DIOSMACYCLOALKANES AS MODELS FOR THE FORMATION OF HYDROCARBONS FROM SURFACE METHYLENES

Progress Report

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Progress Report

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We are making progress on our investigation of the mechanism of olefin exchange with $\text{Os}_2(\text{C}_2\text{H}_4)(\text{CO})_8$. We are probing this system by kinetic study of the reaction of $\text{Os}_2(\text{C}_2\text{H}_4)(\text{CO})_8$ with butyl acrylate (BA) under various pressures of ethylene. Four possible mechanisms for olefin exchange (see page 2) in $\text{Os}_2(\text{C}_2\text{H}_4)(\text{CO})_8$ are simple dissociation I, bridge opening associative II, bridge opening dissociative III, and associative IV (see next page). Mechanism IV has been ruled out by the observation of saturation behavior at high acrylate concentrations which is inconsistent with the rate law derived for this mechanism. Mechanisms I and III are kinetically indistinguishable, but are distinguishable from II. Preliminary kinetic results are consistent with mechanism II and inconsistent with mechanisms I and III since a plot (see Figure on page 3) of the slopes of $(1/k_{\text{obs}} \text{ vs. } 1/[\text{BA}])$ vs. ethylene pressure yields a nonzero intercept.

We have determined $^1\text{J}_{13\text{C}-13\text{C}}$ for the ethylene in $\text{Os}(\text{CO})_4(\eta^2-^{13}\text{C}_2\text{H}_4)$. Furthermore, the molecular structure of $\text{Os}(\text{CO})_4(\eta^2-\text{C}_2\text{H}_4)$ (**1**) has been determined by single-crystal X-ray diffraction. The geometry of **1** is approximately trigonal bipyramidal, with the ethylene carbons twisted out of the equatorial plane by 4.0° . The axial carbonyls of **1** tilt *toward* the coordinated ethylene, with a C1-Os-C1' angle of $171.3(5)^\circ$. In collaboration with Anthony K. Rappé, the optimal geometries of $\text{Os}(\text{CO})_4$, $\text{H}_2\text{Os}(\text{CO})_4$, and **1** have been calculated by Hartree Fock methods. The orbital amplitude contour diagrams of a GVB(6/12) wavefunction for **1** show that the axial bending occurs in order to mix in virtual p_π character and improve backbonding to the equatorial carbonyls; they also show that **1** is best described as a metallacyclopropane.

Four Possible Mechanisms for Olefin Exchange

Mechanism I: Simple Dissociation

$$\text{I.) } \frac{1}{k_{\text{obs}}} = \frac{k_1[\text{O}]}{k_1k_2[\text{T}]} + k_1$$

Mechanism II: Bridge Opening - Associative

$$\text{II.) } \frac{1}{k_{\text{obs}}} = \frac{k_1k_2[\text{O}]}{k_1k_2k_3[\text{T}]} + \frac{k_1}{k_1k_2[\text{T}]} + \frac{1}{k_1}$$

Mechanism III - Bridge Opening - Dissociative

$$\text{III.) } \frac{1}{k_{\text{obs}}} = \frac{(k_4 + k_3)k_2k_1[\text{O}]}{k_1k_2k_3k_4[\text{T}]} + \frac{(k_1 + k_2)}{k_1k_2}$$

Mechanism IV: Associative Exchange

$$\text{IV.) } k_{\text{obs}} = \frac{k_1k_2k_3[\text{T}]}{k_1k_2[\text{O}] + (k_1 + k_2)k_3}$$

[T] = [BA]

Figure

Complexes with three-center, two electron M-H-C (agostic) bonds are of growing interest because they are considered to be key intermediates in industrially important processes such as Ziegler-Natta polymerization reactions and related oligomerizations and dimerizations. Because we would expect a metalacyclopropane to undergo protonation on the ethylene rather than on the metal, we have examined the protonation of $\text{Os}(\text{CO})_4(\text{C}_2\text{H}_4)$ (1).

^1H NMR indicates that an ethyl cation structure with a coordinated solvent is preferred over an agostic one in acetone solution. IR shows that the same is true after crystallization from acetone.

List of Publications

After October 31, 1991

Acknowledging DOE Support

"A Single Crystal Neutron Diffraction Study of $(\mu-\eta^1, \eta^1-\text{C}_2\text{H}_4)\text{Os}_2(\text{CO})_8$, A Model for One Type of Chemisorbed Ethylene", O. P. Anderson, B. R. Bender, J. R. Norton*, A. C. Larson*, and P. J. Vergamini, *Organometallics*, 1991, 10, 3145.

"Alpha vs. Beta Hydrogen Elimination in the Formation of Propene from an Osmacyclobutane", W. Fischer, R. T. Hembre, D. R. Sidler, and J. R. Norton*, *Inorg. Chim. Acta*, 1992. (invited paper for special issue; in press)

"The Structure of $\text{Os}(\text{CO})_4(\text{C}_2\text{H}_4)$, an Osmacyclopropane", B. R. Bender, J. R. Norton*, M. M. Miller, O. P. Anderson, and A. K. Rappé*, *Organometallics*, submitted; being revised in response to the referee's comments.

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