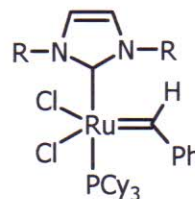


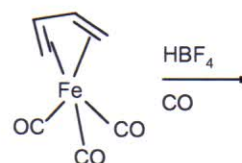
General: Provide for every metal compound the electron count, the number of d-electrons and the formal oxidation state of the metal. In mechanisms do not perform two steps in one – give each separate step. Name every reaction step. Please write legibly (do not use a pencil), if I can't read it, it's considered to be wrong.

1. Given are the compounds $[\text{Pd}(\text{H})\text{CO}(\text{PR}_3)_2]^+$ and $[\text{Pt}(\text{Cl})_3(\text{NH}_3)_3]^+$.

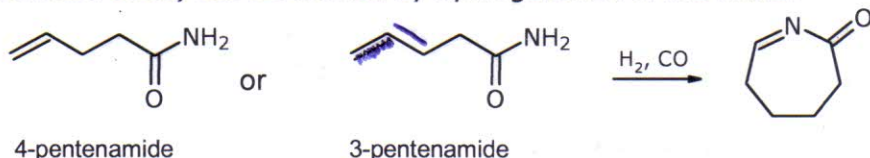
- a. Which charge do you expect for these complexes? Give the electron count, oxidation states and number of d-electrons of the metal centers.
 b. Give electron count, formal oxidation state and number of d-electrons for the Ru complex shown, in both the Fischer and Schrock models.



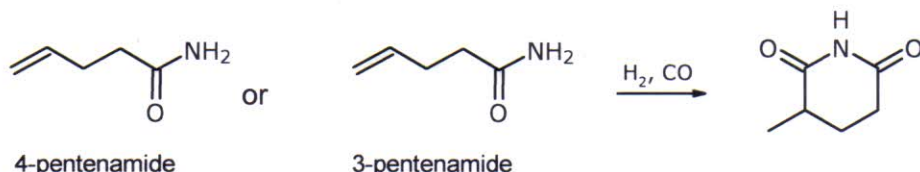
- c. Describe the differences of these models.
 d. Describe the three possible mechanisms for the activation of H_2 at a metal center.
 e. Describe the different binding modes of NO with the formal charges in the ionic electron count. Give the electron count of the compound $[\text{Re}(\text{CH}_3)(\text{CO})(\text{Cp})(\text{NO})]$. What is the formal oxidation state and number of d-electrons of Re?
 f. Give the electron count, oxidation state and number of d-electrons for the iron compound shown. Draw the product that is formed in the reaction and give the electron count, oxidation state and number of d-electrons for the product.



2. We have developed various catalyst for the derivatization of pentenamides, which can potentially be derived from biomass. The reactions are carried out in diglyme (an unreactive ether: $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$) in the presence of a strong acid under a CO/H_2 atmosphere. When using the catalyst precursor $[\text{Rh}(\text{COD})\text{Cl}]$ and a large bidentate phosphorus ligand the following reaction takes place. The product is interesting as caprolactam (a nylon precursor that is produced on Mton scale) can be formed by hydrogenation of the imine.



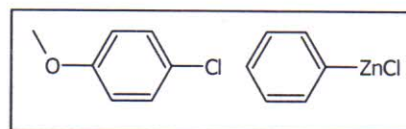
- a. Which three reactions need to take place to make this imine product? Write out the equations and name the reactions.
 b. Provide a mechanism for the first reaction, catalyzed by rhodium.
 c. Provide a mechanism for the second rhodium-catalyzed reaction.
 d. Only low selectivity to the product is obtained when starting from 3-pentenamide, whereas a high selectivity is obtained starting from 4-pentenamide. The undesired product is not the branched isomer, but another product. Can you suggest which product that could be?
 When using the catalyst precursor PdCl_2 and a large bidentate phosphorus ligand the following product is formed instead.



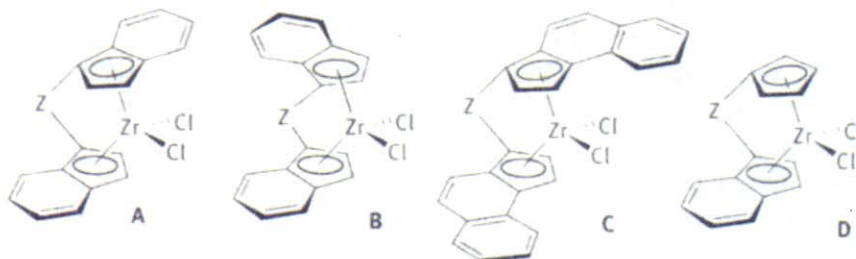
- e. Which reaction needs to take place to make this imide product? Write out the equation and provide a name for the reaction.
 f. Provide a mechanism for this palladium-catalyzed reaction. Can you think of an explanation why the 7-membered ring is not formed?

Organometallic Chemistry and Homogeneous Catalysis

3. In the Negishi coupling reaction a C–C bond is formed between an aryl halide and an organo-zinc reagent. The reaction is catalyzed by complexes such as P_3Pd (P = monodentate P -ligand).

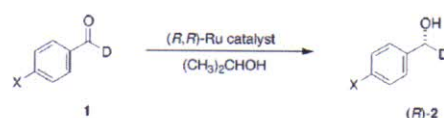


- Compose a possible mechanism for this reaction using the substrates shown in the figure; provide the electron count and oxidation state of the intermediates and name the reaction steps.
 - Complexes such as P_2NiCl_2 can also be used as catalyst precursor. Provide a plausible way for the formation of the active nickel(0) species (NB: avoid the formation of a Ni(IV) intermediate). Which product(s) and side-product(s) do you expect for the two substrates shown?
4. Given the structures of four *ansa*-metallocenes **A–D** in the figure below.



- Provide electron count, formal oxidation state and number of d-electrons of ~~titanium~~ **Zirconium** in the catalyst precursor **A**.
- Rank the compounds from highest to lowest stereoselectivity. Explain your ranking.
- Which of the compounds would give the highest polymer molecular weight? Explain your answer.
- Draw the Fisher projections for the following polypropene pentad structures: i) *mmmm*, ii) *mrrm*, iii) *rrrr*, iv) *mrrm*. How can these pentads be discriminated? What mechanistic information can be obtained from the observation of *mrrm* or *mrrm* pentads?
- The *ansa*-metallocene catalysts give rise to highly linear polymers, whereas late-transition metal catalyst generally give highly branched polymers. Describe the reasons for this difference.

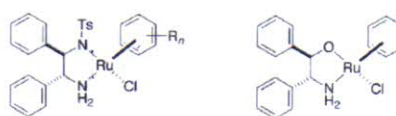
5. The ruthenium compounds shown in the figure (taken from: I. Yamada, R. Noyori, *Org. Letters*, **2000**, *2*, 3425-3427) are good enantioselective transfer hydrogenation catalysts, for which finding Noyori received the Nobel prize in 2001.



- 1
a: X = H d: X = Br
b: X = CH₃ e: X = CF₃
c: X = OCH₃

(*R,R*)-2

- Give the electron count, the number of d-electrons and the formal oxidation state of the metal in compound (*R,R*)-4.
- Provide a mechanism for the transfer hydrogenation shown in the top reaction (**1** → (*R,R*)-2). Watch out: which reagent is missing in the equation? Which byproduct is formed?
- Which byproduct is formed in the reaction shown at the bottom of the figure (**7** → (*S,S*)-2)?
- (Catch-question): Why are the two different enantiomeric products obtained in these two reactions with the same chiral (*R,R*)-catalyst?



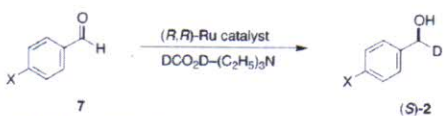
(*R,R*)-3a: η^5 -arene = *p*-cymene

(*R,R*)-3b: η^5 -arene = benzene

(*R,R*)-3c: η^5 -arene = 1,3,5-(CH₃)₃C₆H₃

(*R,R*)-3d: η^5 -arene = (CH₃)₆C₆

(*R,R*)-4



- 7
a: X = H d: X = Br
b: X = CH₃ e: X = CF₃
c: X = OCH₃

(*S,S*)-2

Periodic Table (relevant part)

4	5	6	7	8	9	10	11	12
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd

Re

Pt