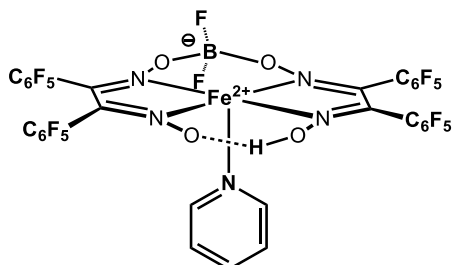


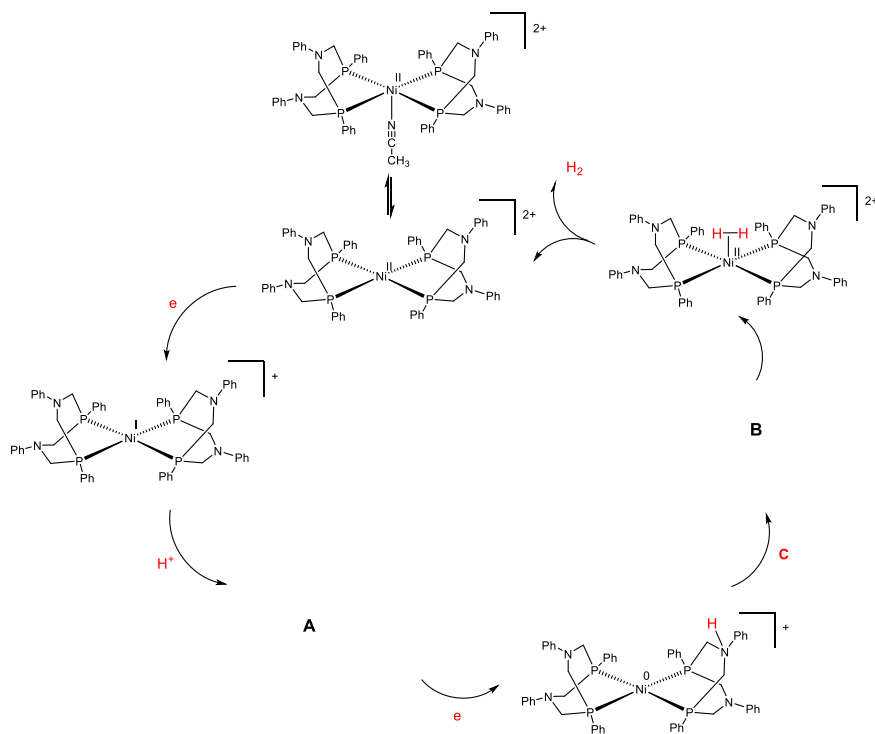
Problem set (exercise) 1

1. The following Fe complex is a molecular electrocatalyst for hydrogen evolution. Propose a bimetallic catalytic cycle for this Fe-catalyzed hydrogen evolution. Specify the oxidation states of the Fe complexes. The initial iron complex before reduction is Fe(II). You don't need to draw the macrocyclic ligand; abbreviate it as "N4", e.g., [FeII(N4)(py)] would be sufficient for the complex in the graph.

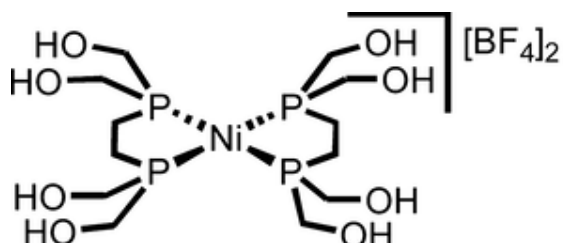


2. The following is a mechanism proposed for hydrogen evolution catalyzed by a Ni complex (you saw it in the class). Some part of the mechanism is incomplete.

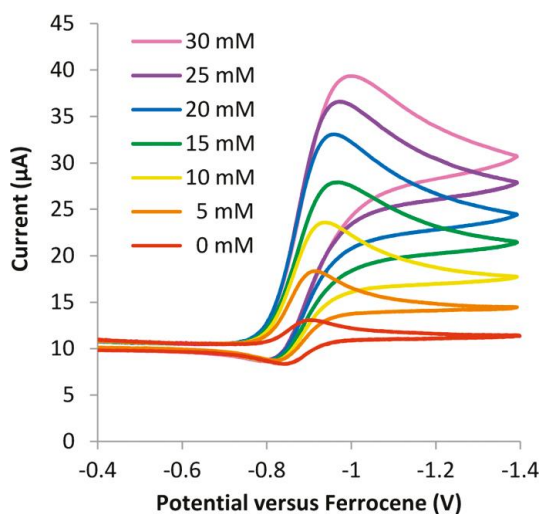
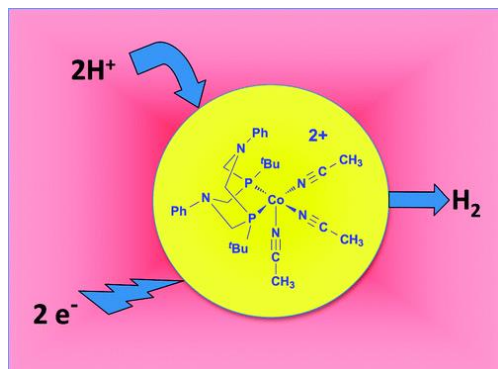
(i) Draw the structures of intermediates A and B. (ii) Label the oxidation state of the Ni in A and B. (iii) What is the reagent C? (iv) Most molecular catalysts operate at high overpotentials, but this catalyst has a high TOF at low overpotentials. Explain why this catalyst can be so efficient?



3. The following complex was shown to be a molecular catalyst for hydrogen evolution in aqueous solution ($\text{pH} = 1$). The function of the hydroxyl groups on the ligand is to enable solubility and stability, but they are not directly involved in catalysis. It was proposed that the first step(s) of catalysis was the reduction of the Ni(II) by 2 electrons to Ni(0). Moreover, the catalysis involved only one nickel center. Based on this information, propose a reasonable mechanism for hydrogen evolution by this catalyst. Please label the oxidation state of the metal in each step. For simplicity, you can represent the starting catalyst as $\text{NiL}(\text{BF}_4)_2$, or $(\text{NiL})^{2+}$.



4. The following figure describes hydrogen evolution catalyzed by a Co complex in acetonitrile. Please answer these questions:

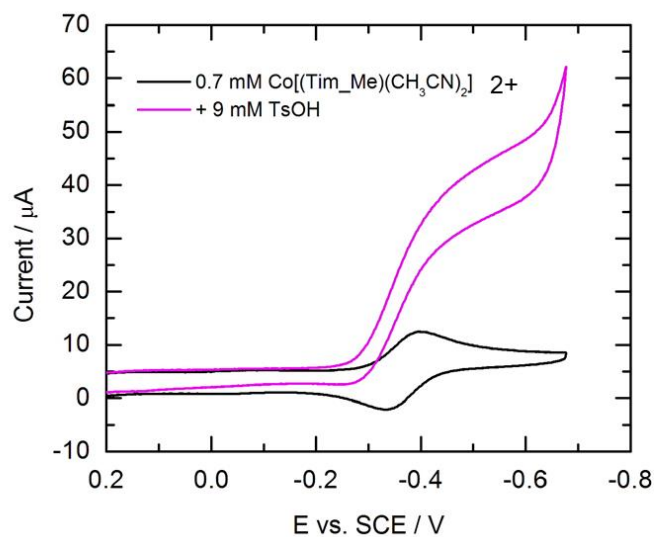
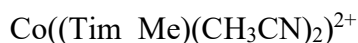
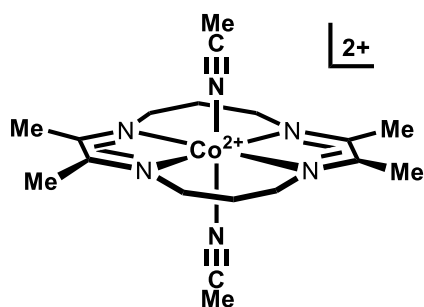


(A): Please label the “catalytic wave” in the above right figure.

(B): $E(\text{HA}) = E(\text{H}^+/\text{H}_2) - 0.059 \times \text{pKa}$. The proton source is 4-bromoanilinium tetrafluoroborate, which has a pKa of 9.43 in acetonitrile. In this solvent, the thermodynamic potential for H^+/H_2 is -0.26 V vs. Ferrocene couple. Based on this information, calculate the overpotential, assuming catalysis occurs at -1.0 V vs. Ferrocene couple. Describe how you get this number.

(C) According to mechanistic study, the catalytic cycle involves only one Co metal. Moreover, a Co(III)-H is involved, and one N atom of the ligand is at some point protonated. Based on this information, propose a catalytic cycle for this system.

5. The following Co complex (called $\text{Co}(\text{Tim_Me})(\text{CH}_3\text{CN})_2$, initially Co is in $\text{Co}(\text{II})$) was shown to be a molecular catalyst for hydrogen.



As shown in the cyclic voltammograms below, the catalysis starts to occur at about -0.4 V vs. SCE, which is close to the potential of $\text{Co}(\text{II})/\text{Co}(\text{I})$. It is known in this system that hydrogen production involves two Co metal ions. Based on this information, propose a mechanism for the reaction. Label the oxidation state of the metal at each step. You can abbreviate the macrocyclic ligand as N4.