Final exam discussion questions for “Iridium Dihydroxybipyridine complexes are Effective Catalysts for Hydrodeoxygenation of Vanillyl Alcohol in Water” by Papish group.

*Organometallics*, **2023**, *42*, 2806-2812. Use these questions to guide your thinking as you read the paper. We will not necessarily discuss all the questions in my office, and I will not collect your written work; you may refer to any notes you take on the paper as we discuss it.

**Preliminaries from the introduction**

1. Why are the authors interested in hydrodeoxygenation (HDO)? As part of your answer, explain what lignin is, and how HDO adds value to it.
2. The authors explain that homogeneous catalysis is better for this reaction as it avoids a competing side reaction with standard heterogeneous catalysts. What is this side reaction?
3. Explain the origin of how NMe2 or OMe provide a “strong p-donor group on the pyridine ring.” Use MO arguments or valence bond arguments to show “evidence for partial p bonding” with these substituents.
4. Explain the three roles attributed to the base. Justify their claims using words and pictures (structures or reactions).
5. The authors claim that catalysis with OH groups near the metal center have the potential for being better catalysis. Explain their reasoning.

**Electron counting**

1. Classify complexes 1 and 2 (chart 1) using the CBC method. Include dn count, VEC, LBN and VN.
2. Repeat this process for the complexes shown in the catalytic cycle (Scheme 5). Is HDO a redox reaction or not?

**Catalysis**

1. what is the “best” catalyst? What makes it the best?
2. What is the “best” base? What makes it the best?
3. By what factor or amount does the base improve catalysis?
4. What is TON and why is it improved with lower catalyst loadings (according to the authors). Does that makes sense to you?
5. The catalyst with 5·10-5 mol% catalyst loading had 997,000 TON while the catalyst with 1·10-4 mol % catalyst loading gave only 836,000 TON. Which catalyst gave more product?
6. The precatalyst (top of Scheme 5) is doubly deprotonated to make the complex at the 12:00 position. We did not cover all of these steps in class but do your best to name them and be able to explain what is happening in each step.

**Discussion**

1. The authors report the pKa of the ligand to be 4.1. explain how they determine it is 99.8% doubly deprotonated at pH 6.8.
2. Is OH- a reasonable leaving group? Do the authors claim this with certainty?
3. What are the advantages of “protic ligands over their aprotic analogs?”
4. Explain the author’s claim that more electron density on Ir leads to activation of the H2 ligand. Use the H2 complex in Scheme 5 and use an MO argument to justify your answer.

The questions we focused on during the oral exam are as follows:

1. What is the CBC classification for complexes 1 and 2 (question 6 above)
2. How do more electron rich ligands help activate H2? (question 17 above)
3. Is it simply electron richness that makes the ligands better?
4. For the “deprotonation step” (at 5pm in the catalytic cycle) what thermodynamic parameter would be good to measure?
5. What is the reaction step where the OH is a “leaving group?” (question 15 above)
6. Carbonate is a good base, why? (expanding on question 9 above)
7. TON (question 11 above)
8. Propose another experiment you would run to help the authors “prove” their mechanism.