rightarrow 1a_{2u}$ transitions will possess some X \rightarrow Rh charge transfer character. The small blue shift in the position of $1a_{1g} \rightarrow 1a_{2u}$ in the $[\text{Rh}_2(\text{bridge})_4\text{Br}_2]^{2+}$ complex is consistent with the proposed fractional charge transfer character.

The mechanism of oxidative addition to $[\text{Rh}_2(\text{bridge})_4]^{2+}$ is under study. We have found that the rate of $\text{C}_2\text{H}_5\text{I}$ addition to $[\text{Rh}_2(\text{bridge})_4]^{2+}$ is comparable to that of CH_3I , and that CH_3OTs reacts extremely slowly. We suspect from these results that the initial step involves Rh(I) attack on a heavy atom in the substrate, yielding $[\text{Rh}_2(\text{bridge})_4\text{I}]^{2+}$ and methyl radical

in the case of CH_3I . A full report of our kinetic and mechanistic studies will be presented in a subsequent paper.

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References and Notes

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- (2) This complex was prepared by a standard method: J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
- (3) Anal. Calcd for $[\text{Rh}_2(\text{bridge})_4](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$: C, 66.37; H, 5.41; N, 10.75. Found: C, 65.59; H, 5.49; N, 10.24.
- (4) According to simple Hückel theory, the tetramer, hexamer, and octamer transition energies are given by: $E_{D_2} = E_D + \beta$; $E_{D_3} = E_D + 2^{1/2}\beta$; $E_{D_4} = E_D + [(5^{1/2} + 1)/2]\beta$; $E_D = E(1a_{2u} \rightarrow 2a_{1g})$ and $\beta = \beta_{1a_{2u}} + \beta_{2a_{1g}}$. Theory and experiment accord closely for $\beta = -5500 \text{ cm}^{-1}$: $E_{D_2}(\text{calcd}) = 12\,500$, $E_{D_2}(\text{obsd}) = 12\,820$; $E_{D_3}(\text{calcd}) = 10\,220$, $E_{D_3}(\text{obsd}) = 10\,080$, $E_{D_4}(\text{calcd}) = 9\,100$, $E_{D_4}(\text{obsd}) = 8\,770 \text{ cm}^{-1}$. The broad absorption system centered at about 1735 nm (5760 cm^{-1}) probably represents overlapping bands owing to oligomers with $n > 4$. For $n = \infty$, the calculated limit is $E_D + 2\beta$, or 7000 cm^{-1} .
- (5) When the I_2 oxidation was performed at high concentrations of $[\text{Rh}_2(\text{bridge})_4]^{2+}$, a green intermediate species was observed. The concentration of this intermediate was maximal for the stoichiometric ratio $2[\text{Rh}_2(\text{bridge})_4]^{2+}:\text{I}_2$. Furthermore, the concentration of the intermediate was found to be proportional to $[[\text{Rh}_2(\text{bridge})_4]^{2+}]^2$. The green species is formulated as $[\text{I-D-D-I}]^{4+}$.
- (6) Anal. Calcd for $[\text{Rh}_2(\text{bridge})_4\text{I}_2](\text{I}_3)_2$: C, 15.0; H, 1.50; N, 7.05; I, 63.5. Found: C, 15.8; H, 1.65; N, 7.09; I, 62.2.
- (7) Anal. Calcd for $[\text{Rh}_2(\text{bridge})_4\text{Br}_2](\text{Br}_3)_2$: C, 19.67; H, 1.98; N, 9.17. Found: C, 19.97; H, 1.93; N, 9.06.
- (8) Anal. Calcd for $[\text{Rh}_2(\text{bridge})_4(\text{CH}_3\text{I})](\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$: C, 60.66; H, 5.09; N, 9.69. Found: C, 58.74; H, 5.08; N, 9.29.
- (9) R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975).
- (10) Complexes of the type $[\text{Rh}_2(\text{CNR})_6\text{X}_2]^{2+}$ obtained by mixing solutions of $[\text{Rh}(\text{CNR})_4]^+$ and *trans*- $[\text{Rh}(\text{CNR})_4\text{X}_2]^+$ (R = alkyl; X = halide) have been reported [A. L. Balch and M. M. Olmstead, *J. Am. Chem. Soc.*, **98**, 2354 (1976)]. These adducts exhibit electronic spectral properties that are very similar to those of analogous $[\text{Rh}_2(\text{bridge})_4\text{X}_2]^{2+}$ complexes. Of the two structures for $[\text{Rh}_2(\text{CNR})_6\text{X}_2]^{2+}$ species suggested by Balch and Olmstead, our results favor the one containing a direct Rh(II)-Rh(II) bond in preference to the Rh-X-Rh-X alignment. Balch and Olmstead also argued that their spectral data were more consistent with a Rh(II)-Rh(II) bonded species.

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Book Reviews*

Aldehydes—Photometric Analysis. Volume 3. By EUGENE SAWICKI and CAROLE R. SAWICKI. Academic Press, New York and London, 1976. xiv + 341 pp. \$26.75.

Volumes 1 and 2 of this work, which is a part of the series "The Analysis of Organic Materials" edited by Belcher and Anderson, appeared last year and have been reviewed; four more volumes are promised. This work is really of more general applicability than its title suggests, for its concern is with analysis of other types of substances, which can be converted to aldehydes in one way or another. The authors anticipated future development of the subject by including discussions of other reactions that give rise to aldehydes, even when no analytical application has yet been published.

More than 30 aldehydes, including acetaldehyde, aldoses, aldosterone, and various amino aldehydes, are covered in this volume, but the actual emphasis is on the substances from which they can be formed. Under acetaldehyde, for example, are considered acetals, 2-alkenes, ethylene oxide, several glycols, phenothiazines, pyruvic acid, etc. The aldehydes are taken up in alphabetical order, so one should have the full set, but this volume like the earlier ones, is separately indexed. It looks very useful.

Concise Etymological Dictionary of Chemistry. By S. C. BEVAN, S. J. GREGG, and A. ROSSEINSKY. Applied Science Publishers, Barking, Essex, 1976. ix + 140 pp. £7.00.

This is a rather small book, especially in terms of the number of words defined. Nevertheless, it is adequate and promises to be very useful. Its purpose is, of course, not so much to define words as to give their origin and the roots, mostly Greek and Latin, from which they are derived. Many of these etymologies are obvious, such as "citric acid" from citrus, but such words as "eutrophication" (from Greek roots for "well" and "to nourish"), and "griseofulvin" (from Latin roots for gray and yellow) become more comprehensible when their origins are explained. An understanding of these matters can be helpful when the necessity arises to coin new terms.

It is not difficult to spot gaps in a work of this kind (hosts of natural products are omitted, on practical grounds), but they are not serious. A more important fact is that the definitions given consistently show a high level of scientific as well as etymological scholarship. There are

also occasional euphemisms of charming delicacy, as in the etymology of "viscous", which comes from the Latin for "full of bird lime". This term might be put to new use by authors wishing to dispute a referee's unkind comments, by alleging that the referee is truly viscous.

Immunology. Readings from Scientific American. Edited by F. M. BURNETT. W. H. Freeman & Co., San Francisco, Calif. 1976. vi + 275 pp. \$14.00 (hard cover); \$7.00 (soft cover).

The chapters in this book are reproductions of the authoritatively written and sumptuously illustrated articles that originally appeared in "Scientific American". Those selected date from 1955, stated by the editor to mark the beginning of modern immunology. In that year, the Salk vaccine came into general use; the advances since then "have been specially concerned with bringing immunology into step with the rest of biology . . .". The understanding of protein biosynthesis and of the role of DNA in coding information brought consideration of immunology to the molecular level during the past twenty years. There is much to interest organic and biological chemists in this book, which is especially helpful in providing broad orientation to those who are not specialists in the area.

Carbanions: Mechanistic and Isotopic Aspects. By E. BUNCEL (Queen's University). Elsevier Scientific Publishing Co., Amsterdam, The Netherlands, 1975. x + 270 pp. \$30.80.

This book is a clear and highly readable account of some of the mechanistic and structural aspects of carbanion chemistry. The presentation is at an introductory level and would be suited to undergraduate as well as graduate students. Chapter One is a very good introduction to structural considerations for carbanions and the kinetic and equilibrium acidity of carbon acids. The remaining six chapters discuss the topics of stereochemistry of carbanion reactions, tautomerism, nonclassical carbanions, enolate and homoenolate rearrangements, orbital symmetry control in carbanion rearrangements, and carbanions in reactions of organometallic compounds. Discussion of the last topic is primarily restricted to electrophilic substitution reactions of mercury, silicon, and tin. No discussion of the role of carbanions in synthesis is attempted. The book has over 700 references, up to 1973, and has an author and reasonably complete subject index.

Michael W. Rathke, Michigan State University

Book Reviews

* Unsigned book reviews are by the Book Review Editor.