

Ligand Effects in Metal-Mediated Selective Oxidation. A Comparison of Cyclopentadienyl and Trimetaphosphate Supporting Ligands in Cyclooctadienyliridium(I) Complexes

V. W. Day,^{a,1a} T. A. Eberspacher,^{1a} W. G. Klemperer,^{a,1b} and B. Zhong^{1b}

Departments of Chemistry
University of Nebraska, Lincoln, Nebraska 68588
University of Illinois, Urbana, Illinois 61801

Received July 26, 1993

Revised Manuscript Received January 31, 1994

The 1,5-cyclooctadiene complex $[(C_8H_{12})Ir(P_3O_9)]^{2-}$ reacts stoichiometrically with 0.5 equiv of O_2 in an extremely unorthodox³ fashion, yielding the hydroxylated allyl complex $[(C_8H_{11}OH)Ir(P_3O_9)]^{2-}$ by way of an isolable, isomeric oxametallacyclic intermediate,⁴ as shown in Scheme 1. The similarity⁴ between the polyoxoanion-supported organometallic system and the solid oxide-supported system Ag/Al_2O_3 ⁵ raises questions concerning the role played by the $P_3O_9^{3-}$ polyoxoanion ligand in the O_2 oxidation chemistry of Scheme 1. We have therefore prepared a cyclopentadienyl complex analogous to a, $[(C_5H_5)IrCp']$, where $Cp' = 1,3-C_5H_3(SiMe_3)_2$, and examined its reactivity toward molecular oxygen. Unlike the trimetaphosphate complex, the cyclopentadienyl complex is extremely unreactive toward oxygen, failing to react even at elevated temperatures in solvents such as benzene (80 °C), toluene (110 °C), and 1,2- $C_2H_4Cl_2$ (80 °C) after 12 h. After extensive experimentation, however, we have devised forced conditions under which $[(C_5H_5)IrCp']$ can be oxidized and find that a pathway different from that of Scheme 1 is followed, namely oxidative dehydrogenation, as shown in Scheme 2. The difference in behavior between these two systems can be attributed to an unusual property of the $P_3O_9^{3-}$ ligand, its ability to act as a flexidentate ligand.

Complex d, $[(C_5H_5)IrCp']$, is prepared⁶ in 82% yield from $[IrCl(C_5H_5)]_2$ ⁷ and $LiCp'$ ⁸ in tetrahydrofuran solution. It reacts with O_2 (1 atm) in a sealed NMR sample tube at 75 °C in 0.06 M 1,1,2,2- $C_2D_2Cl_4$ (TCE) solution to form the two isomeric ketone complexes e and f shown in Scheme 2 with a half-time of about 4 h. At this point, 50% conversion, the yield of e plus f is 70% and the e:f ratio is 2.5:1. When prepared on a larger scale, e and f can be separated and purified by column chromatography, and their solid-state structures have been determined using single-crystal X-ray diffraction techniques (see Figure 1).⁶ The minor product f can be prepared in higher yield by reacting complex d with 3-chloroperoxybenzoic acid.⁶ Although e and f are not interconverted under the reaction conditions employed for O_2 oxidation of d, complex e is further oxidized under these conditions, as might be expected from its structural similarity with d. Several experiments identify the reaction of complex d with O_2 in TCE as a free-radical chain process. An induction period is observed, and the oxidation is completely suppressed by small amounts (0.03 equiv) of the free-radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol.^{9a} The reaction is accelerated by the free-radical

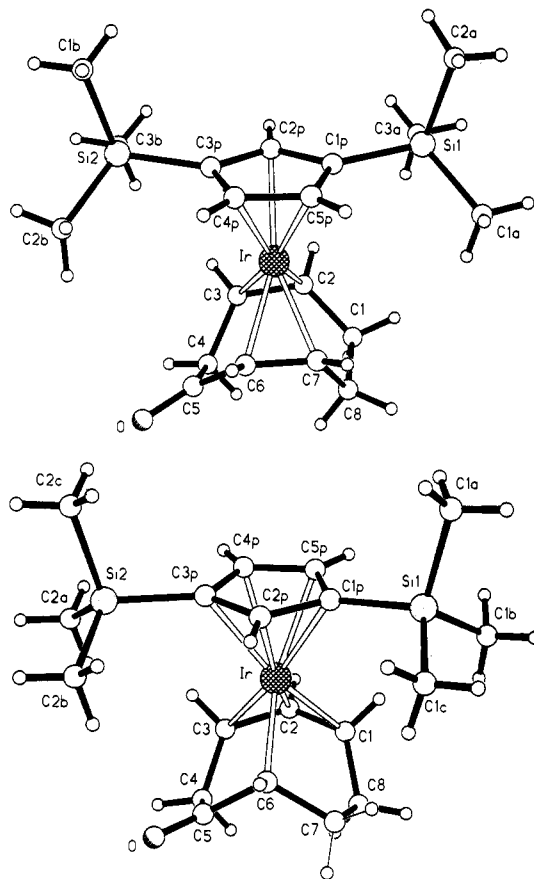
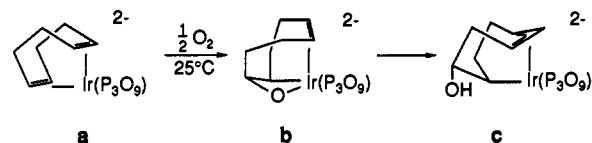
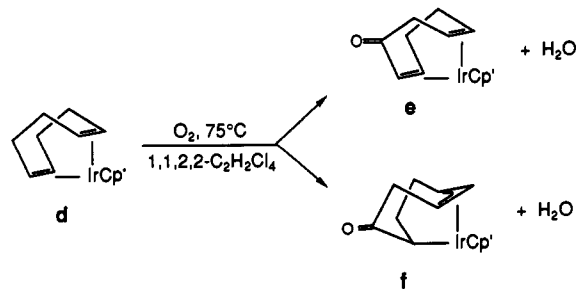


Figure 1. (a) Perspective drawing of the solid-state structure of $(\eta^2, \eta^2-C_8H_{10}O)Ir[\eta^2-1,3-C_5H_3(Si(CH_3)_3)_2]$, e. The Ir and Si atoms are represented by large cross-hatched and dotted spheres, respectively. Oxygen and carbon atoms are represented by medium-sized shaded and open spheres, respectively, while hydrogen atoms are represented by small open spheres. (b) Perspective drawing of the major component of the (disordered) asymmetric unit in crystalline $(\eta^1, \eta^3-C_8H_{10}O)Ir[\eta^2-1,3-C_5H_3(Si(CH_3)_3)_2]$, f, with all atoms represented as in Figure 1a. The $\eta^1, \eta^3-C_8H_{10}O$ ligand is disordered in the lattice; 62% of the time C_5 is a ketonic carbon and 38% of the time it is a methylene carbon; 38% of the time C_7 is a ketonic carbon and 62% of the time it is a methylene carbon. The two methylene hydrogens shown on C_7 were computer-generated at idealized positions for this drawing but not included in the structural model, which was least-squares refined.

Scheme 1



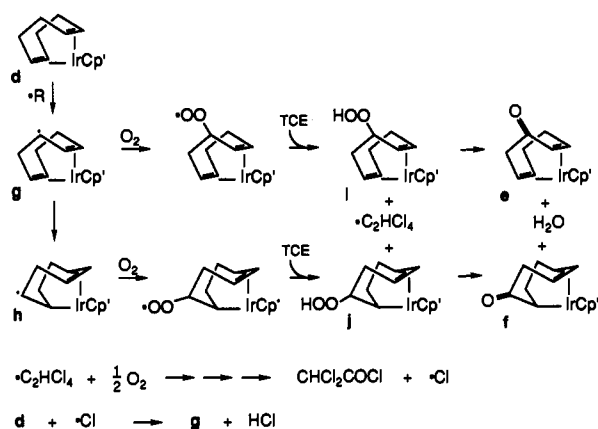
Scheme 2



- (1) (a) University of Nebraska. (b) University of Illinois.
- (2) Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345.
- (3) Jørgensen, K. A.; Schiott, B. *Chem. Rev.* **1990**, *90*, 1483.
- (4) Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 2031.
- (5) Van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, *35*, 265.
- (6) Roberts, J. T.; Madix, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 8540.
- (7) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Kahn, T. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.
- (8) Lappert, M. F.; Singh, A. *Inorg. Synth.* **1990**, *27*, 168.
- (9) Emanuel, N. M.; Denisov, E. T.; Maizus, Z. K. *Liquid-Phase Oxidation of Hydrocarbons*; Plenum: New York, 1967; (a) p 225 (b) p 141.

initiator *tert*-butyl hydroperoxide:^{9b} the half-time is reduced to about 20 min at 75 °C by 0.03 equiv of initiator. The radical

Scheme 3



chain reaction is propagated not by compound **d**, however, but by TCE. Complex **d** is stable for at least 24 h at 75 °C in the presence of 0.03 equiv of *tert*-butyl hydroperoxide and excess O₂ in benzene or toluene solution; less than 5% decomposition occurs in 1,2-C₂H₄Cl₂ (DCE) solution. Free-radical, chlorine-photo-sensitized O₂ oxidation has been observed for TCE but not for DCE under the same reaction conditions.¹⁰ This difference in reactivity is well-understood¹⁰ in terms of the exothermicity of the dissociation of the chloroethoxy radical intermediates involved. Reaction of CHCl₂CCl₂• with 0.5 equiv of O₂ yields CHCl₂CCl₂O•, whose dissociation to CHCl₂COCl and Cl• is exothermic by about 16 kcal/mol.¹⁰ The corresponding C–Cl dissociation in CH₂ClCHClO• is exothermic by only about 4 kcal/mol.¹⁰ As a result, TCE but not DCE is capable of propagating long-chain oxidation.¹⁰

A mechanism for [(C₈H₁₂)IrCp'] oxidation is proposed in Scheme 3. The radical **g** produced by a chain initiator undergoes rearrangement to **h**, ultimately producing the isomeric hydroperoxides **i** and **j**. The hydrogen atom source for products **i** and **j** is the TCE solvent, which propagates the chain using Cl• radicals produced upon reaction of C₂HCl₄• with O₂ (see above).¹⁰ The route to isomeric hydroperoxide ligands is modeled after the autoxidation of free 1,5-cyclooctadiene, which is known to afford a mixture of 2,6-cyclooctadien-1-yl hydroperoxide and 2,5-

cyclooctadien-1-yl hydroperoxide.¹¹ Conversion of the two isomeric hydroperoxides into the corresponding ketones has ample precedent both as a free-radical¹² and as a metal-initiated or -catalyzed¹³ process.

Comparison of the mechanisms proposed for [(C₈H₁₂)IrCp'] oxidation above and [(C₈H₁₂)Ir(P₃O₉)]²⁻ oxidation elsewhere⁴ shows initial O₂ attack at the C₈H₁₂ ligand in the former case and at the Ir(I) metal center in the latter. Given that the iridium center in the cyclopentadienyl complex has an 18-electron configuration and that the free ligand requires elevated temperatures for autoxidation, the inertness of this complex toward oxygen is not surprising. The same considerations would apply to the trimetaphosphate complex, were it not for the unsymmetric bonding mode observed for the κ³-O-P₃O₉³⁻ ligand in [(C₈-H₁₂)Ir(P₃O₉)]²⁻.² Here the two oxygen atoms coordinated to iridium *trans* to the olefin ligands have normal, 2.18-Å Ir–O bond lengths. The third oxygen atom occupying the apex of a square-pyramidal coordination polyhedron forms a very weak, 2.70-Å bond to the iridium center. As a result, this ligating atom might undergo facile dissociation, allowing O₂ attack at the metal center and subsequent formation of a reactive O₂ complex, [(η⁴-C₈H₁₂)Ir(η²-O₂)(κ²-O-P₃O₉)]²⁻. We are currently investigating this possibility by studying the oxidative addition chemistry of [(C₈H₁₂)Ir(P₃O₉)]²⁻.

Acknowledgment. This research was supported by the National Science Foundation.

Supplementary Material Available: Details of sample preparations and reaction conditions, crystal structure reports, listings of positional and thermal parameters, listings of bond lengths and angles, and perspective structure drawings for compounds **e** and **f** (41 pages); structure factor tables (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(11) Farrissey, W. J.; Perry, R. H.; Stehling, F. C.; Chamberlain, N. F. *Tetrahedron Lett.* 1964, 48, 3635.

(12) Howard, J. A. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 8, p 250.

(13) (a) Fusi, A.; Ugo, R.; Fox, F.; Pasini, A.; Cenini, S. *J. Organomet. Chem.* 1971, 26, 417. (b) Arzoumanian, H.; Blanc, A. A.; Metzger, J.; Vincent, J. E. *J. Organomet. Chem.* 1974, 82, 261.

(10) (a) Bertrand, L.; Franklin, J. A.; Goldfinger, P.; Huybrechts, C. *J. Phys. Chem.* 1968, 72, 3926. (b) Bertrand, L.; Exsteen-Meyers, L.; Franklin, J. A.; Huybrechts, G.; Olbregts, J. *Int. J. Chem. Kinet.* 1971, 3, 89.