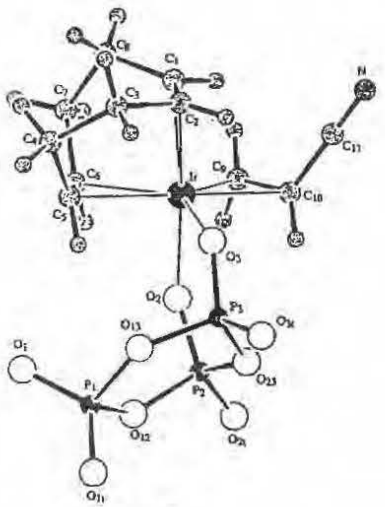
Studies of the Mechanism of C-O Bond Formation in a Polyoxoanion-Supported Oxairidacyclobutane Complex

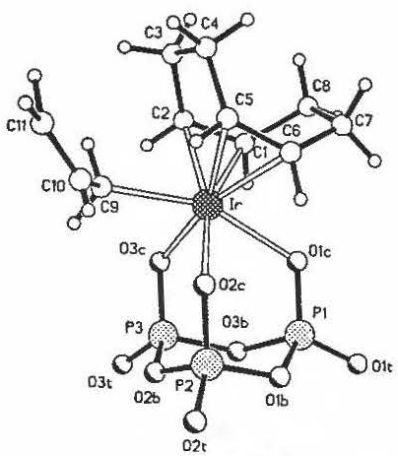
Jie Chen Final Seminar June 11, 1993

Olefin oxidation is an important industrial process, and its mechanism has been extensively studied [1]. Oxametallacyclobutane complexes have frequently been invoked as olefin oxidation intermediates since they were first proposed by Sharpless [2]. However, only one such complex, $[(C_8H_{12}O)Ir(\kappa^3O\text{-}P_3O_9)]^{2-}$ (**2**), has ever been synthesized by O_2 oxidation of an olefin complex, namely, $[(C_8H_{12})Ir(\kappa^3O\text{-}P_3O_9)]^{2-}$ (**1**) [3]. In this reaction, oxygen forms a C-O bond selectively with a coordinated olefinic carbon of complex **1** to yield **2**. The mechanism of this unique, selective formation of the C-O bond in the oxametallacyclobutane complex **2**, however, is not clear. An intermediate has been observed at low temperatures in the ^{31}P NMR spectrum as a set of three multiplets (-12, -14, -21 ppm) in an AMX spin system, and has been proposed to be a bidentate $(P_3O_9)^{3-}$ complex [3].

The goal of this research has been to study the formation mechanism of the oxametallacyclobutane complex **2**. The synthesis of cyanoolefin complexes of **1**, $[(C_8H_{12})Ir(\text{cyanoolefin})(\kappa^2O\text{-}P_3O_9)]^{2-}$, which contain bidentate $(P_3O_9)^{3-}$ ligands [4], was undertaken to verify the previous assignment of the ^{31}P NMR spectrum of an intermediate observed during the low temperature O_2 oxidation of **1**. The anion $[(C_8H_{12})Ir(CH_2{=}CHCN)(\kappa^2O\text{-}P_3O_9)]^{2-}$ has the solid-state structure **a** containing a trigonal bipyramidal iridium center and a bidentate $(P_3O_9)^{3-}$ ligand. In solution, two isomers are observed, corresponding to metal binding to



a

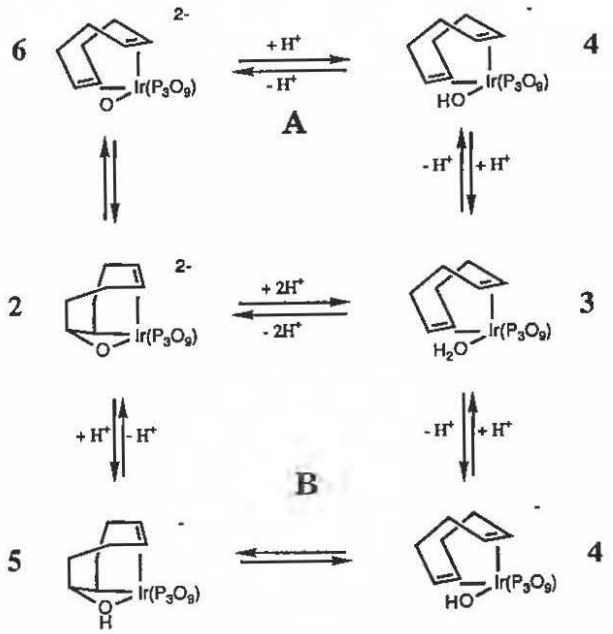


b

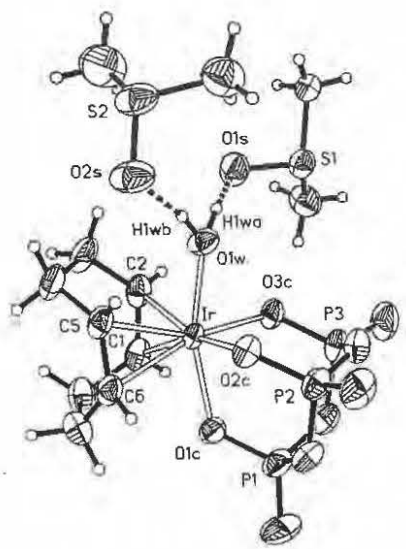
different faces of $CH_2{=}CHCN$, and are in an equilibrium with **1** and $CH_2{=}CHCN$. The ^{31}P NMR resonance at -21 ppm is assigned to P_1 in **a** since an uncoordinated $(P_3O_9)^{3-}$ has a ^{31}P NMR resonance at -21 ppm, and the resonances at -12 and -14 ppm are assigned to P_2 and P_3 because tridentate $(P_3O_9)^{3-}$ ligands are known to have chemical shifts in -1 to -14 ppm region [3, 5]. The intermediate that formed upon low temperature oxidation of **1** has ^{31}P NMR chemical shifts of -12, -14, and -21 ppm [3]. Therefore, this intermediate is a $(\kappa^2O\text{-}P_3O_9)^{3-}$ complex. Further investigation of the conversion of this intermediate to the oxametallacyclobutane complex **2** indicates that the intermediate is not an O_2 analogue of the cyanoolefin complexes, $[(C_8H_{12})Ir(\eta^2\text{-}O_2)(\kappa^2O\text{-}P_3O_9)]^{2-}$. The intermediate converts to **2** without reacting with **1**, whereas the O_2 analog requires **1** to form **2**.

The allyl complex $[(C_8H_{12})Ir(\kappa^3O\text{-}P_3O_9)(C_3H_5)]^-$ was synthesized from $[(C_8H_{12})Ir(\kappa^3O\text{-}P_3O_9)]^{2-}$ and allyl iodide. This complex was prepared in order to examine the equilibrium between tridentate trimetaphosphate coordination and bidentate trimetaphosphate coordination, when both modes are allowed by the 18-electron rule. The resulting Ir(III) complex has the σ-allyl structure **b**, instead of a π-allyl structure containing a bidentate $(P_3O_9)^{3-}$ ligand which requires the replacement of an oxygen ligand (σ-donor) by an olefin group (π-acceptor). However, such a replacement occurs in **a** when the oxidation state of iridium is +1. The high electron density on Ir(I) is delocalized onto the π-acceptor acrylonitrile ligand by back-bonding [6]. Dioxygen, on the other hand, might adopt either η^1 or η^2 coordination mode with a $(\kappa^3O\text{-}P_3O_9)^{3-}$ ligand or a $(\kappa^2O\text{-}P_3O_9)^{3-}$ ligand, respectively, since the competition occurs between two oxygen donors and no preference is predicted.

To gain insight into the C-O bond formation mechanism of the oxametallacyclobutane complex **2**, both the reactivity of **2** and alternative routes to **2** have been investigated. Specifically, a unique, reversible conversion of the oxametallacyclobutane complex **2** to the aquo olefin complex $(C_8H_{12})Ir(OH_2)(\kappa^3O\text{-}P_3O_9)$ (**3**) was discovered. Two possible interconversion pathways have been considered, as shown in Scheme 1: pathway A involves an



Scheme 1



3

iridium oxo intermediate and follows the Sharpless mechanism; pathway B resembles the mechanism of the Wacker process [7]. Low temperature deprotonation of **3** with triethylamine leads to a hydroxide olefin complex, $[(C_8H_{12})Ir(OH)(\kappa^3O\text{-}P_3O_9)]^-$ (**4**). This hydroxide complex cannot be further deprotonated by triethylamine to form an iridium(III) oxo complex, $[(C_8H_{12})Ir(O)(\kappa^3O\text{-}P_3O_9)]^{2-}$. Therefore, pathway A is not followed. This is not surprising since no terminal oxo complexes of d^6 transition metals are known [8], presumably because π-accepting orbitals are necessary for stabilizing a terminal oxo group [9].

The interconversion between **3** and **4** follows pathway B in Scheme 1. At ambient temperature, the coordinated OH group in **4** attacks a coordinated olefin, resulting in a protonated oxametallacyclobutane complex, $[(C_8H_{12}OH)Ir(\kappa^3O\text{-}P_3O_9)]^-$ (**5**). The hydroxyl proton in this complex can easily be abstracted by triethylamine. The attack of a nucleophilic OH

group on a coordinated olefin resembles the mechanism of the Wacker process where a hydroxide group attacks a coordinated ethylene [7]. Yet it is different from the Wacker process in that the OH group is coordinated, rather than free. Protonation of **2** to form **3** also follows pathway B, as expected by microscopic reversibility.

The C-O bond in the oxametallacyclobutane complex **2** is formed from a nucleophilic coordinated hydroxo ligand and an electrophilic coordinated C=C double bond. This mechanism supports the proposed O_2 oxidation mechanism of $[(C_8H_{12})Ir(\kappa^3O\text{-}P_3O_9)]^{2-}$ to form the oxametallacyclobutane complex **2** where an iridium μ-oxo dimer intermediate, rather than an iridium terminal oxo intermediate, is involved [3]. Given that the Ir-OH oxygen is sufficiently nucleophilic to attack a coordinated olefin, it is reasonable to expect that the Ir-O-Ir oxygen is also nucleophilic enough to attack a coordinated olefin.

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