

Recommended Reading: 24, 27.1-27.7 (3rd edition); 24, 25.1-25.7 (4th edition)

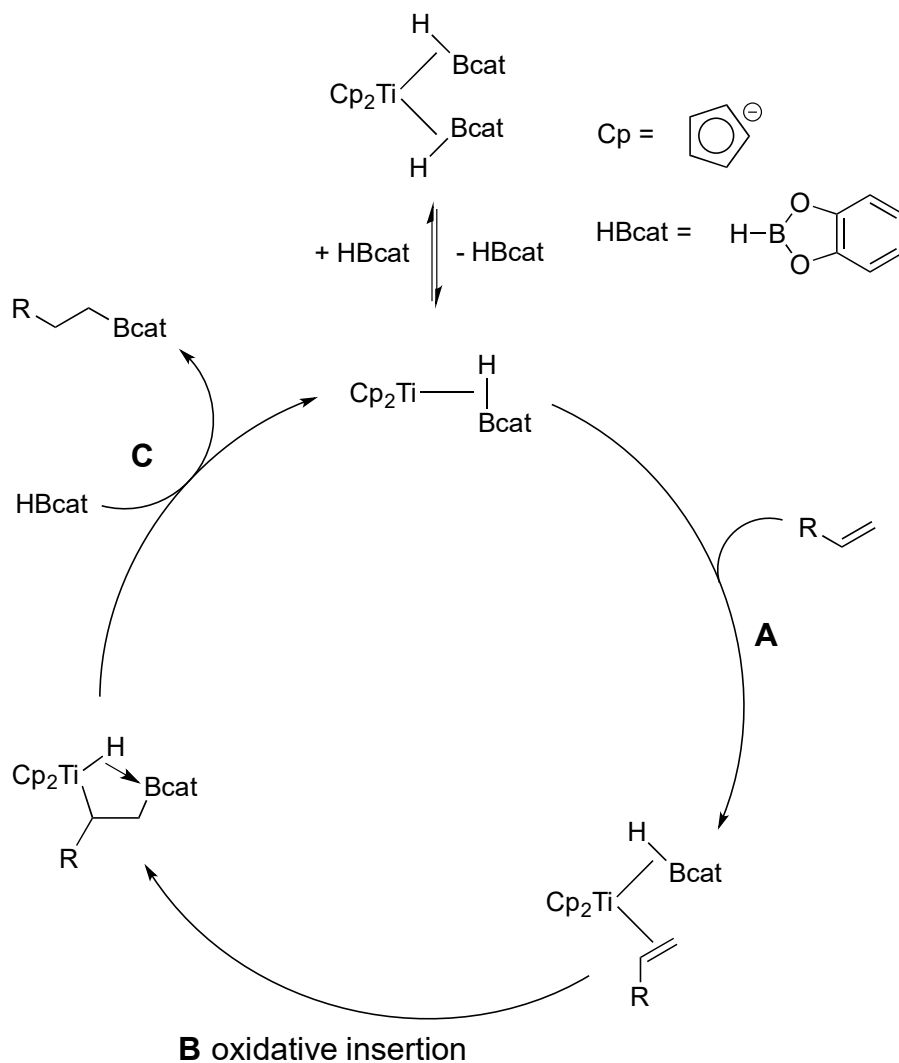
Ch 102 – Problem Set 8

Due: Thursday, June 8 – Before Class

Problem 1 (1 point)

The hydroboration of alkenes is an important transformation in organic methodology. Cp_2TiMe_2 has been reported to act as a pre-catalyst for addition of HBcat across olefins by first generating $\text{Cp}_2\text{Ti}(\text{HBcat})_2$. The catalytic cycle is shown below.

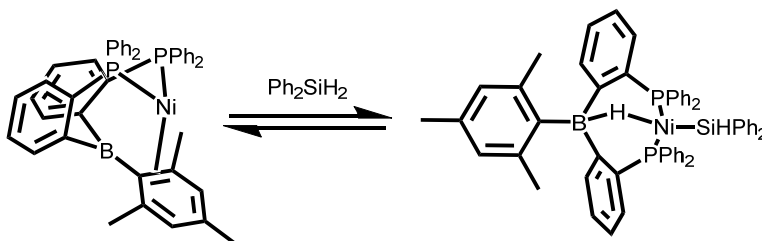
a) For each intermediate, provide the Ti oxidation state, d-electron count, and total valence electron count. Provide the names of the elementary steps for **A** and **C**.



b) Given that steps **B** and **C** are relatively irreversible, what would be the product(s) of the addition of DBcat to 1-decene under the Ti-catalyzed conditions?

Problem 2 (2 points)

- A) The bisphosphine borane nickel compound pictured below reacts reversibly with diphenyl silane to do oxidative addition and reductive elimination of one of the Si-H bonds. Give the valence electron count, d-electron count and formal oxidation state for each of the Ni compounds. (Hint: 4 coordinate boron has a formal charge that must be accounted when counting e⁻.)



- B) The Ni compound pictured above also acts as a catalyst for the hydrosilylation of benzaldehydes (overall reaction shown below). Kinetic measurements showed a linear dependence of the reaction rate on the concentration of the Ni catalyst at 3 different catalyst loadings (1.25 mol%, 2.5 mol% and 5 mol%). Kinetic measurements also showed that the reaction rate was invariant with changing concentrations of Ph₂SiH₂ and *p*-dimethylaminobenzaldehyde. Write a rate law for this reaction consistent with the provided kinetic data.

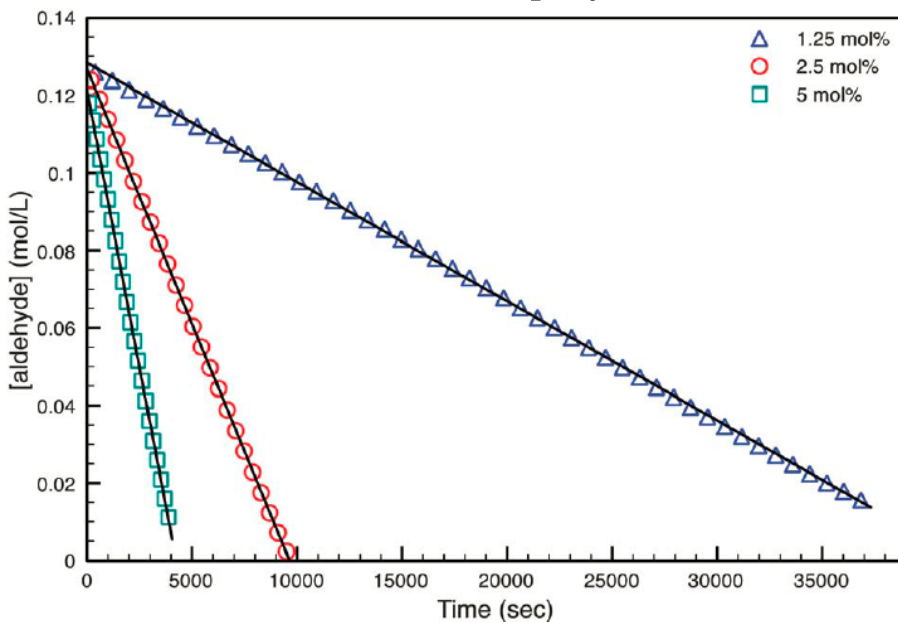
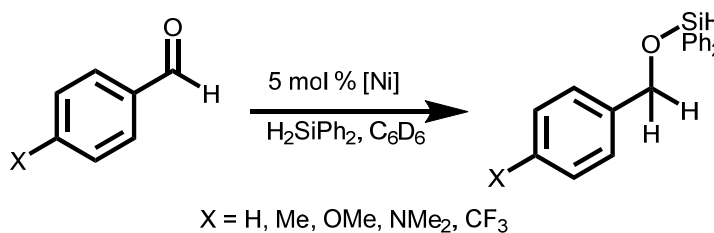
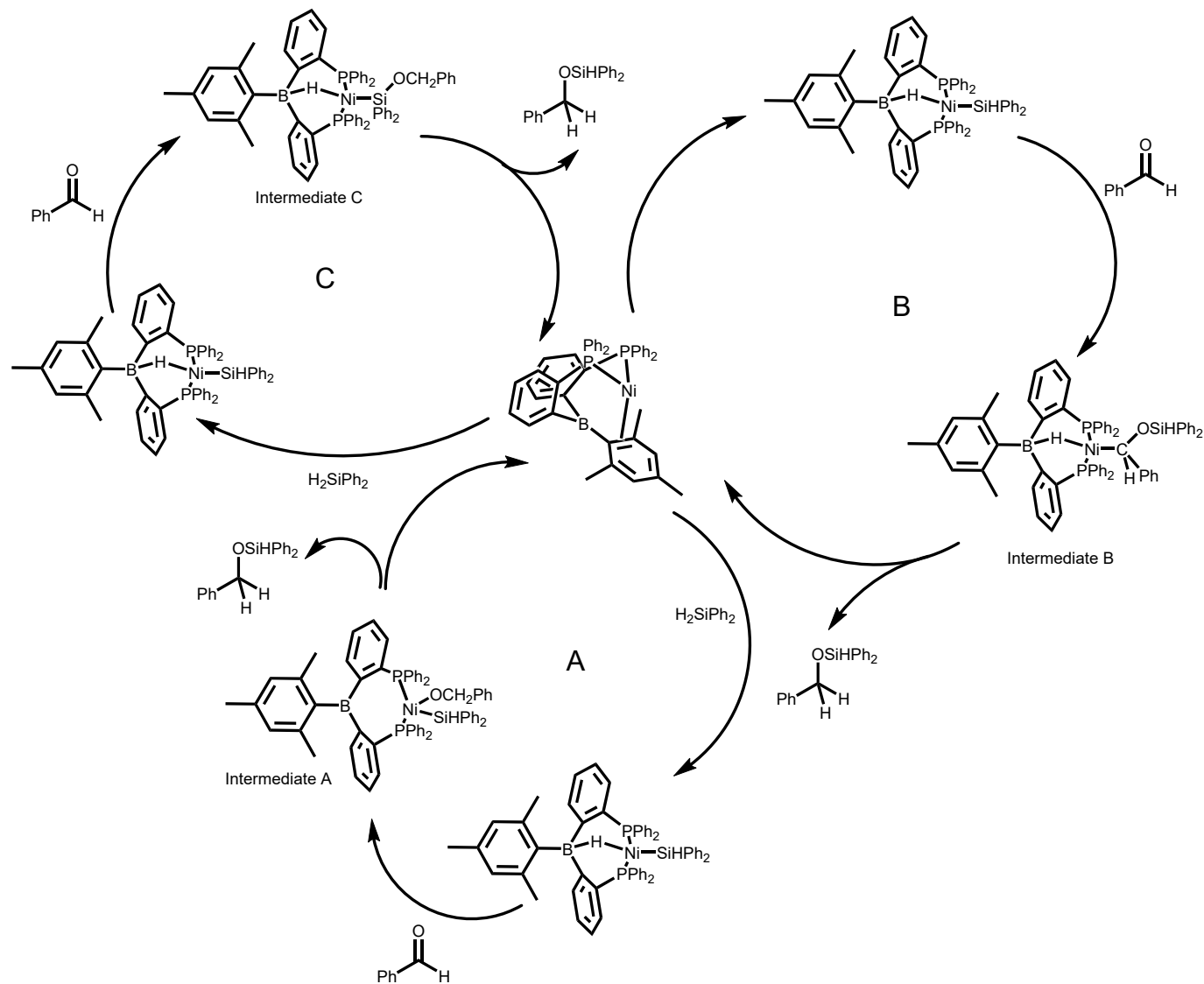


Fig. 4 Plot of aldehyde concentration *versus* time for the hydrosilylation of *p*-dimethylaminobenzaldehyde by 1.25, 2.5, and 5 mol% 1.

C) ^1H , ^{13}C and ^{31}P NMR studies of the catalytic hydrosilylation of benzaldehyde under turnover conditions revealed a diamagnetic intermediate species that displays peaks corresponding to the Ni-diphosphine motif bound to the two reagents upon some chemical transformations. This species was observed to have an up-field resonance consistent with a metal hydride. Using benzaldehyde with a ^{13}C label on the carbonyl carbon a doublet (corresponding to single bond C-H coupling) was observed specifically for this carbon position in the proton-coupled ^{13}C NMR spectrum. Three possible mechanisms are outlined below for the hydrosilylation of benzaldehyde, with proposed structures of the detectible intermediate labeled as Intermediate A, B, or C. Which of the mechanisms is consistent with the experimental data? Explain how you can rule out the other two choices.



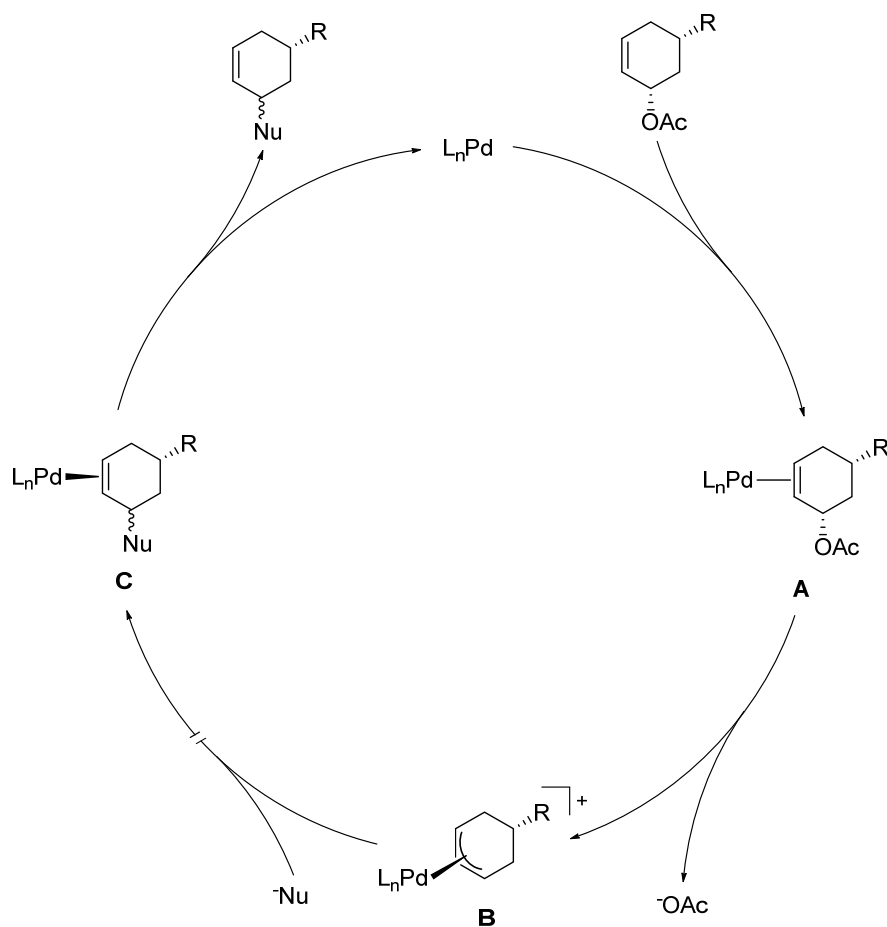
D) For the catalytic cycle you chose in part C identify which step is the rate determining step using your rate law from part B. Label all the elementary steps on your chosen cycle with the type of transformation (sigma-bond metathesis, insertion, α -H abstraction etc...)

Problem 3 (2 points)

Part I

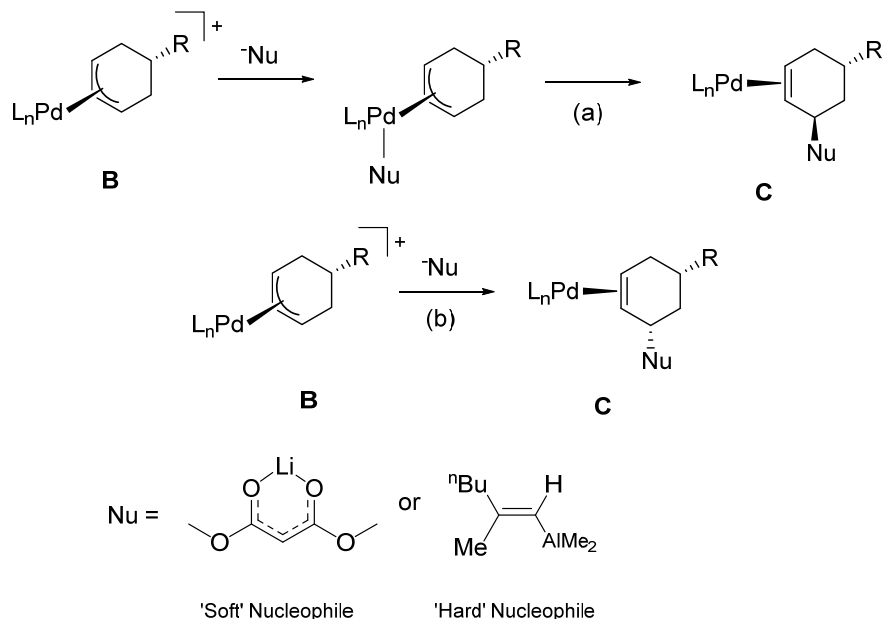
Reactions with allylic electrophiles can suffer from unpredictable regio- and stereo-selectivities. A common example of selective additions to allylic organic fragments include Michael addition to α,β -unsaturated ketones. The Tsuji-Trost reaction is an example of a transition-metal catalyzed allylic addition reaction which can occur with predictable regio- and stereospecificity (Scheme 1). In this reaction, a palladium (0) catalyst forms an η^3 - π -allyl complex with an olefin adjacent to a leaving group (either halogens, carbonates, or, shown below, esters). Nucleophilic addition (often a carbon nucleophile, but sulfur, nitrogen, and phosphorous nucleophiles are also reported) is accomplished to afford substitution at the allylic position.

Scheme 1



In the case of the substrate above, the nature of the nucleophile determines which face the ring is substituted on. Nucleophiles either substitute via direct attack on the allylic fragment, or through initial binding of the metal center (Scheme 2).

Scheme 2



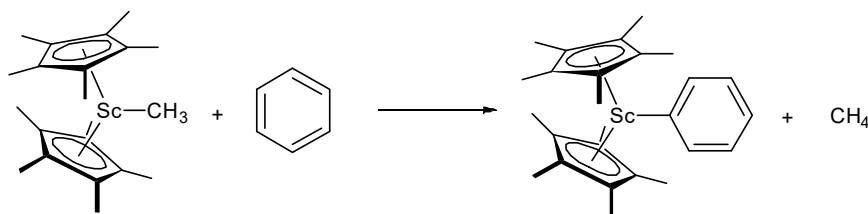
a) For metal complexes **A**, **B**, and **C**, assign valence electron count, metal oxidation state, and d electron counts. Assume L = phosphine and $n = 2$.

b) For the two possible mechanisms of nucleophile addition (Scheme 2), provide the type of organometallic elementary transformation in steps (a) and (b).

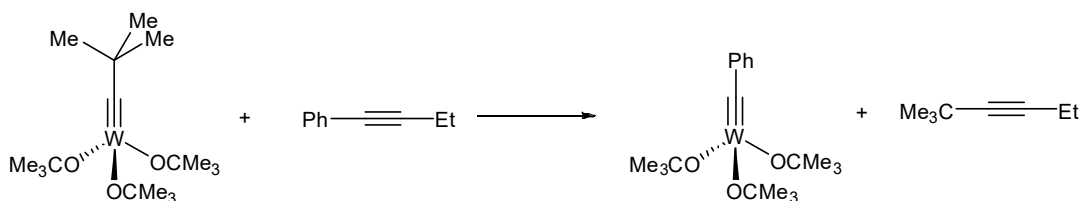
Part II

For the reactions given below, name the type of elementary organometallic transformation, and provide a mechanism of the reaction including any transition states as discussed in lecture. Provide the valence electron count, metal oxidation state, and d electron count of the metal-containing starting materials.

a)



b)



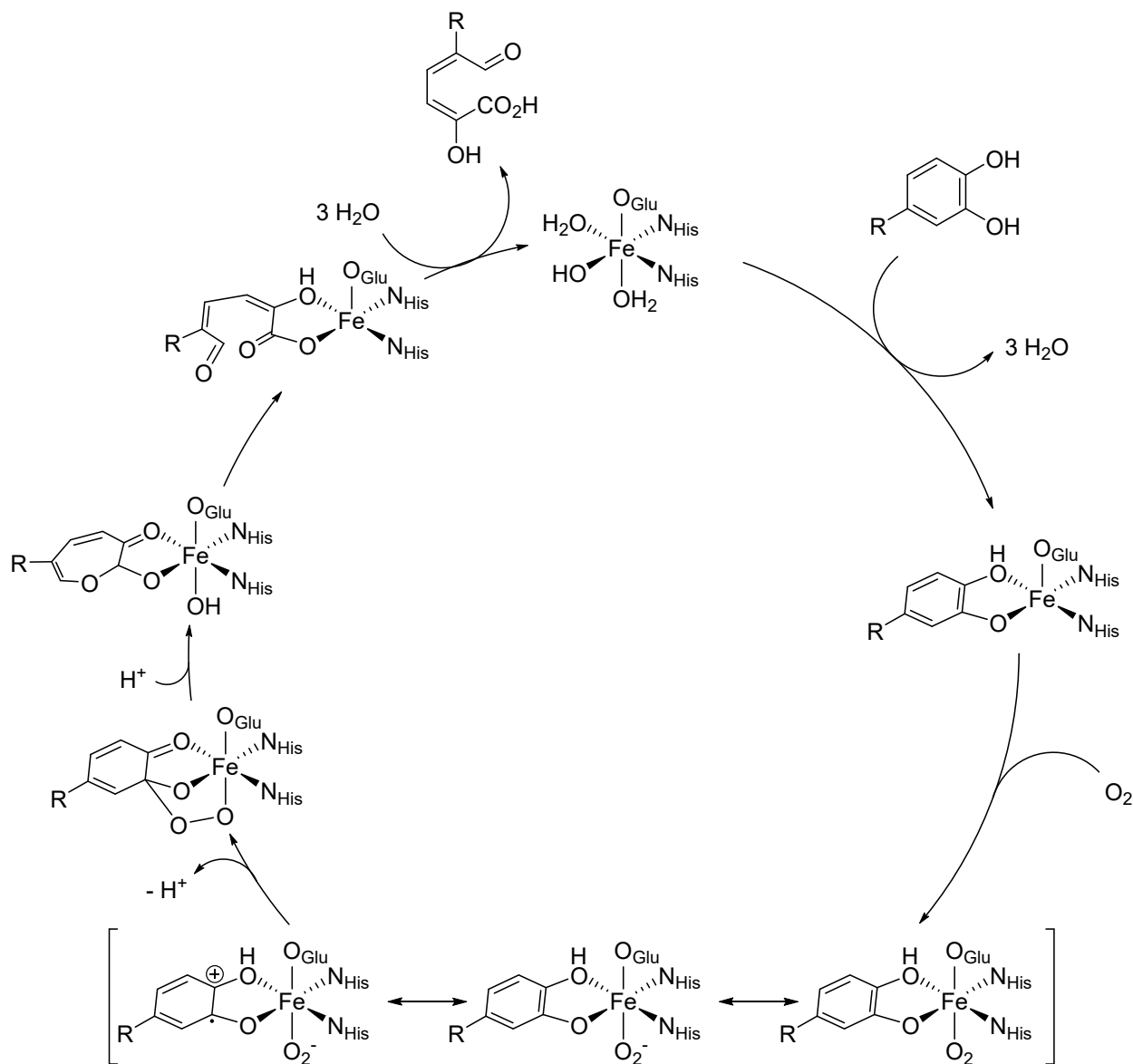
c)



Problem 4 (3 points)

Part I

The structure of the Fe enzyme that conducts extradiol cleavage of catechols was mentioned in class. The enzyme has a tetramer structure. A crystal structure was obtained that captured four unique iron-oxygen species in each tetramer. The catalytic cycle for the Fe-catalyzed oxidation of a catechol substrate in the enzyme is shown below:



a) For the above catalytic cycle, write the overall balanced chemical reaction. Indicate what atoms serve as the net oxidants and reductants in the reaction.

b) Indicate the Fe oxidation state for each intermediate in the cycle. Note that many examples of Fe^{II} are known to react with O₂, while that is not the case for Fe^{III}.

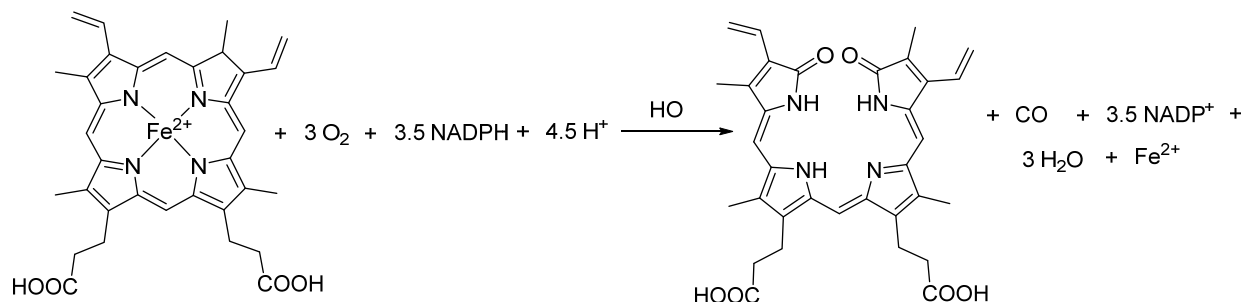
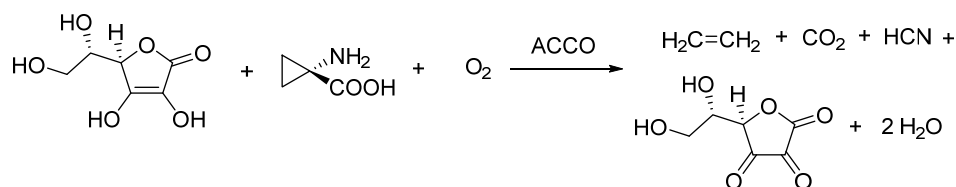
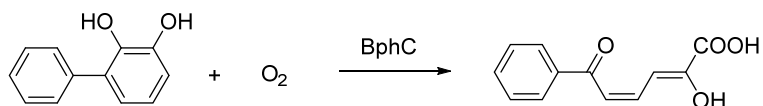
c) Label all O₂-derived ligands as superoxide, peroxide, oxide, etc.

d) If isotopically labeled dioxygen were used in the catalytic reaction, indicate where those ^{18}O atoms would appear in the products.

e) Indicate if the above conversion corresponds to oxidase vs oxygenase reactivity.

Part II

For each of the enzyme-catalyzed reactions listed below: (1) label the oxidizing agents and reducing agents, (2) give the oxidation state of all atoms that have experienced a change in oxidation state, (3) identify the reaction as being carried out by an oxygenase or oxidase enzyme.



Part III

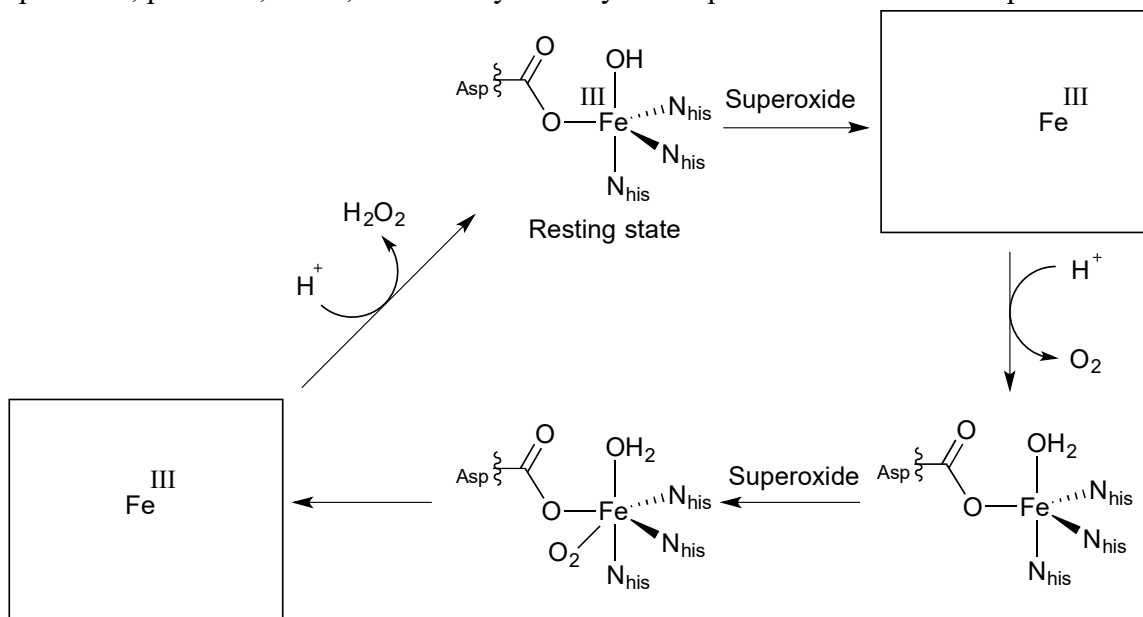
Reactive oxygen species (ROS) such as superoxide (O_2^-) and hydrogen peroxide (H_2O_2) are regarded as deleterious side-products of the normal metabolism of dioxygen. Three important classes of enzymes are responsible for converting such deleterious ROS to innocuous species such as O_2 and H_2O .

- Superoxide dismutases (SOD) catalyze the disproportionation of superoxide to hydrogen peroxide and oxygen.
- Peroxidases catalyze the oxidation of hydrogen peroxide to water.
- Catalases (peroxide dismutase) catalyze the disproportionation of hydrogen peroxide to water the dioxygen.

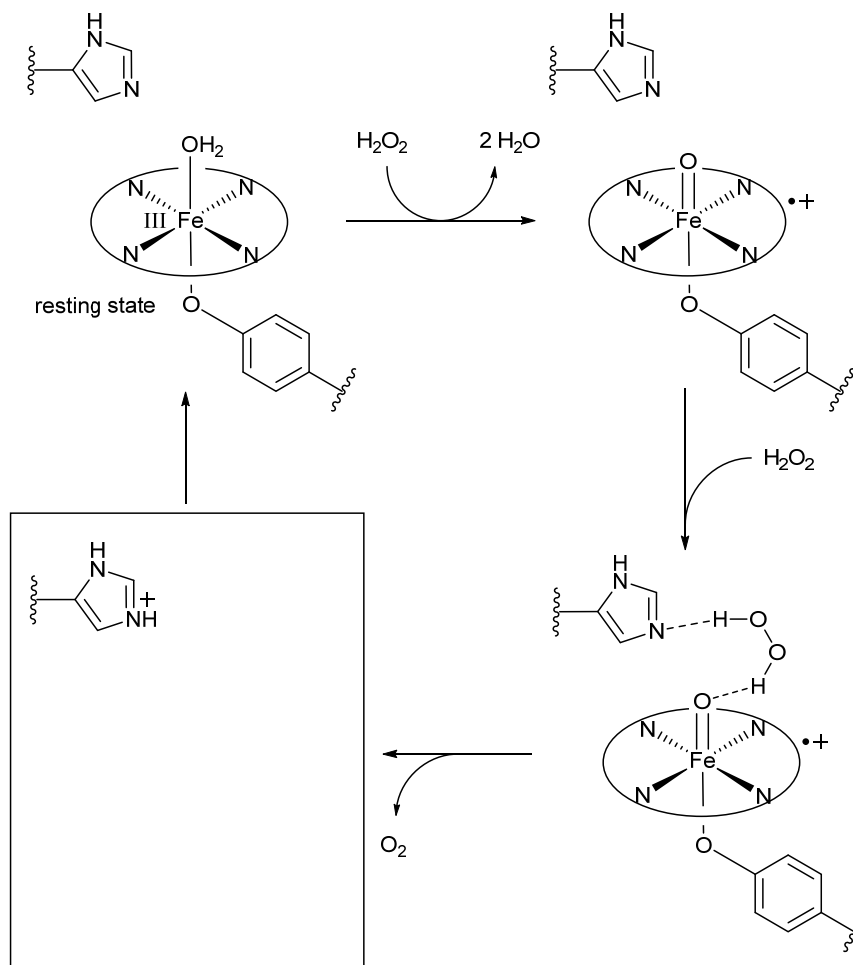
1) Provide balanced equations for the above three processes using protons and electrons as necessary.

Four classes of SODs are known: Fe-SOD, Mn-SOD, CuZn-SOD, and Ni-SOD. An incomplete, proposed mechanism of Fe-SOD is shown below.

- 2) Provide missing structures and assign oxidation states to all Fe centers. Label the O₂-derived ligands as superoxide, peroxide, oxide, etc. Clearly identify the steps that involve a redox process.



- 3) The identity of the axial ligand has an important effect in the reactivity of Fe porphyrin cofactors, as mentioned in class. The active site of catalase enzymes have a phenoxide donor from a Tyr residue. Furthermore, there is a conserved His residue near the Fe center. Provide missing structures and assign oxidation states to all Fe centers in the scheme below.



Problem 5 (2 points)

Pick a topic of interest from the recommended reading (descriptive chemistry) in bold at the beginning of this problem set. Prepare two power point slides including relevant *descriptive chemistry* (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, electron count, symmetry, MO theory, vibrational spectroscopy, etc.) and some application of the provided software (since MO theory and vibrational spectroscopy were covered in class, you are now expected to include some molecular orbital pictures / MO diagram analysis / IR / Raman analysis). Attach a printout of the slides to your solution of the problem set, and email the TAs the slides in pdf format by 12:00 noon on the due date. Please format file names as "FirstName_LastName_PSET#" and include your name on the first slide.