

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 π -donor group on the pyridine ring.” Use MO arguments or valence bond arguments to show “evidence for partial π 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

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

Catalysis

- 8) what is the “best” catalyst? What makes it the best?
- 9) What is the “best” base? What makes it the best?
- 10) By what factor or amount does the base improve catalysis?
- 11) What is TON and why is it improved with lower catalyst loadings (according to the authors). Does that makes sense to you?
- 12) The catalyst with $5 \cdot 10^{-5}$ mol% catalyst loading had 997,000 TON while the catalyst with $1 \cdot 10^{-4}$ mol % catalyst loading gave only 836,000 TON. Which catalyst gave more product?
- 13) 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

- 14) The authors report the pK_a of the ligand to be 4.1. explain how they determine it is 99.8% doubly deprotonated at pH 6.8.
- 15) Is OH^- a reasonable leaving group? Do the authors claim this with certainty?
- 16) What are the advantages of “protic ligands over their aprotic analogs?”
- 17) Explain the author’s claim that more electron density on Ir leads to activation of the H_2 ligand. Use the H_2 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 H_2 ? (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.