###### PCET and Pourbaix

*To prepare for discussion, write out the answers to these questions and bring them with you to class.*

These questions are based on a figure from Rountree *et al.* *Inorg. Chem.* **2019**, *58*, 6647. In this work, Jillian Dempsey’s group at the University of North Carolina examined the mechanism by which a nickel-containing catalyst brings about the reduction of H+ to form H2.

1. The complex that acts as a catalyst for H2 formation is [Ni(PPh2NBn2) 2]2+.
2. The neutral (PPh2NBn2) ligand is formally named 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclooctane.

The structure of this ligand has been started for you below. Fill in the missing substituents and add lone pair electrons to **all** atoms that could potentially coordinate to the nickel ion.



1. What is the oxidation state of nickel in this complex and how many *d* electrons does it have?
2. When nickel is coordinated by two (PPh2NBn2) ligands (each coordinating through only one type of possible coordinating atom), a quasi-square planar complex forms. This initial complex is called [NiII]2+.

Where is this initial complex located on the Pourbaix diagrams in Figure 3 (below)?

3. The authors say that “In abbreviations, an ‘H’ located to the left of Ni in a label indicates the hydrogen is a hydride while an ‘H’ located to the right of Ni in a label indicates it is bound to the ligand.” When hydrogen is a hydride, it is binding directly to the nickel metal center.

1. Draw the Lewis structure of hydride. What is its charge?
2. Look carefully at the diagrams shown in parts A and B in Figure 3. How are they different in terms of which type(s) of H are involved?
3. Pourbaix diagrams are used in environmental chemistry to demonstrate the forms in which an element will exist (also called the element’s speciation) under various pH and environmental potential conditions. In this adaptation, the authors have changed the traditional format so that the diagrams are depicting the applied potential (*y*-axis) vs the pKa of the proton-donating acid (*x*-axis).
4. Start with the [NiII]2+ complex in either of the diagrams shown in Figure 3A or 3B. When you proceed in the direction of increasingly negative applied potential and cross *horizontal* lines on the diagram, what happens to the complex? (You can answer this question without reading the article.)
5. Now start with the [Ni0] complex at the bottom-right corner of the diagram in Figure 3B. As you move in the more acidic direction across the diagram, what happens to the complex?