Table I. Vibrations of **1** and Their IR Polarizations[a]

ν, cm^{-1}			
Raman	IR	K	$\phi_{C=C}$[b]
619	619	0.17	0°
	640	0.36	90°
	889	0.19	0°
	1004	0.27	39 ± 7°
	1161	0.27	39 ± 7°
	1184	0.38	90°
1265	1264	0.39	90°
	1274	0.38	90°
1358	1359	0.36	90°
	1446	0.24	31 ± 6°
1557[c]	1557	0.37	90°
	2856	0.29	44 ± 7°
	2904	0.36	90°
	2953	0.31	49 ± 7°

[a] Argon matrix, 12 K. [b] Absolute value of the angle between the IR transition moment and the $\pi\pi^*$ polarization direction. [c] Assigned as the C=C stretch. Calculated frequency, 1546 cm^{-1} (MNDO × 0.915), calculated $\phi_{C=C} = 90°$.

unreacted **3** and, particularly at the higher temperatures, a stable product to which we assign the structure **4**.[7] The evidence for structure **1** is (i) a 1557-cm^{-1} band in the C=C stretching region, relatively weak in the IR (Figure 1), but the strongest of all the Raman bands. The shift relative to **5** (1685 cm^{-1}) is compatible with strong double pyramidalization of **1**. (ii) A broad UV band peaking at 245 ± 15 nm, compatible with the expected lowering of the $\pi\pi^*$ excitation energy. Irradiation at 248 nm bleaches both the UV and the IR bands associated with **1** and increases the IR peaks of **4**; no additional products are detected. (iii) Above ~165 K in the neat sample, which is quite rigid, and already above ~40 K in the much less viscous argon-matrix-isolated sample, the IR bands of **1** gradually disappear and those of the known[5] 2 + 2 dimer of **1** grow; a GC comparison with an authentic sample (SE-30 column) confirms that the dimer is the chief product formed on warm-up.

A partially aligned sample of matrix-isolated **1** resulted by photoselection upon irradiation with linearly polarized 248-nm light (KrF laser) in ~70% conversion to **4**. The IR dichroic ratios, d_i, were converted to the orientation factors [$K_i = \langle\cos^2 i\rangle = d_i/(d_i + 2)$, i is the angle between the ith transition moment direction and the laboratory axis Z defined by the electric vector direction of the 248 nm light; the angular brackets indicate averaging over the molecular assembly].[8,9] The K_i values fall into three categories, separated by margins far in excess of the experimental error (about ±0.03): (i) $K = 0.17$–0.19, (ii) $K = 0.36$–0.39, (iii) $0.24 < K < 0.31$ (Table I). Assuming the 248-nm absorption to be polarized along the C=C axis x, we must have $K_x < K_y = K_z$. Since $\sum_u K_u = 1$, groups i and ii belong to mutually perpendicular transitions and are within experimental error, $K_x = 0.20$, $K_y = K_z = 0.40$.

Since in group iii we observe five lines with K_i values very different from both 0.20 and 0.40, these are not polarized along x, y, or z. The absolute values of the angles $\phi_{C=C}$ between the x axis (C=C) and the IR transition moment directions were obtained from the IR dichroic ratios and the above K_x and K_y values by standard procedures[8-10] (Table I). Both the experimental and the calculated polarization of the C=C stretching vibration are perpendicular to the C=C bond, as expected for a doubly pyramidal olefin. Molecular symmetry must be lower than C_{2v}, and C_2 is the most likely candidate that still preserves orthogonality among many of the transition moments. This is also the symmetry that was obtained from calculations. The calculated pyramidalization angle at the doubly bonded carbons was 47.8° (MM2), 43.5° (MNDO), and 40.6° (STO-3G), close to the tetrahedral value of 54.7°.

After scaling, the MNDO calculation reproduced very well the 1557-cm^{-1} frequency of the C=C stretch in **1**. A value of 1546 cm^{-1} was obtained with a multiplicative correction factor of 0.915, which fits the MNDO calculated frequencies for ethylene and tetramethylethylene to experiment. The MNDO heat of hydrogenation is 47 kcal/mol more negative than the MNDO value for **5**, suggestive of a very highly strained C=C bond.

In conclusion, the first highly reactive representative of a class of doubly pyramidalized olefins has now been directly observed. It has an unusually low-frequency C=C stretching vibration and a low-energy $\pi\pi^*$ excited state.

Acknowledgment. This work was supported by the National Science Foundation. The MNDO calculations were performed by using a computer program kindly provided by Prof. M. J. S. Dewar and modified by Dr. J. W. Downing. We are grateful to Prof. K. Morokuma and Dr. N. Koga for the STO-3G geometry optimization.

---

(7) A full characterization of this isolated product by ^{1}H and ^{13}C NMR will be reported later.

(8) Thulstrup, E. W.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 5594 and references therein. Radziszewski, J. G.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 3289.

(9) Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light. Solute Alignment by Photoselection, in Liquid Crystals, Polymers, and Membranes*; VCH Publishers: Deerfield Beach, FL, 1986.

(10) Raabe, G.; Vančik, H.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 671.

Synthesis and Characterization of High-Valent Oxo-Olefin and Oxo-Carbonyl Complexes. Crystal and Molecular Structure of $W(O)Cl_2(CH_2{=}CH_2)(PMePh_2)_2$

Fu-Min Su,[1a] Clive Cooper,[1a] Steven J. Geib,[1b]
Arnold L. Rheingold,[1b] and James M. Mayer*[1a]

Department of Chemistry, University of Washington
Seattle, Washington 98195
Department of Chemistry, University of Delaware
Newark, Delaware 19716

Received January 16, 1986

Transition-metal oxide compounds catalyze or perform a number of reactions of olefins, including oxidation, polymerization, and metathesis.[2] The active sites for most of these processes are thought to contain terminal oxo ligands. Olefin binding to the metal center has often been suggested as an important step in these reactions but has not as yet been directly observed.[3-5] For example, olefin complexes have been proposed in osmium tetraoxide oxidations,[3] in epoxidations by cytochrome P-450 enzymes,[4] and in tungsten-catalyzed metathesis reactions.[5] We wish to report the first examples of metal complexes containing both simple olefin and terminal oxo ligands. The only previous example of an oxo-olefin compound is an adduct of a very unusual olefin, tetracyanoethylene: $Mo(O)[C_2(CN)_4](S_2CNR_2)_2$.[6] We have also isolated the first carbonyl-terminal oxo complex.[7] The properties of these novel compounds indicate that π-back-bonding can be

---

(1) (a) University of Washington. (b) University of Delaware.

(2) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. Cullis, C. F.; Hucknall, D. J. *Catalysis* (*London*) **1982**, *5*, 273–307. Banks, R. L. *Ibid.* **1981**, *4*, 100–129. Clark, A. *Catal. Rev.* **1969**, *3*, 145–173.

(3) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120–3128. Hentges, S. G.; Sharpless, K. B. *Ibid.* **1980**, *102*, 4263–4265. Nugent, W. A. *J. Org. Chem.* **1980**, *45*, 4533–4534. See also: Rappé, A. K.; Goddard, W. A., III *Ibid.* **1982**, *104*, 448–456.

(4) Collman, J. P.; Brauman, J. I.; Kodadek, T.; Raybock, S. A.; Et al. *J. Am. Chem. Soc.* **1985**, *107*, 2000–2005, 4343–4345, and references therein.

(5) Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73–83. See also: Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491–7496.

(6) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 8640–8641. Ricard, L.; Weiss, R. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 217–220.

0002-7863/86/1508-3545$01.50/0

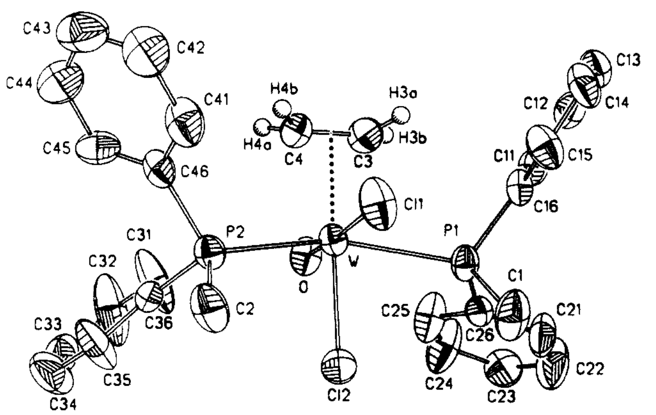

Figure 1. ORTEP drawing of $W(O)Cl_2(C_2H_4)(PMePh_2)_2$ (**2**) with 35% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) not mentioned in the text: W–Cl(1), 2.495 (3); W–Cl(2), 2.444 (3); W–P(1), 2.594 (3); W–P(2), 2.575 (3); W–C(3), 2.218 (12); W–C(4), 2.221 (12); P(1)–W–C1(1), 82.1 (1); P(2)–W–Cl(1), 82.1 (1); P(1)–W–Cl(2), 80.4 (1); P(2)–W–Cl(2), 79.8 (1); Cl(1)–W–Cl(2), 89.6 (1); O–W–Cl(1), 176.1 (2); O–W–Cl(2), 94.2 (2); O–W–C(3), 90.6 (4); O–W–C(4), 90.7 (4); Cl(1)–W–CTR, 85.4 (3); Cl(2)–W–CTR, 175.0 (3) (CTR = midpoint of C(3)–C(4)).

an important interaction for high-valent metal–oxo species.

Ethylene, propylene, and 1,3-butadiene all react rapidly with *cis-mer*-$W(O)Cl_2(PMePh_2)_3$ (**1**)[8] at 40 °C, liberating one phosphine ligand to form $W(O)Cl_2(CH_2{=}CHR)(PMePh_2)_2$ in 50–75% yields (**2–4**, eq 1).[9] Compounds **2–4** are yellow, air-stable

$$\underset{\mathbf{1}}{W(O)Cl_2(PMePh_2)_3} + CH_2{=}CHR \rightarrow W(O)Cl_2(CH_2{=}CHR)(PMePh_2)_2 + PMePh_2 \quad (1)$$

$$\mathbf{2}, R = H \qquad \mathbf{3}, R = Me \qquad \mathbf{4}, R = CH{=}CH_2$$

solids which are soluble in organic solvents; only **2** is stable to air in solution.

Crystals of **2** were grown by slow evaporation of a benzene solution and were fully characterized by an X-ray crystal structure.[10] The coordination geometry about the tungsten center can be described as a distorted octahedron with the ethylene ligand occupying one site (Figure 1). The phosphine ligands occupy trans positions in the octahedron although the P–W–P angle is only 154.7 (1)°. This suggests that there is significant steric crowding between the phosphine groups and both the oxo and ethylene ligands (angles: O–W–P = 98.3, 98.8 (2)°, CTR–W–P = 99.2, 99.2 (3)°; CTR is the ethylene centroid). The terminal oxo group exerts substantial steric influence because of the short W–O bond (1.714 (6) Å) and because in general a multiple bond occupies more space than a single bond.[11] The ethylene ligand lies cis to the oxo group (angle: O–W–CTR = 90.7 (3)°) and is oriented perpendicular to the tungsten–oxygen multiple bond. The ethylenic carbon–carbon bond length of 1.404 (17) Å is substantially longer than that of free ethylene (1.337 (2) Å) and is typical of ethylene adducts of low-valent metal centers such as η-$C_5Me_5(PPh_3)Rh(CH_2CH_2)$: 1.408 (16) Å.[12]

The geometries of the olefin complexes **2–4** in solution appear to be similar to the structure of **2** in the solid state on the basis of ^1H, ^{31}P, and ^{13}C NMR spectra.[13] For instance the ^1H NMR spectra of **2** at 25 and 80 °C show two resonances for the four ethylene protons, which indicates that ethylene rotation is slow on the NMR time scale with an activation barrier greater than 17 kcal/mol.[14] The NMR spectra of **4** indicate that the butadiene ligand is bound to tungsten through only one double bond since the coordinated olefinic resonances are similar to those of **2** and **3** and distinguished from the uncoordinated vinylic resonances.

Analogous carbon monoxide and *tert*-butyl isocyanide complexes can also be made by the displacement of a phosphine ligand in **1** in yields of 70% (eq 2). Compound **5** is the first example

$$W(O)Cl_2(PMePh_2)_3 + L \rightarrow W(O)Cl_2(L)(PMePh_2)_2 + PMePh_2 \quad (2)$$

$$\mathbf{5}, L = CO \qquad \mathbf{6}, L = CNCMe_3$$

of a transition-metal complex with both carbonyl and terminal oxo ligands. NMR data indicate that the light purple adducts **5** and **6** have octahedral geometries similar to the structure of **2**.[13] The IR spectra of **5** and **6**, like those of **2–4**, have a strong band in the region 955–960 cm^{-1} due to the tungsten–oxygen multiple bond.[15] The carbonyl and isonitrile stretching frequencies are 2006 and 2130 cm^{-1}, indicative of substantial metal-to-ligand π-back-bonding.

Significant back-bonding in these compounds is surprising because of the high (+4) formal oxidation state of the tungsten.[7,16] Metal–terminal oxo complexes with d^2 configurations (like **1–6**) are usually diamagnetic with the two d electrons paired in an orbital that lies perpendicular to the metal oxygen bond (d_{xy} when the z axis is taken as coincident with the M–O vector).[15,17] Back-bonding therefore occurs predominantly to the ligands cis to the oxo group and, as found in **2–6**, this is the preferred site for a π acid ligand. π-Back-bonding to an olefin ligand is maximized when the π^* acceptor orbital lies perpendicular to the metal–oxygen bond, as seen for **2**.[18] The substantial barrier to ethylene rotation is another indication of the importance of π-

---

(7) There are examples of carbonyl–imido and carbonyl–nitrido complexes: $W(NAr)(CO)(S_2CNR_2)_2$ (ν(CO) = 1912 cm^{-1}): Hillhouse, G. L.; Haymore, B. L. *J. Organomet. Chem.* **1978**, *162*, C23–C26. See also: Hillhouse, G. L.; Haymore, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 1537–1548. $Re(NAr)Cl_3(CO)(PPh_3)$ (ν(CO) = 2040 cm^{-1}): La Monica, G., Cenini, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1145–1149; *Inorg. Chim. Acta* **1978**, *29*, 183–187. Ru and Os(VI) nitrido–carbonyl complexes: Belmonte, P. A. University of Illinois Chicago Circle, personal communication, 1985.

(8) Carmona, E.; Sânchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797–801.

(9) For example, compound **2** was prepared by stirring a benzene solution of **1** (0.35 g in 15 mL) at 40 °C under 1 atm of ethylene for 30 min. Filtration, evaporation of most of the solvent, and addition of petroleum ether gave 0.20 g (74%) of yellow **2**.

(10) Crystal data for $W(O)Cl_2(C_2H_4)(PMePh_2)_2$ (**2**): orthorhombic, *Pbca*; a = 13.189 (3) Å, b = 27.229 (5) Å, c = 15.581 (2) Å, V = 5596 (2) Å^3, Z = 8, D_c = 1.66 g cm^{-1}, 23 °C. A Nicolet R3 diffractometer was used to collect 5769 data ($4° \leq 2\theta \leq 53°$) of which 3200 data with $F_o > 4\sigma(F_o)$ were used in the solution and refinement. An empirical absorption correction was applied to all data (μ(Mo Kα) = 46.87 cm^{-1}). Structure was solved by heavy-atom methods. All remaining non-hydrogen atoms were located on subsequent difference Fourier syntheses. Methyl and phenyl hydrogens were calculated. Ethylene hydrogens were located on a Fourier difference map, isotropically refined, and fixed at 0.96 Å from carbon. Structure refined to R_F = 4.58% and R_{wF} = 4.74%; *GOF* = 1.024, highest final difference peak, 0.63 e/Å^3 (between C(31) and C(32)).

(11) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980, p 39. Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 709–716.

(12) Porzio, W.; Zocchi, M. *J. Am. Chem. Soc.* **1978**, *100*, 2048–2052. See also: Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *Ibid.* **1983**, *105*, 1136–1143.

(13) Full spectroscopic data for **2–6** are included in the supplemental material. Selected NMR data for **2**: ^1H (C_6D_6) δ 2.24, 2.77 (m, 2 H each, $CHH'{=}CHH'$), 2.43 (t, 6, J_{PH} = 4 Hz, PCH_3Ph_2); ^{13}C δ 53.8 (t, $^1J_{CH}$ = 156 Hz, C_2H_4); $^{31}P\{^1H\}$ 18.3 (s, $^1J_{WP}$ = 268 Hz). For **3**: $^{13}C\{^1H\}$ δ 60.2, 65.8, 27.1 (s, $CH_2{=}CHCH_3$); $^{31}P\{^1H\}$ δ 20.1, 21.3 (d, $^2J_{PP}$ = 161, $^1J_{WP}$ = 273 Hz). For **4**: $^{13}C\{^1H\}$ δ 57.8, 71.7, 145.7, 113.9 (s, $CH_2CHCHCH_2$); $^{31}P\{^1H\}$ δ 17.2, 20.4 (d, $^2J_{PP}$ = 163, $^1J_{WP}$ = 260 Hz). For **5**: $^{13}C\{^1H\}$ δ 234.6 (CO); $^{31}P\{^1H\}$ δ 14.8 (s, $^1J_{WP}$ = 326 Hz); $\nu(^{13}CO)$ = 1961 cm^{-1}.

(14) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 96.

(15) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459–517. Dori, Z. *Prog. Inorg. Chem.* **1981**, *28*, 239–307.

(16) High-valent olefin complexes are very rare, to our knowledge limited to W(IV) and Pt(IV) species: Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. Green, M. L. H.; Mahtab, R. *Ibid.* **1979**, 262. Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1985**, *107*, 1793–1794.

(17) A more complete discussion of bonding in metal–oxo compounds is given in: Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454.

(18) Similar arguments have been presented to explain the structures of d^2 oxo–acetylene compounds: Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1997–2006. Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713–7721. Bennett, M. A.; Boyd, I. W. *J. Organomet. Chem.* **1985**, *290*, 165–180 and refs therein. Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Organometallics* **1985**, *4*, 422–423 and refs therein.

back-bonding in these d^2 oxo compounds. The molybdenum–oxo–TCNE complex, the known imido–carbonyl complexes, and most of the reported oxo–acetylene compounds are isoelectronic with **1–6** and adopt the same basic structure, presumably for the same electronic reasons.[6,7,18]

The ethylene, carbonyl, and isonitrile complexes exhibit moderate thermal stability, with less than 10% decomposition after 24 h at 90 °C in benzene solution in a sealed tube. The propylene and butadiene complexes, however, are substantially decomposed within 24 h at 40 °C. The decompositions of **2–4** appear to proceed via loss of the olefin ligands. The thermal stability parallels the ligand substitution reactions that interconvert **1–6**: the strength of metal–ligand bonding appears to vary in the order $CH_2{=}CH_2 \sim CO \sim CNCMe_3 \gg CH_2{=}CHCH{=}CH_2 > PMePh_2 \sim CH_2{=}CHMe$.

This work indicates that olefins and other π-acid ligands can bind strongly to transition-metal oxide species if the metal is in a d^2 configuration. We have not as yet observed rearrangement of an oxo–olefin complex to an oxametallacyclobutane (suggested to occur in osmium tetraoxide and chromyl chloride oxidations[3]) or observed formation of CO_2 from the oxo–carbonyl compound. These processes may be unfavorable in this system because of the strength of the tungsten–oxygen multiple bond and the presence of π-back-bonding interactions. Studies are in progress to explore the reactivity of these and other high-valent olefin and carbonyl complexes.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Graduate School Research Fund of the University of Washington.

Supplementary Material Available: Spectroscopic data for **2–6** and tables of analytical data for **2–5** and crystallographic data for **2**: atomic coordinates, bond distances and angles, anisotropic temperature factors, hydrogen atom coordinates, and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Book Reviews *

Chemistry of Pyrotechnics: Basic Principles and Theory. By John A. Conkling (Washington College). Marcel Dekker: New York and Basel. 1985. vi + 190 pp. $49.75. ISBN 0-8247-7443-4.

A book of this sort can be counted on to awaken the sleeping pyrotechnician in most chemists. In this case, the reader has to be patient while the author discusses elementary chemistry, physics, and thermodynamics in the first three chapters. Thereafter come chapters on Pyrotechnic Principles, Ignition and Propagation, Heat and Delay Compositions, Color and Light Production, and Smoke and Sound. In these later chapters appear many formulations. The approach is generally more empirical than the title suggests, but scientific explanations appear throughout. The references are generally to secondary sources. Safety is emphasized repeatedly. Two small appendixes deal with Obtaining Pyrotechnic Literature and Mixing Test Quantities of Pyrotechnic Compositions. The book provides a good overall perspective, but the later parts might be considered unsuitable for a reader whose weak technical background makes the early chapters necessary, and the chemist who might make use of the later chapters is not likely to need the introductory material. A 6-page index completes the work.

Metallo-organic Chemistry. By Anthony J. Pearson (Case Western Reserve University). John Wiley & Sons: New York. 1985. xi + 398 pp. $29.95.

Several textbooks covering the organometallic area have appeared in the last few years, and this is one of the best. The literature is covered up to mid-1982, and (unlike some other recent texts) Pearson has done a good job of providing key literature references throughout. The author's expressed intent was "to provide a basic coverage of the chemistry of organo-transition metal complexes and to set this in the context of their application in synthetic organic chemistry", and he does this very well.

The first chapter deals with the basic bonding (using the frontier MO approach) and electron-counting concepts which are used extensively in the text. Chapter two addresses fluxionality and dynamic equilibria and surveys some common organometallic reaction types with an emphasis on some of the classic catalytic processes (such as olefin metathesis and polymerization, the Wacker process, hydrogenation, etc.) in the field. Chapters three through nine cover the descriptive chemistry of carbon ligands, arranged with respect to ligand hapticity (σ-alkyl; carbene and carbyne; alkene and alkyne; allyl; diene; dienyl; arene and triene). These chapters nicely incorporate (1) syntheses, (2) physical characteristics of complexes, (3) reactivities of organometallic complexes, especially with regard to their organic synthetic uses, and (4) mechanistic considerations, including detailed stereochemical information. The illustrations and figures are descriptive, clear, and plentiful; stereochemistry is always faithfully shown when known.

The text was written primarily for "synthetic organic chemists whose education has so far neglected organometallic chemistry", but inorganic chemists will find it equally valuable as a reference work since their education has historically neglected detailed synthetic *applications* of metals to organic synthesis.

Gregory L. Hillhouse, *University of Chicago*

Biochemistry of Dioxygen. By L. L. Ingraham and D. L. Meyer (University of California, Davis). Plenum Press: New York. 1985. xi + 287 pp. $45.00. ISBN 0-306-41948-3.

While the intended audience for this book is the research biochemist, it will certainly also be of great value to the organic or bioorganic chemist working in the area or who contemplates doing research in the area of oxygen metabolism or related areas where results could have consequences for the more biochemically oriented metabolism studies. The book includes a timely survey of work reflecting the title as well as related areas, viz, the chemistry of ground-state oxygen, singlet oxygen, peroxides, and superoxide ion. The latter topics serve as an introduction to a systematic survey of the enzyme systems involved in dioxygen metabolism. This survey is organized around characteristics of the enzyme-activated dioxygen reactions with categories in which dioxygen (1) reacts as a one-, two-, or four-electron acceptor from the substrate or (2) reacts as a two-electron acceptor and an oxygen atom donor, or (3) reacts as a two oxygen atom donor. The book also includes important chapters on the related subjects of dioxygen toxicity and bioluminescence.

The introductory chapters on ground-state dioxygen, etc., include properties, reactions, and, where appropriate, methods of generating the subject oxidant or compounds. The emphasis is on aspects of these topics that are pertinent to the subsequent chapters on enzyme activation of dioxygen. The chapters on the various types of enzymes are generally organized to include the type of reaction catalyzed, what is known about the structure of the enzyme type, specific examples of the type, and current views on the mechanism of action of the enzyme type.

The book is interpretive at many points, particularly where competing mechanisms are reviewed and discussed. In general, this reviewer found such discussions to be balanced and informative. However, in discussing the mechanism of quenching of singlet dioxygen by β-carotene, the authors characterize the interaction of single dioxygen and ground-state singlet β-carotene to give triplet dioxygen and excited triplet β-carotene as being quantum-mechanically forbidden, which it is not. This view may have led the authors to their stated belief that the available evidence on the competing mechanisms for singlet dioxygen quenching by β-carotene is not sufficient to confirm or eliminate any of the proposed mechanisms. To this reviewer the balance of the evidence would seem to favor quenching by energy transfer.

The strength of this book is the bringing together in an organized fashion the great range of subjects fitting the title. The book suffers from too many typographical errors to be easily excused on this point. such errors are particularly damaging in figures, where misinterpretation is likely.

In summary, the authors have done a service to those working or

---

*Unsigned book reviews are by the Book Review Editor.