

Print Name: _____

2 HOURS TO ANSWER ALL 3 QUESTIONS

EACH QUESTION IS COMPOSED OF 3 SECTIONS (A+B+C)

EACH SECTION CARRIES 10%. EACH QUESTION CARRIES 30% TOTAL

AN ADDITIONAL 10% WILL BE AWARDED

BASED UPON THE FOLLOWING REQUIREMENT:

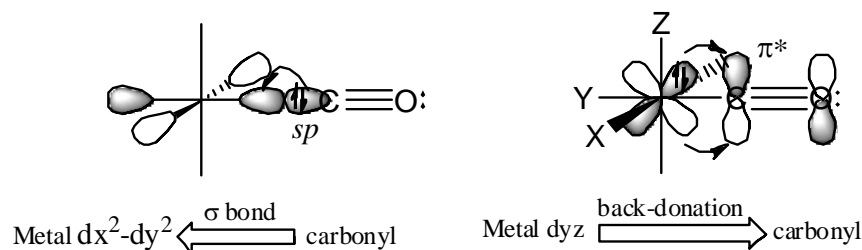
Wherever possible give further details to illustrate any specific point you would like to get across and justify your answer. This may include:

- **metal oxidation state**
- **coordination number and complex geometry/symmetry**
- **total valence electron count of the complex (18VE rule)**
- **a metal-ligand bonding schematic**
- **a description of the steric/electronic nature of reagent and/or substrate**
- **additional intermediates not explicitly shown in a catalytic cycle.**

Question 1

- a) Explain the below trend in CO bond vibrational frequency $\nu(\text{CO})$ using the Dewar-Chatt-Duncanson model.

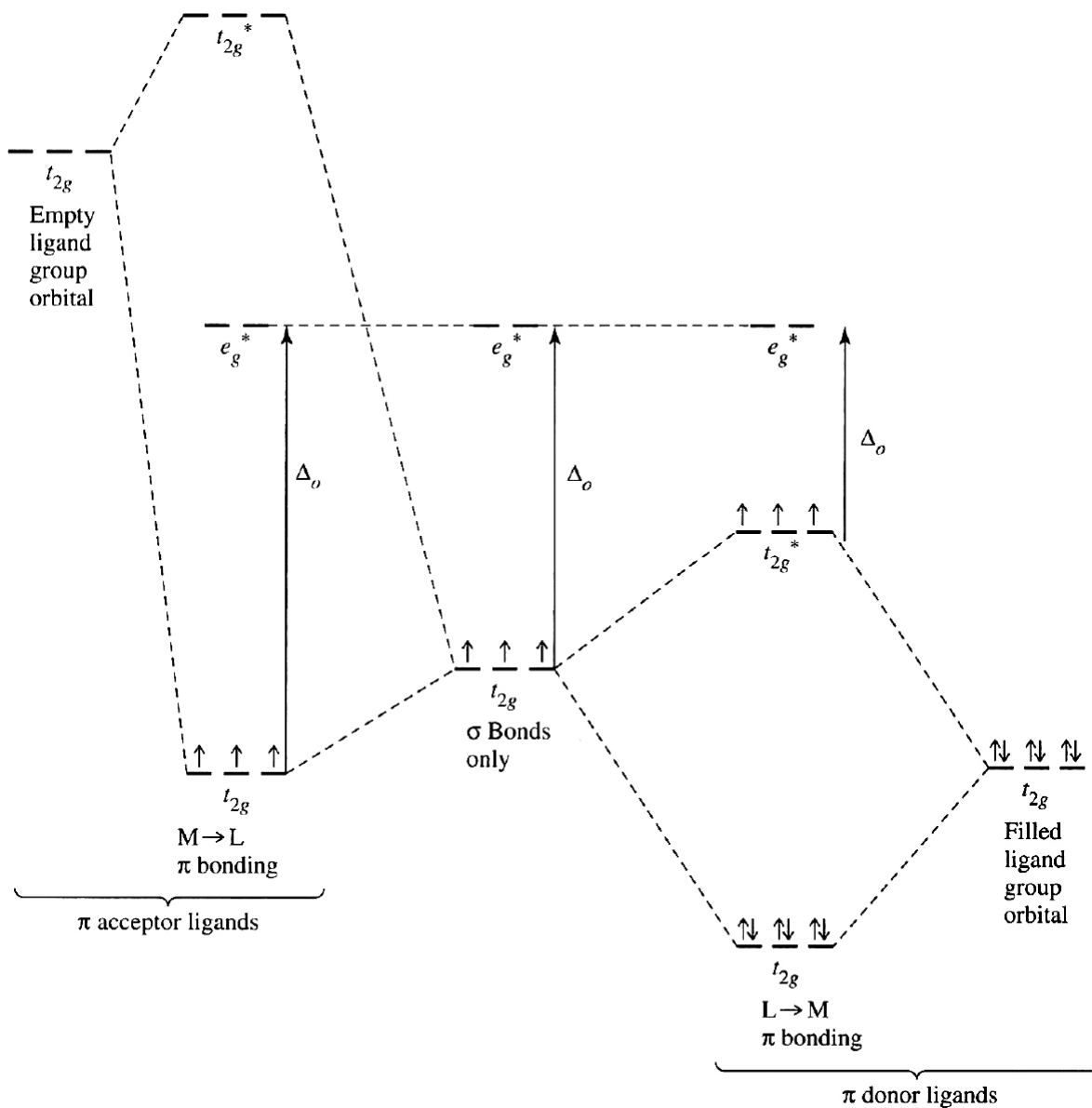
	$\nu(\text{CO}) \text{ cm}^{-1}$
$[\text{Ti}(\text{CO})_6]^{2-}$	1748
$[\text{V}(\text{CO})_6]^-$	1859
$\text{Cr}(\text{CO})_6$	2000
$[\text{Mn}(\text{CO})_6]^+$	2100
$[\text{Fe}(\text{CO})_6]^{2+}$	2204



- all complexes have CN = 6 and are of O_h symmetry.
- all complexes are metal hexacarbonyls
- all complexes have 6 d -valence electrons

As we progress from Ti(2-) to V(-) to Cr(0) to Mn(1+) to Fe(2+) the electron count on the nuclei is identical however the proton count at the central nuclei increase resulting in a net increase in electronegativity as we follow the above trend. The increase in electronegativity reduces the extent of π -back-donation from the central metal d_{xy} , d_{xz} and d_{yz} orbitals such that population of the $t_{2g} \pi^*$ ligand SALC orbitals is reduced. Reduced population of the $t_{2g} \pi^*$ ligand SALC orbitals on CO therefore gives rise to a higher bond order between carbon and oxygen (somewhere between 2 and 3). This can be observed via an increase in the $\nu(\text{CO})$ stretching frequency in the IR spectrum. This is most obvious, for example, if we compare the least electronegative metal center Ti(2-) where $\nu(\text{CO}) = 1748 \text{ cm}^{-1}$ relative to the most electronegative metal given in Fe(2+) where $\nu(\text{CO}) = 2204 \text{ cm}^{-1}$.

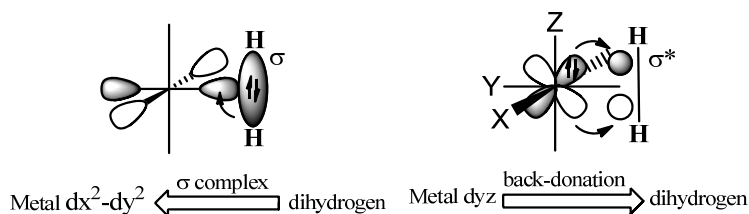
- b) For an O_h complex draw the influence π -acceptor and π -donor bonding interactions on the frontier orbitals.



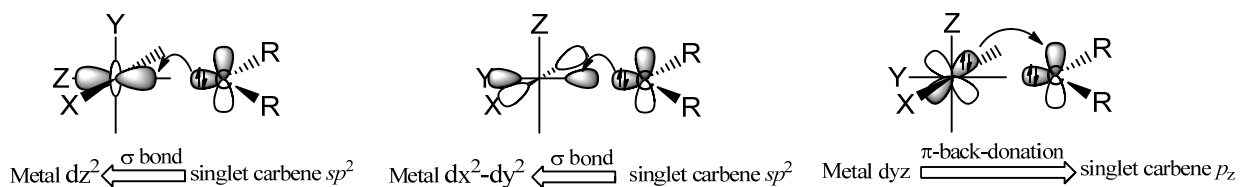
π acceptor ligands result in $M \rightarrow L$ π bonding, a larger Δ_o favoring low spin configurations with an increased stability. π donor ligands result in $L \rightarrow M$ π bonding, a smaller Δ_o favoring high spin configurations and a decreased stability.

c) Using molecular orbitals draw the bonding scheme for the following classes of metal complex, inclusive of any π -bonding:

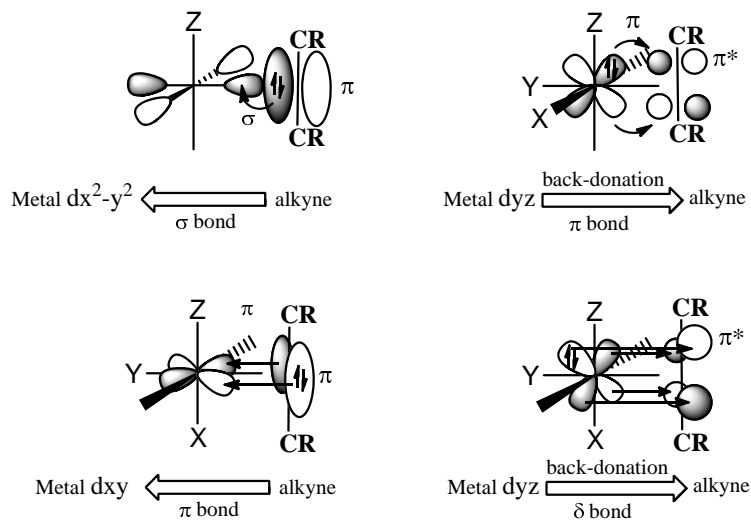
i) Metal dihydrogen complex



ii) Fischer carbene



iii) Metal alkyne

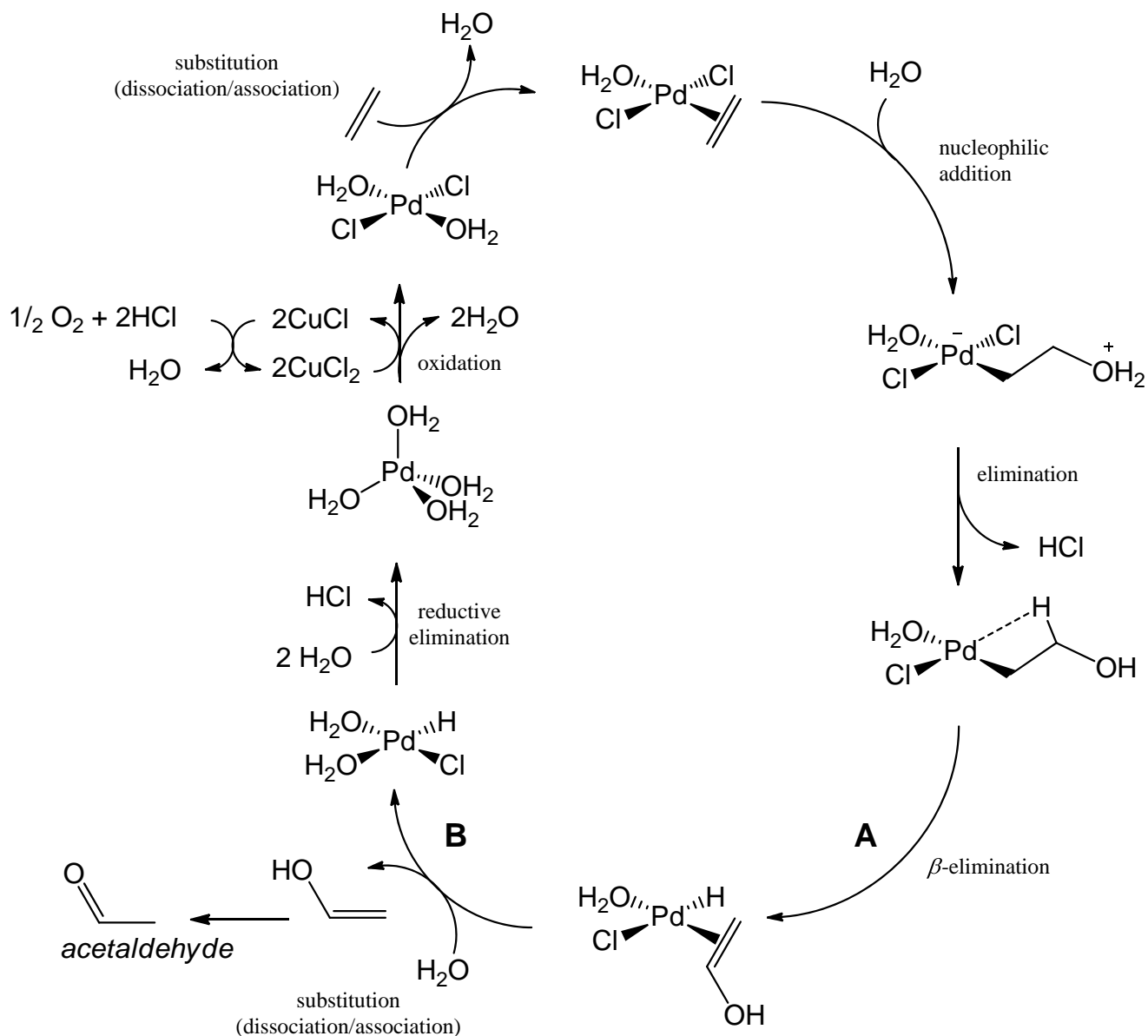


Question 2

a) Below is the catalytic cycle for the Wacker oxidation process.

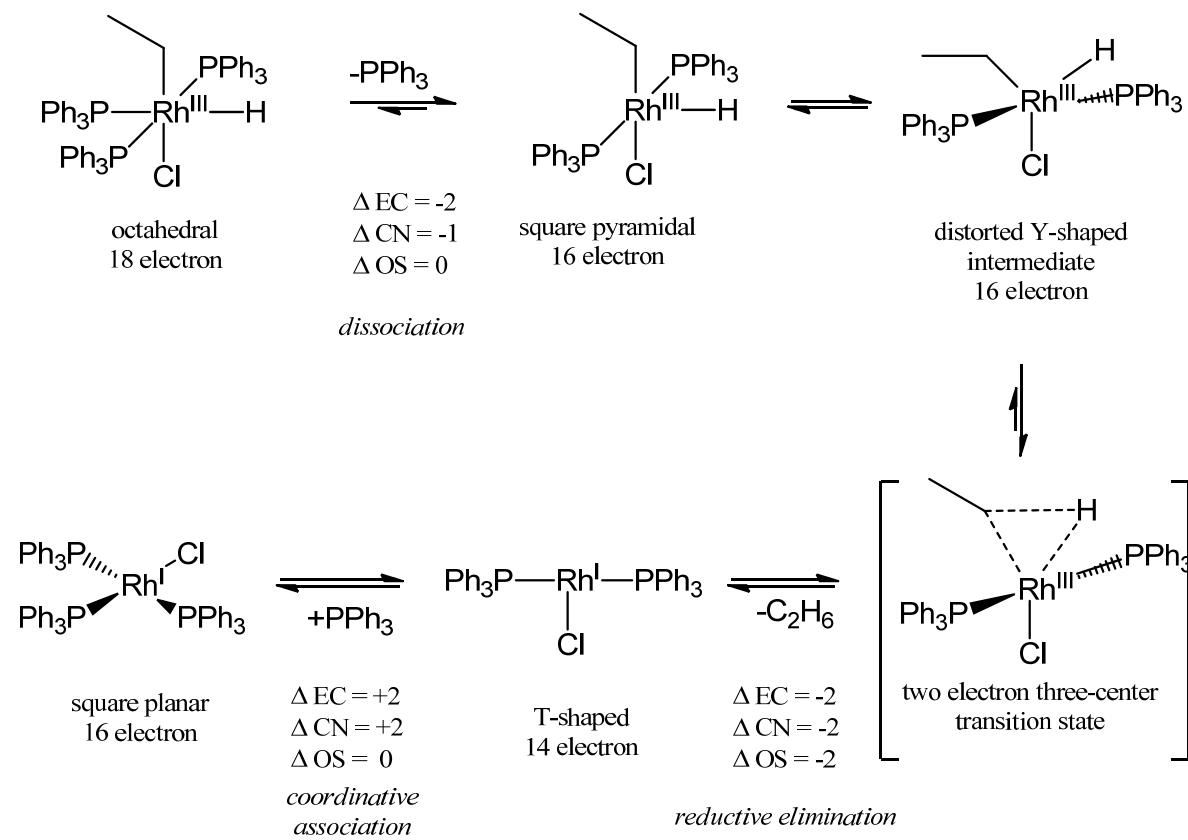
Determine catalytic intermediates following reactions A and B.

What role does CuCl_2 play in the catalytic cycle.

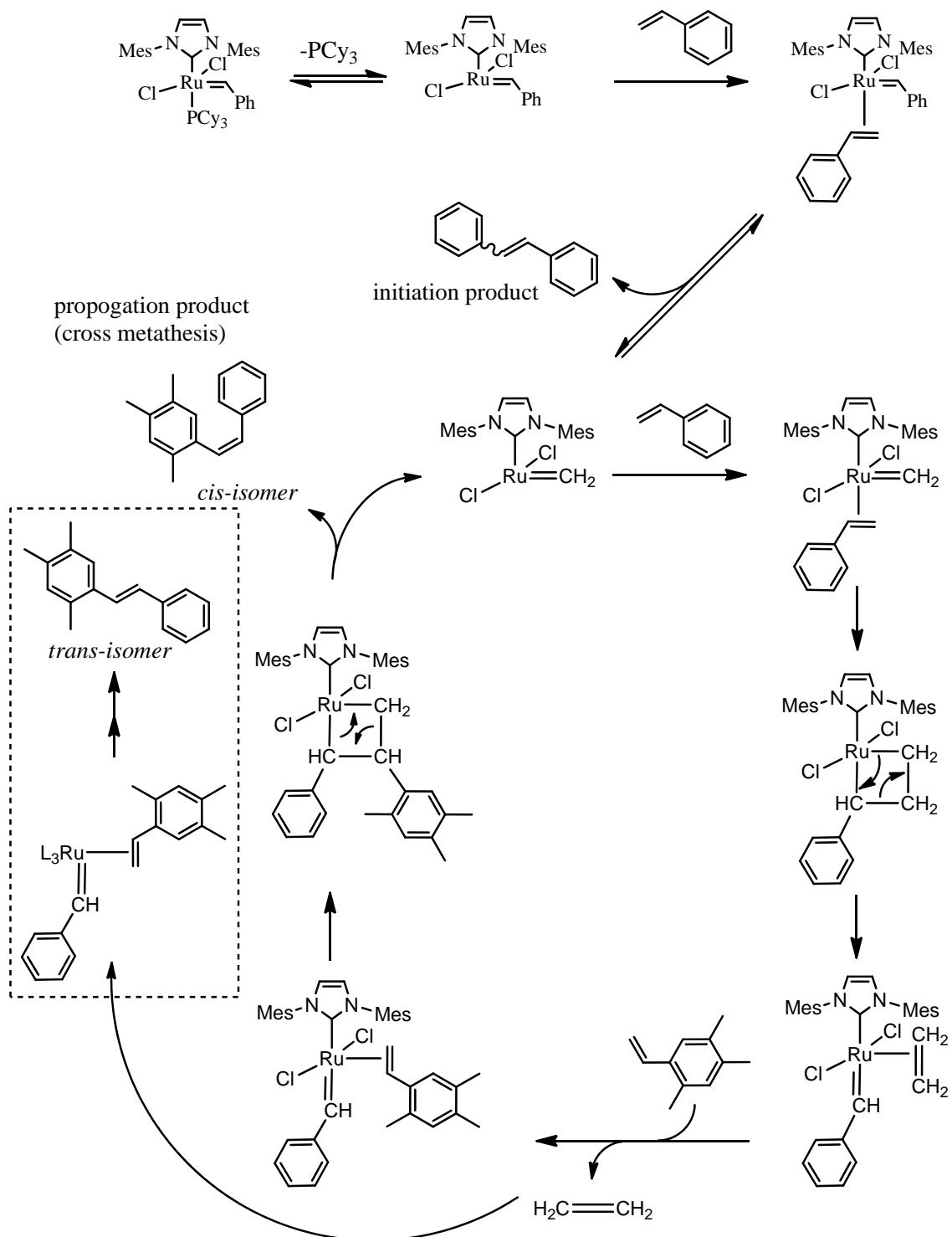


CuCl_2 is used as an oxidizing agent to regenerate Pd(II) in a stoichiometric (2:1) redox reaction producing two equivalents of cuprous chloride CuI . The latter complex is air sensitive and is reoxidized back to Cu(II) in the presence of O_2 and HCl .

- b) Draw the kinetically favored reductive elimination mechanism for the following complex.

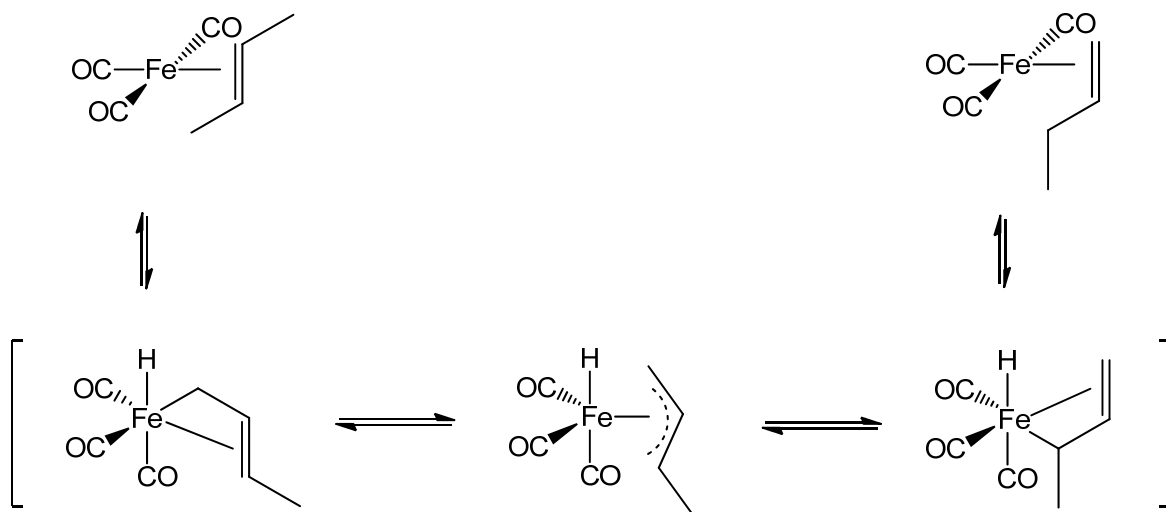


c) Draw a complete catalytic cycle for the following reaction.



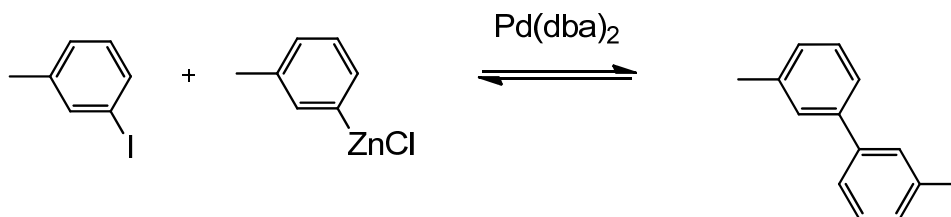
Question 3

a) Draw a mechanism for the following isomerization.

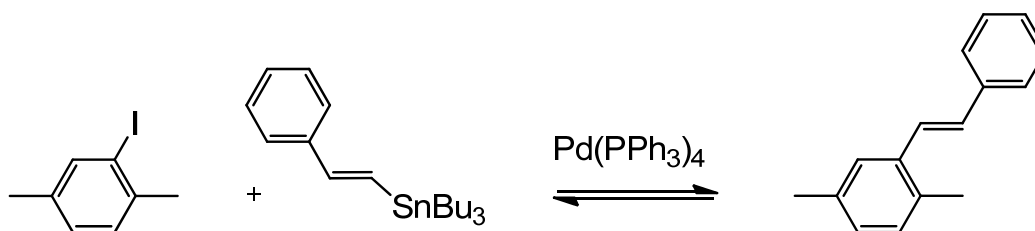


b) Name each of the following reactions accordingly and suggest anticipated products

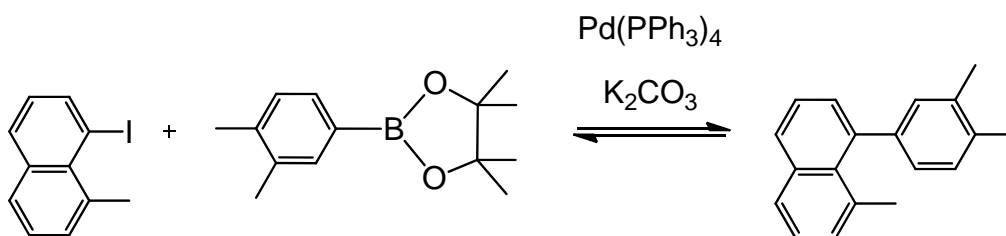
Negishi coupling



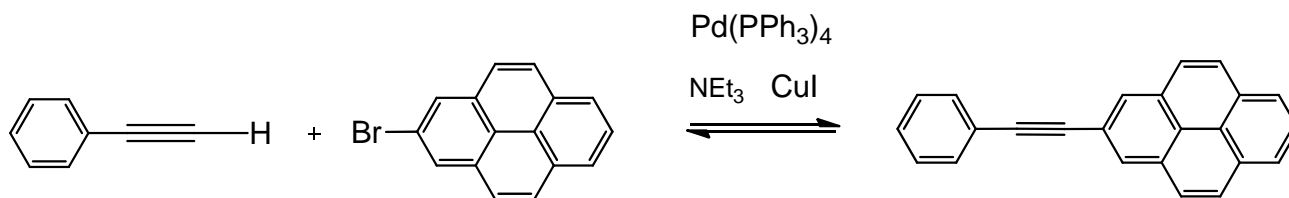
Stille coupling



Suzuki-Miyaura coupling



Sonogashira coupling



c) Draw a complete catalytic cycle for the final reaction from 3(b)

