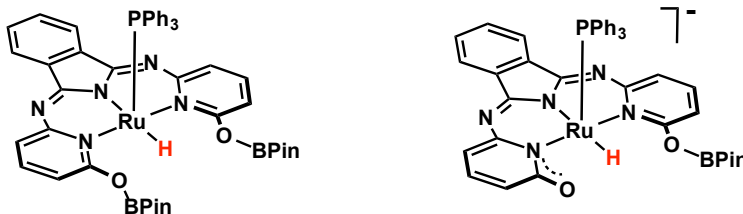


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Hypothesis Generation: The Figure below shows a pair hydroboration catalysts. These only differ in protonation state (make sure you identify where). Using your understanding of basic hydroboration mechanisms from organic chemistry, predict which of the two catalysts is best suited for hydroboration. Provide chemical reasoning for your answer.



The following literature discussion will guide you through the recent report on proton-responsive hydroboration catalysts reported by Geri and Szymczak (*J. Am. Chem. Soc.* **2015**, *137*, 12808-12814 doi: 10.1021/jacs.5b08406). All Figure numbers below refer to images from the manuscript that is an open-source, ACS AuthorChoice paper.

Reactivity

1. Identify what part of each molecule in the Figure above (same as hypothesis handout) would be the nucleophile and rank the compounds in order of increasing nucleophilicity. Justify your answer.
2. For each of the reactions in Figure 3 from the paper, describe the acid-base reaction taking place in words or re-draw the structures and clearly mark the acidic proton and acceptor.
 - a. (*Optional*) Would you predict that O1–H1 in compound **2** changes its conformation to point out into solvent in compound **3**? Briefly explain why or why not.
 - b. (*Optional*) After making your prediction download the CIF files for this paper from the Supporting Information and visualize the structure of **3** using a free software package like Mercury. Is the representation of **3** in Figure 3 misleading when it comes to the chemical reason for this conformational change?
3. Can **2** activate hydrogen? Provide evidence from the paper to support your answer.
4. Which protonation form of the catalyst is responsible for hydrogen activation?
5. Read section “E–H Heterolysis: Reactions and Kinetics”. How did the authors prove the connectivity and H locations in **5**?
 - a. (*Advanced*) Suggest another experiment the authors could do to further support the location of the hydrogen atoms in **5**.

Electron Counting (*Optional*) You can include the linked Learning Object here on electron counting for metal complexes featuring proton-responsive ligands if you want

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your students to practice that for the species in Figure 3. Link: [Kecking over Electron Counting Formalisms? An In-Class Exercise in Counting Electrons for Ru Complexes with Proton-Responsive Ligands in the CBC and Ionic Methods](#)

Symmetry (*Optional*)

1. What is the point group of **1–4**, based on the ChemDraw cartoons, as drawn in the Figure 3? Sketch a key symmetry operation (superimposed on the molecule) for each to justify your answer.
2. Does the NMR agree with your point group assignment for **2**? Support your answer with data from the paper.
3. What feature revealed in the X-ray structure potentially explains the lower symmetry of **2** compared to its solution structure?
 - a. (*Advanced*) Explain the physical origin for this discrepancy.

Catalysis

1. Look at the author's proposed mechanism in Figure 6. What protonation state of the metal-ligand complex do they suggest is responsible for hydroboration catalysis?
 - a. (*Optional*) Have the students discuss whether the proposed mechanism is an inner- or outer-sphere hydroboration mechanism. See the linked Learning Object if you need to introduce your students to inner- vs. outer-sphere reactivity.
2. Draw the structure of the borane (HBPin) used in the reaction mechanism in Figure 6.
3. Think back to your sophomore level organic course. If NaBH₄ was to reduce a nitrile, what part of that molecule acts as the nucleophile? What part acts as the electrophile?
4. Compare this to the transition state on right hand side of Figure 6. What part of the molecule is the nucleophile? What part of the molecule is the electrophile?
 - a. (*Optional*) Suggest a role of the 2-pyridone arm in stabilizing this transition state.
5. How does the protonation state of the Ru complex (**1**) enable or inhibit the hydroboration of nitriles as shown in the mechanism in Figure 6?

Hypothesis Revision (*Optional*) At this point you have a lot of information about how this catalyst works and how the different protonation states affect its reactivity. Revisit your original prediction about which of the two catalysts is best suited for hydroboration reaction. Provide chemical reasoning for your answer. You may want to consider how protonation influences the nucleophilicity of the catalyst.

Catalytic Activity

1. Compare the redox potentials of **1**, **2**, and **3**. Provide an explanation for the differences in potentials using electronic arguments.
2. Do you think the redox potentials of compounds **1**, **2**, and **3** relate to the nucleophilicity of each compound? Briefly explain why or why not.
3. Briefly describe in words the reaction equation in Figure 5.

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4. What is meant by turnover frequency (TOF)? You may need to search for a meaning for this term as it is not defined in the manuscript.
5. Figure 5 compares the TOFs of different catalysts. Based on the TOF for **1**, **2**, and **3**, which is the best catalyst?
 - a. Revisit your answer to Question 2 in this section. Did you predict this result?
6. The authors report TOF values for **7**, **8**, and **9** relative to **1**. Briefly explain whether a large or small number indicates that the catalyst is better than **1**.
7. Does 4-methylphenolate (**9**) catalyze this reaction? Provide evidence to support your answer.
 - b. (*Optional*) Reflect on the mechanism in Figure 6. Would you classify that as an inner- or outer-sphere mechanism? Does the catalytic behavior of **9** support or refute this mechanism?
4. Read the “Mechanistic Analysis” section. What experimental evidence do the authors provide to support the proposed mechanism in Figure 6? Be specific in your answer by providing statements and spectroscopic evidence that they used to reach this conclusion.
 - c. (*Optional*) How did the authors rule out the role of Ru nanoparticles in this catalysis, which are commonly formed under reducing conditions such as those they employed?

Reflection Write a paragraph analyzing the differences between your original prediction and your final prediction. Additionally, summarize the key chemical lessons that you learned in the process of reading this article.