**LITERATURE DISCUSSION – STUDENT HANDOUT**

This literature discussion is centered on the following article: “Regeneration of an IrIII Complex Active for Alkane Dehydrogenation Using Molecular Oxygen” by Kate E. Allen, D. Michael Heinekey, Alan S. Goldman, Karen I. Goldberg, *Organometallics*, **2014**, *33*, 1337-1340. (DOI: /10.1021/om401241e)

Please go to the ACS website and find and download a copy of the paper. Print it out and as you read the paper, make notes on the paper and bring these to class with you. We will be using this paper to answer the following questions:

1. What chemical problem is addressed in this paper? Why is this problem important?

2. What is a “pincer” complex? What elements are commonly used in pincer ligands for coordinating directly to the metal atom? Why would you use a pincer ligand when designing a transition metal complex?

3. Consider reaction (2) (p. 1137). Provide electron counts and oxidation states for the metal centers in both iridium complexes (1a and 2a). Does the oxidation state of iridium change? Which species is oxidized? Which is reduced? Consider Reaction 3 and answer these same questions.

4. Calculate the differences in enthalpy and entropy for the dehydrogenation of octane to 1-octene at 298 K. Is the reaction endo- or exothermic? Rationalize the sign associated with the difference in entropy. Calculate the difference in free energy for this dehydrogenation reaction at 298 K. Is this reaction spontaneous under these conditions? (Use the attached table for the energy values.)

5. Calculate the free energy of the *hydrogenation* (reduction) of O2 to H2O. Can the hydrogenation of oxygen be used to drive the dehydrogenation of octane forward? Explain why or why not. (Use the attached table for the energy values.)

6. Once again, consider reaction (2). What is happening to the two hydrogen atoms removed from n-octane to produce 1-octene? Into what products are they incorporated, and in what form?

7. Write out the hypothetical catalytic cycle that results from addition of equations (2) and (3). (Hint: the cycle is actually described to some extent in the two sentences directly below equation (3).) Give one reason why this cycle might not function as drawn. (Hint: See the author’s note in Ref 7.)

8. Consider reaction (3). Where does the water ligand come from? (Hint: Look at the reagents and count atoms.)

9. Consider Figure 1 and the corresponding discussion in the text. What features in the 1H NMR spectra lead the authors to invoke the formation of an unknown intermediate/s?

10. Figure 1 shows the NMR spectra from 3.7 - 6.7 ppm of complexes 1a (top trace) and 2a (bottom trace). This region focuses on which protons of the pincer ligand? (Draw the ligand and circle or otherwise indicate the protons.)

a) Consider the methylene protons of complex 1a. Why do they show up as a singlet in the NMR spectrum of 1a (top trace)? (Hint - what is the point group of the complex?)

b) Consider the methylene protons of complex 2a. Why do they show up as an apparent quartet in the NMR spectrum of 2a (bottom trace)?

11. Under what conditions is intermediate 4a formed? What is the evidence that it is NOT the same species as intermediate 3a (give three reasons)?

12. By the end of the paper it is clear that the authors do not have a definite structure for 4a. However, there are several suggested ligands that might be present.

a) What structural feature do they all share?

b) What experiments were carried out to support this proposal?

c) Write out a reaction between H2O2 and [MnO4]- under acidic conditions and balance it using the half-reaction method.

13. What kind of reactivity does complex 1a show in the presence of H2O2? Why would this create a problem for determining the presence of a peroxo- ligand (-OOH) for complex 3a?

14. You’ve read through the paper and discussed several of the results and how they support the conclusions of the paper. If you were the Primary Investigator writing a grant proposal to the NSF or DOE to continue this work, what would you propose as the next step in the project?