Studies on the Mechanism of Oxygen Atom Transfer
from Molecular Oxygen to Ir Coordinated Cyclooctadiene

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Oxidations using O_2 account for 7 of the 12 largest heterogeneous catalytic processes used in industry today [1]. Four of these 7 processes are hydrocarbon oxidations and use oxidized transition metal catalysts. The epoxidation of ethylene over Ag supported Al_2O_3 is the largest of these hydrocarbon oxidations (5.37 billion pounds in 1988 - the 28th largest commodity chemical produced in the U.S.) and proceeds with >80% selectivity with carbon dioxide and water as the only byproducts [2,12a].

Little is known about the molecular mechanism the Ag/Al_2O_3 catalyzed O_2 epoxidation of ethylene. The goal of this work has been to study the reaction of molecular polyoxoanion-supported Ir cyclooctadiene complexes with oxygen in an effort to isolate and characterize intermediates and gain an understanding of the mechanism by which O_2 oxidations occur. Development of these schemes may aid in identification of factors influencing reactivity and ultimately allow control via synthetic design.

The cyclooctadiene complex $[(C_8H_{12})Ir-(P_3O_9)][(n-C_4H_9)_4N]_2$, **a**, is known to react in solution with O_2 to form $[(C_8H_{11}OH)Ir(P_3O_9)][(n-C_4H_9)_4N]_2$, **f**, according to the following reaction:

$$[(C_8H_{12})Ir(P_3O_9)][(n-C_4H_9)_4N]_2 + O_2 \rightarrow$$

$$[(C_8H_{11}OH)Ir(P_3O_9)][(n-C_4H_9)_4N]_2$$
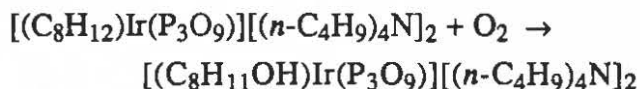
Both **a** and **f** have been characterized by single crystal x-ray diffraction [4] and the structure of the anions are shown in the top and bottom of Figure 1, respectively. Examination of the structural relationships between these two complexes does not lead to a clear understanding of how this interesting process occurs.

The purpose of this research is to examine the mechanism by which **a** proceeds to **f**. This reaction was first explored by O_2 uptake experiments to determine that each atom of O_2 was incorporated into a molecule of **a**. Sealed tube ^{31}P NMR experiments were then performed to follow the transformation of **a** to **f** and establish the presence of intermediates and the relationship between these species.


Figure 1.
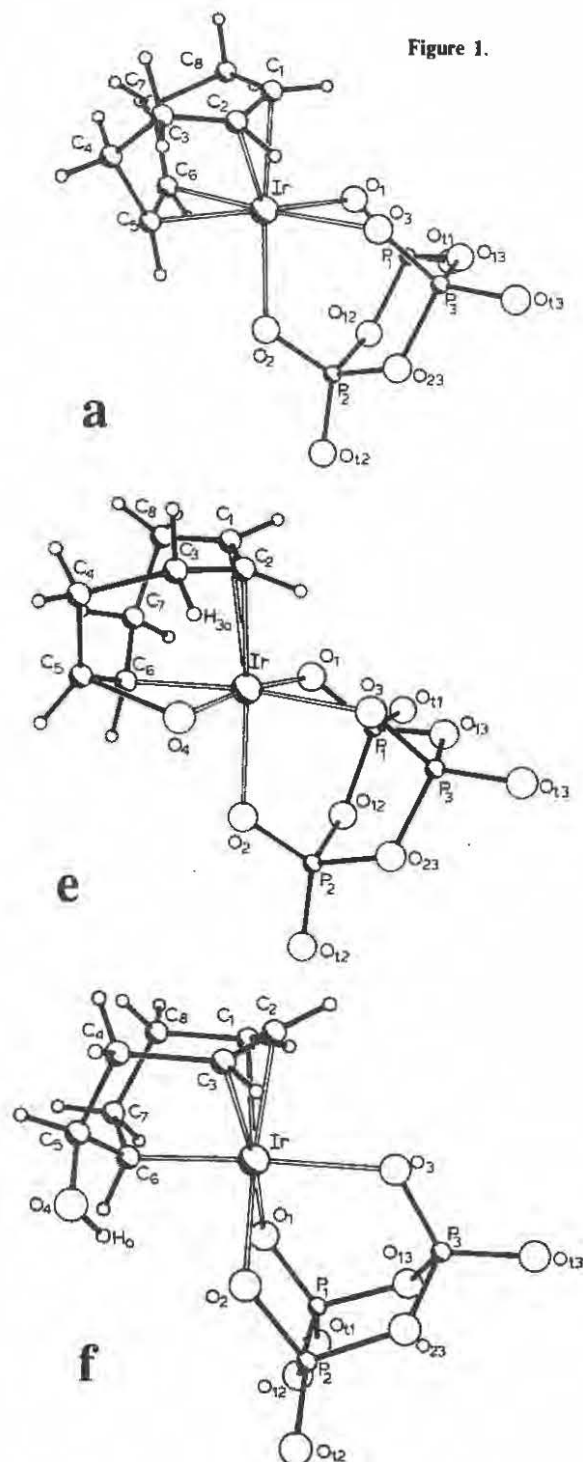
One of these intermediates, the oxametallacyclobutane complex $[(C_8H_{12}O)Ir(P_3O_9)]$-$[(n\text{-}C_4H_9)_4N]_2$, **e**, was isolated and structurally characterized and is shown in the middle of Figure 1 [5]. The $(P_3O_9)^{3-}$ fragment of **e** is the adamantane structure with Ir replacing one of the $[P=O]^{3+}$ vertices. Pseudo-octahedral coordination geometry at the Ir(III) center is defined by three terminal $(P_3O_9)^{3-}$ oxygen atoms (O_1, O_2, and O_3), an olefinic C=C bond (C_1-C_2), and the carbon (C_6) and oxygen (O_4) atoms of an oxametallacyclobutane ring. The structures **a** and **e** are related by insertion of an O atom into a C-Ir bond of **a**. The structure of **f** is related to that of **e** by proton transfer from the allylic carbon (C_3) of **e** to the oxygen atom of the oxametallacyclobutane ring and bond formation between Ir and the allylic carbon (C_3).

Two other species, **d** and **g**, have been observed by ^{13}C and ^{31}P NMR spectroscopy and their proposed structures are shown in the Scheme. On the basis of these observations, a mechanism has been proposed detailing the incorporation of the O atom from oxygen into **a** and its subsequent reactivity.

In the Scheme, this proposed mechanism is shown. Oxygen initially binds to the 18-electron Ir center in **a** to form the η^1-O_2 complex **b**. A complex utilizing η^2-O_2 coordination of the type observed in species such as $[Ir(PPh_3)_2(CO)Cl(O_2)]$ [6] is disfavored since such a complex containing η^4-C_8H_{12} and κ^2O-P_3O_9 ligands would have a 20-electron valence configuration. This type of η^1-O_2 coordination has been proposed for O_2 adducts of the 18-electron d^8 Ir(I) complexes $[(C_8H_{12})Ir(phen)Y]$ (Y = I-, SCN-; phen = phenanthroline) [7]. The η^1-O_2 intermediate **b** reacts with a second Ir center to form the μ-η^2-O_2, κ^3O-P_3O_9 complex, **c**. Complex **c** then undergoes internal redox [8] to form an isomeric Ir(III) oxo complex, **d**, whose coordinated oxygen atoms are inserted into Ir-C bonds to complete the transformation into **e**.
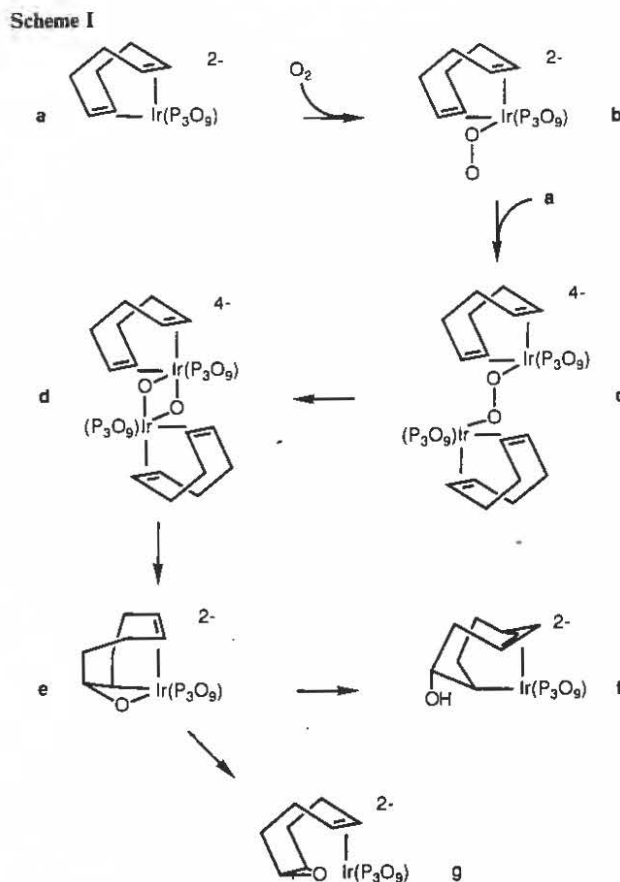
Scheme I

Analogous oxygen atom transfer from the Ir(III) oxo complex, $[(C_5Me_5)Ir(O)]_2$, to PPh_3 has been observed [9]. A plausible 18-electron structure for **d** containing η^4-C_8H_{12} and κ^2O-$P_3O_9^{3-}$ ligands is shown in the Scheme. This structure is supported by nmr data for the first reaction intermediate observed at -20°C in CH_3CN. The X part of the observed ABX ^{31}P multiplet is assigned to the phosphorus atom in the uncoordinated phosphate group of the κ^2O-$P_3O_9^{3-}$ ligand since its chemical shift (-21.5 ppm) is similar to that for free $P_3O_9^{3-}$ in CH_3CN (-22.0 ppm) [10]. Eight distinct ^{13}C nmr resonances are observed for the η^4-C_8H_{12} ligand.

It is interesting to note that oxametallacyclobutane complexes are frequently invoked as reaction intermediates for olefin epoxidation [11]. Thermal activation of the oxametallacyclobutane complex **e** may yield **f**, however, and not an epoxide such as **g**. In this context it should be noted that the heterogeneous catalyst Ag/Al_2O_3 does not effectively catalyze selective epoxidation of olefins containing acidic allylic hydrogens [12].

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