Organometallic Chemistry 2023 Exam 1
May 15, 2025; 8:30 AM PST

Directions: This is a closed notes exam. Answer the following questions to the best of your ability. There are **12 questions**, 17 pages, and the exam is **110 points total.** There are 3 bonus questions worth 12 points as part of question 5, question 9 and at the end. You have **2 hours** to complete this exam. All answers must be written on the pages provided. Please write legibly. If you have a question, raise your hand and a TA will come to you.

NAME:____

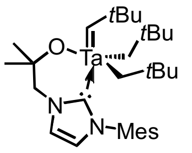
Problem	Available Points	Earned Points
1	13	
2	19	
3	5	
4	7	
5	7	
5 bonus	3	
6	11	
7	9	
8	10	
9	3	
9 bonus	2	
10	6	
11	12	
12	8	
bonus	7	

TOTAL:________________/110 (+12 bonus)

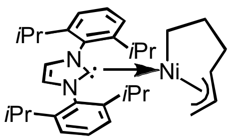
1. (**13 points total, 0.5 point each element**) Fill out the *d*-block on the blank periodic table. *If you are unsure of any of the elements you may ask the TAs for assistance but will receive a penalty.* There are 26 *d*-block elements (ignoring row 12). Please ignore Lanthanum and Actinium.

3	4	5	6	7	8	9	10	11	12
IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB
3B	4B	5B	6B	7B		8		1B	2B
									30 **Zn** Zinc 65.39
									48 **Cd** Cadmium 112.411
57-71									80 **Hg** Mercury 200.59
89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [269]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicium [277]

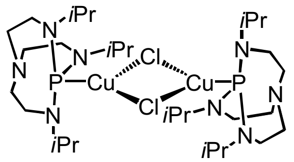
2. (**19 points total, 1 point each**) Provide the metal oxidation state, d-electron count, and overall electron count for each complex. For complex **IV**, please also predict whether there is Ni–Ni bond.



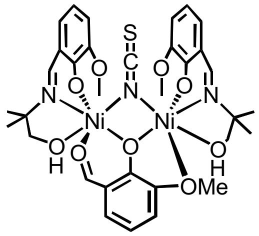
I



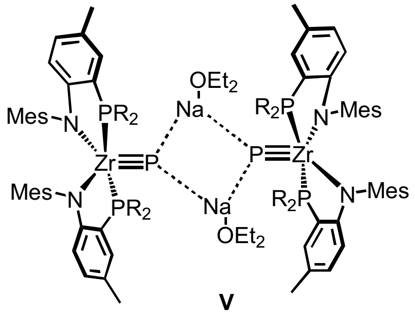
II



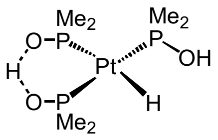
III



IV



V

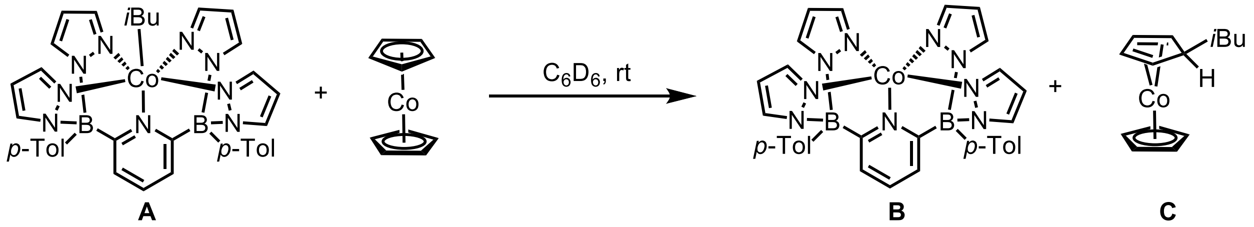


VI

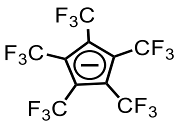
Complex	Metal oxidation state	d-electron count	Total electron count	M-M bond order
I				N/A
II				N/A
III				N/A
IV				
V				N/A
VI				N/A

3. (**5 points total**) The reaction of **A** with cobaltocene at room temperature yields **B** and **C**.

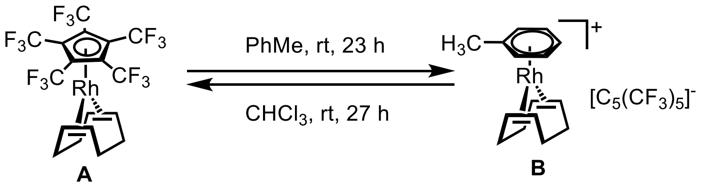
- **a)** Provide the metal oxidation states, d-electron counts, and overall electron counts of all four Co complexes. (**4 points**)
- **b)** Explain why cobaltocene is a good one-electron reductant. (**1 point**)



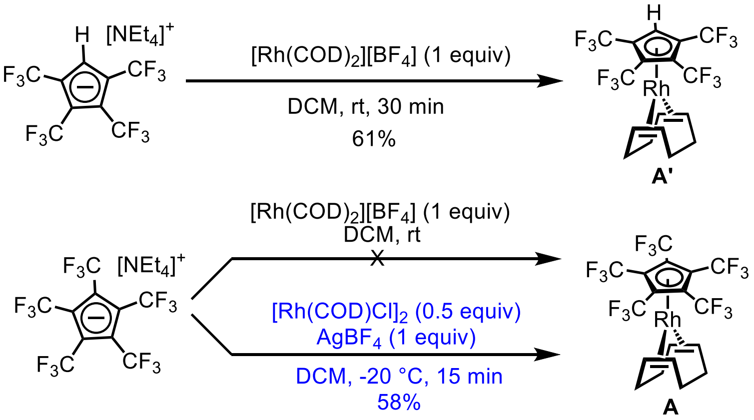
4. (**7 points total**) Rh Complex **A** with a perfluorinated Cp* ligand (structure shown below) was first synthesized in 2022.



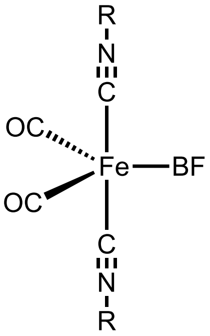
a) When complex **A** was dissolved in toluene, complex **B** was formed, with the perfluorinated Cp* fully displaced by toluene. Complex **B** has toluene as the coordinating ligand, and the perfluorinated Cp* as a weakly coordinated anion (WCA). The reverse of this reaction was achieved by dissolving complex **B** in chloroform. Explain why these two reactions took place. (**3 points**)



b) The reaction of $[C_5(CF_3)_4H][NEt_4]$ with $[Rh(COD)_2][BF_4]$ afforded the Rh complex **A'** with a coordinated tetrakis(trifluoromethyl)cyclopentadienyl ligand. However, subjecting the perfluorinated Cp* anion to the same conditions did not yield the corresponding Rh complex **A**. Instead, another condition (shown in blue) was used. Please explain the different reactivities. (**4 points**)

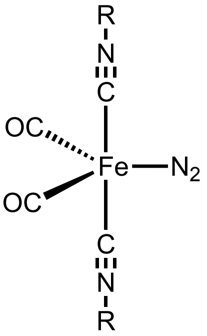


5. (**7 points total, plus 3 bonus points**) The following compound **A** synthesized by the Figueroa lab is a seminal example of diatomic boron monofluoride coordination to metal:



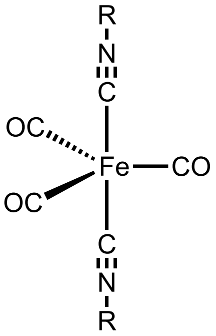
A

v(CN) = 2056 cm^{-1}



B

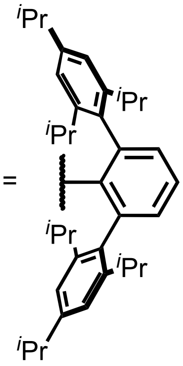
v(CN) = 2075 cm^{-1}



C

v(CN) = 2092 cm^{-1}

R =



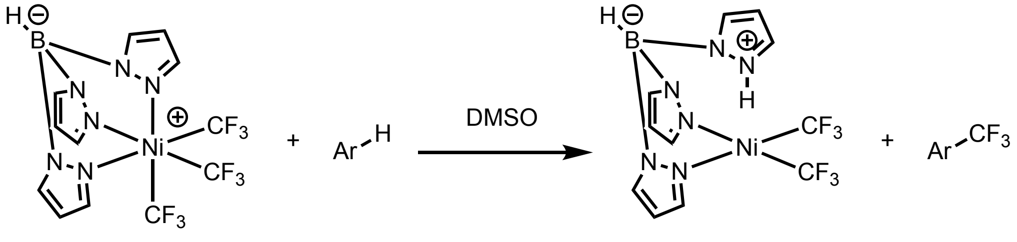
a) Draw out the metal-ligand orbital interactions involved in bonding between iron and the isonitrile ligands in **A**. Please label each orbital drawn. (**3 points**)

b) Order the electron density of Fe in compounds **A** – **C** from most electron rich to electron poor. Explain. (**3 points**)

c) Based on the electron density of Fe, deduce whether BF is a stronger or weaker σ-donor than CO. (**1 point**)

Bonus: DFT calculations revealed that the B–F bond in **A** is most accurately described as a single bond. Would you expect the B–F bond in **A** be longer, shorter, or roughly the same as the B–F bond in the non-ligating BF molecule? Explain. (**3 points**)

6. (**11 points total**) In 2019, Sanford lab reported a Ni-mediated C–H trifluoromethylation.



A **B**

a) For complexes **A** and **B**, **provide the oxidation state of Ni** and match the complexes with the appropriate d-orbital splitting diagram (located in the following page). (**3 points**)

b) Consider all the ligands of **A** and **B** strong field ligands. Fill out the electrons in the orbital splitting diagrams and **predict the magneticity** of each complex. (**4 points**)

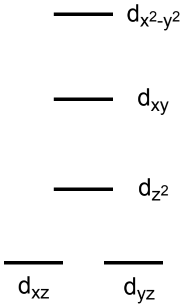


Diagram I

Complex __

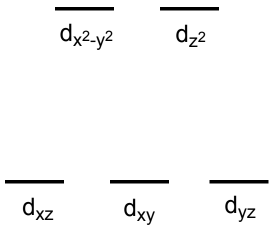
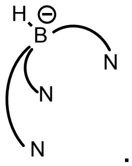


Diagram II

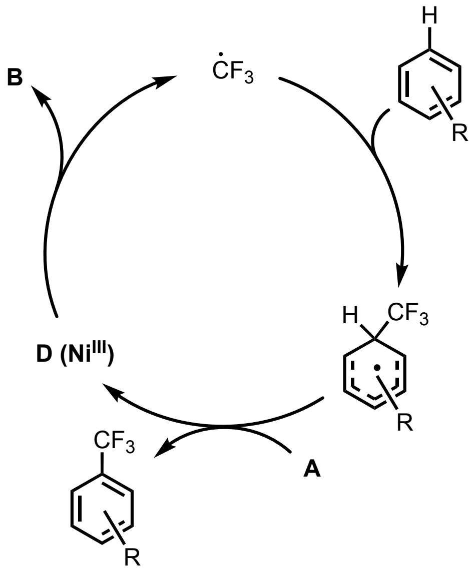
Complex __

c) Mechanistic studies revealed that the reaction proceeds via a radical chain mechanism. Please provide the structures of charge-neutral intermediates **C** and **D** (Hint: solvent coordination is present in **C**). You may abbreviate the tridentate ligand as  . (**4 points**)

Initiation

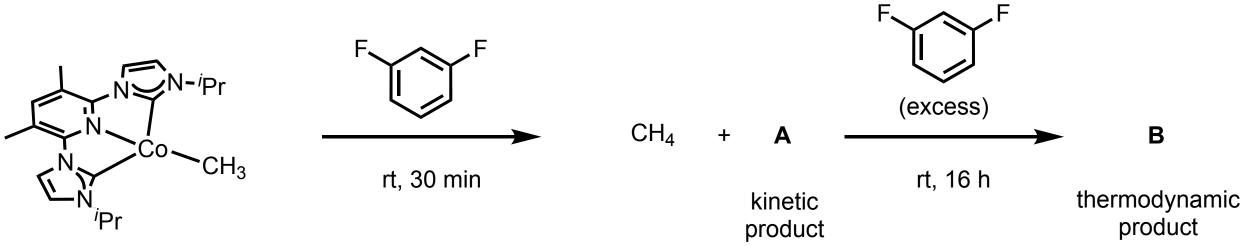
$$\mathbf{A} \xrightarrow[\text{slow}]{\text{DMSO}} \mathbf{C}\ (\mathbf{Ni^{III}}) + \dot{C}F_3$$

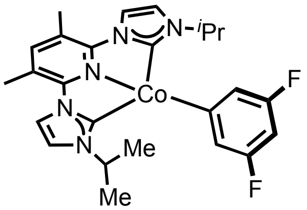
Propagation



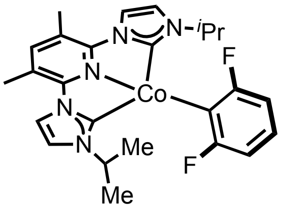
(Please provide your answers in the following page)

7. (**9 points total**) In 2023, Chirik lab achieved a Co catalyzed site selective C–H borylation reaction. In their stoichiometric studies, they discovered an interesting phenomenon that the major product of the reaction is time dependent.





Complex 1

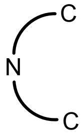


Complex 2

a) Provide the Co oxidation state, d electron count and total electron count of the starting complex. (**1 point**)

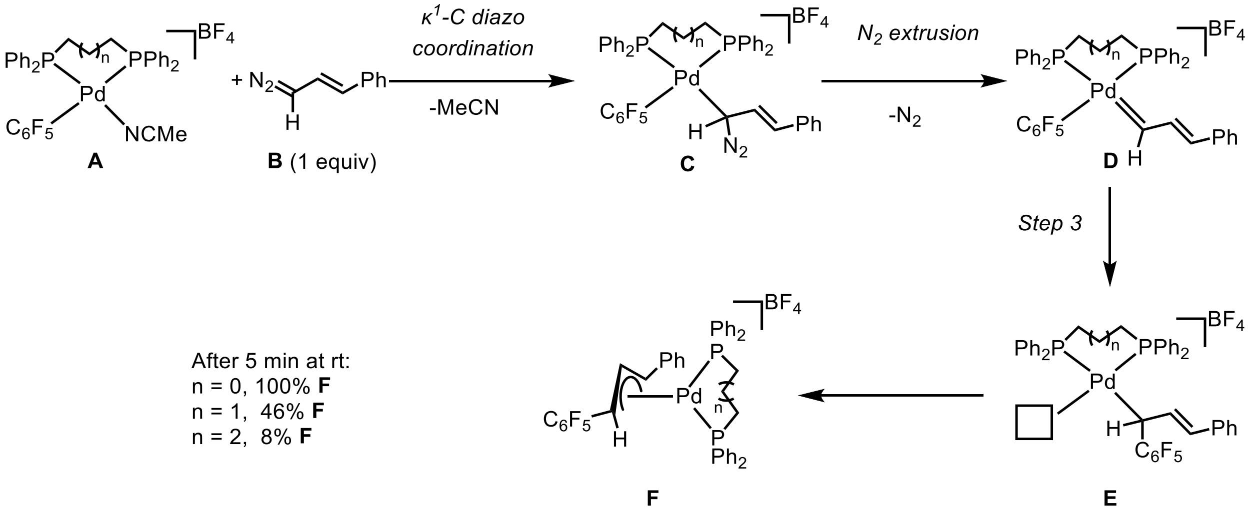
b) Match products **A** and **B** with the complexes 1 and 2. Explain your rationale. (**3 points**)

c) DFT calculations suggest that C–H oxidative addition is the rate determining step for the formation of **A**. Propose an experiment to evaluate the DFT result. (**2 points**)

d) No isomerization between **A** and **B** was observed in the absence of difluorobenzene, while excess difluorobenzene promotes full isomerization from **A** to **B**. Propose a mechanism for the isomerization and explain the necessity of excess difluorobenzene. You may abbreviate the tridentate ligand as 

. (**3 points**)

8. (**10 points total**) A recent study reported the carbene-aryl coupling using Pd complexes with bidentate phosphine ligands of different linker lengths. The reaction of Pd complex **A** and diazo compound **B** gave complex **F** of descending yields when the ligand was switched from dppe (*n* = 0) to dppp (*n* = 1) and then to dppb (*n* = 2). No significant formation of side product was detected. Experimental and DFT results combined supported a reaction pathway shown below.



After 5 min at rt:
n = 0, 100% **F**
n = 1, 46% **F**
n = 2, 8% **F**

a) Give the metal oxidation states, d electron counts, and overall electron counts of complexes **C**, **D**, and **F**. (**3 points**)

b) What elementary step is step 3 (the conversion of **D** to **E**)? (**1 point**)

c) What are the hapticities of the allyl ligand **E** and **F**? (**1 point**)

d) For the complex with n=1, the additions of 1, 2, and 3 equivalents of **B** were tested. After 5 minutes of reaction, the yield of **F** was found to increase linearly with respect to the equivalents of **B**. What does it suggest about the mechanism of the diazo coordination step. (**2 points**)

e) Rationalize the trend in yield across the ligand series (dppe, dppb, and dppp). (**3 points**)

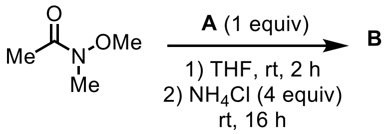
9. (**3 points total, plus 2 bonus points**) Heating a mixture of n-butyl magnesium bromide with a slight excess of sodium borohydride in dry THF to reflux for 24 h yielded a new soluble compound **A** together with white precipitate.

$$^{n}\mathrm{BuMgCl} + \mathrm{NaBH_4} \xrightarrow{\text{THF, reflux, 24 h}} \textbf{A} + \text{white precipitate}$$

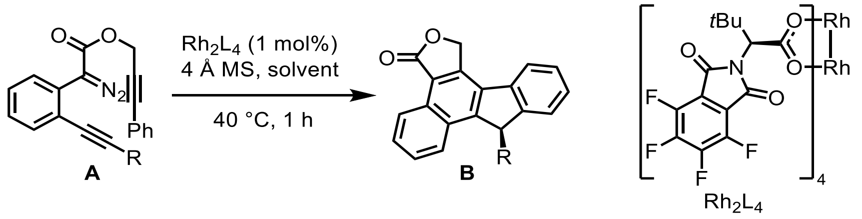
a) Propose the molecular formula of **A** (as its monomeric form). (**1 point**)

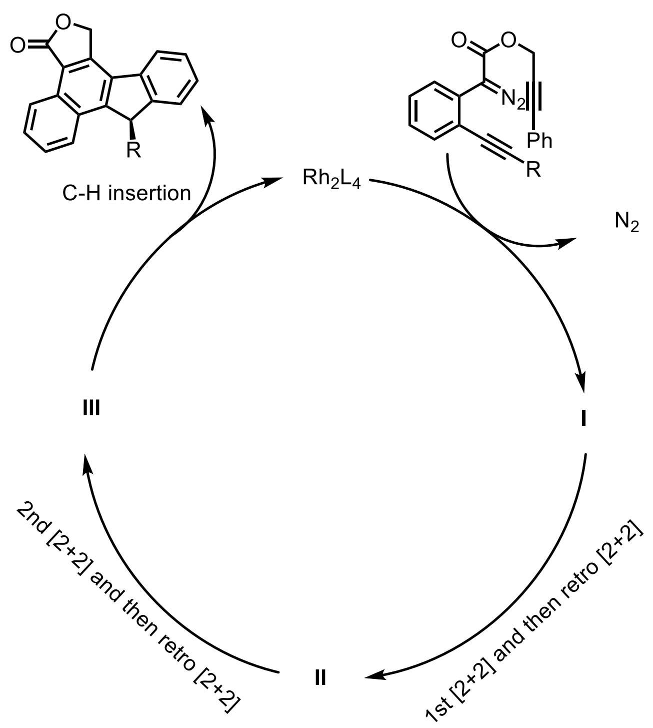
b) Various spectroscopic techniques were used to characterize compound **A**, and in all spectrum, there were some minor peaks that cannot be assigned to compound **A**. Vapor diffusion of petroleum ether into a THF solution of **A** yielded crystals of the formula $Mg(BH_4)_2 \cdot 3THF$. Explain what process could account for the above observation. (**2 points**)

Bonus: Predict the organic product **B** of the reaction between Weinreb amide and compound **A**. (**2 points**)

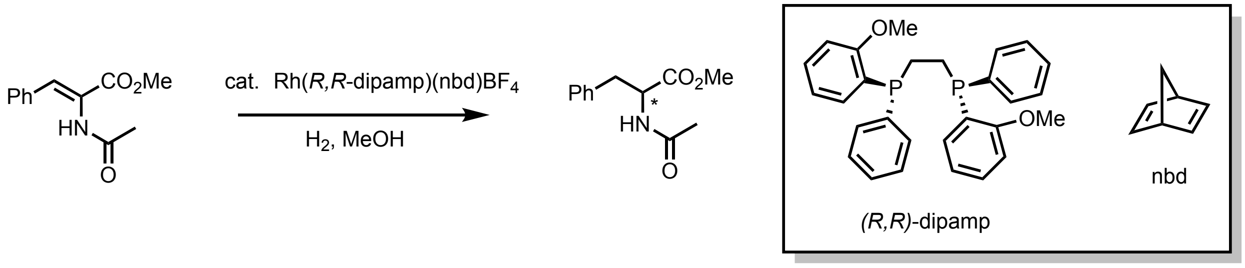


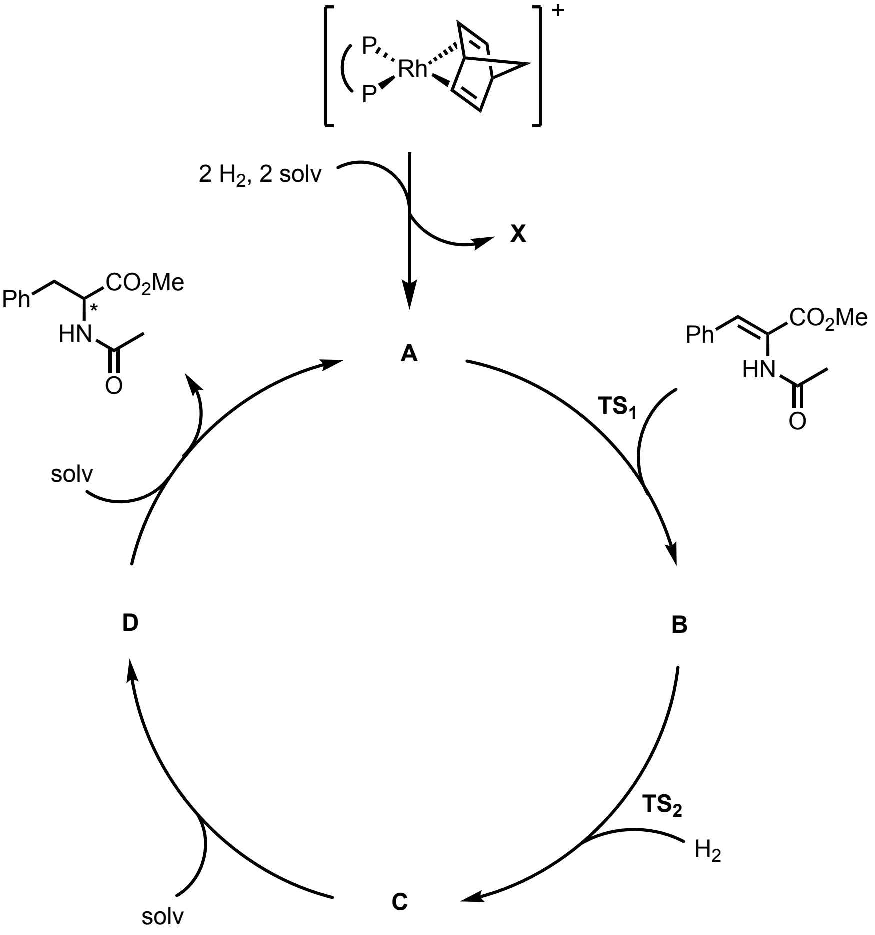
10. (**6 points total**) A Rh-catalyzed double carbene/alkyne metathesis followed by C–H functionalization yields compound **B**. Complete the catalytic cycle by proposing the structures of **I**, **II**, and **III**. You could represent Rh_2L_4 as [Rh].





11. (**12 points total**) The mechanism of asymmetric hydrogenation of methyl-(*Z*)-α-acetamidocinnamate was studied in detail by Landis and Halpern:

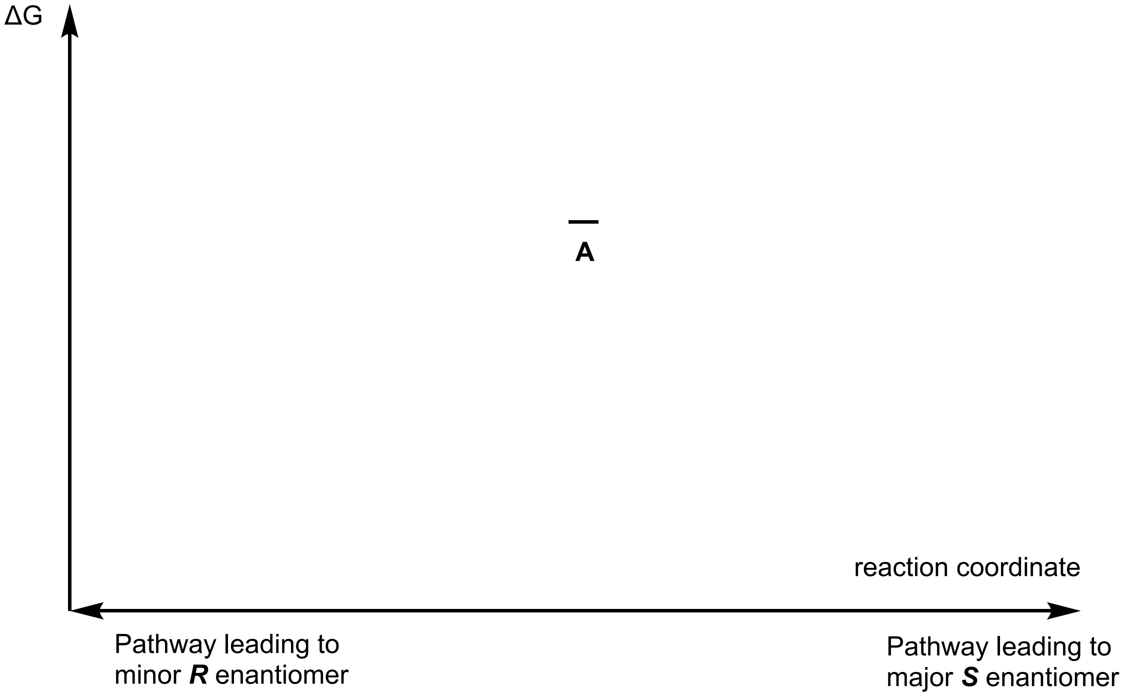




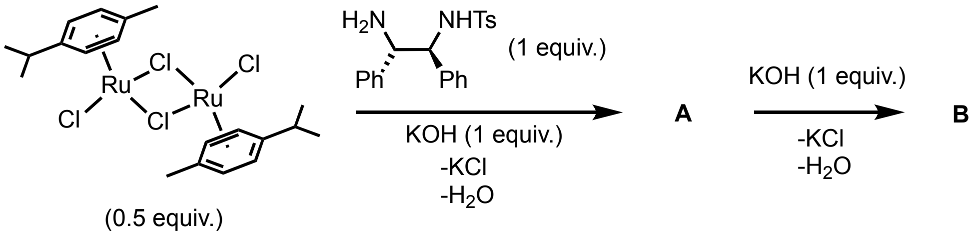
a) Organic byproduct **X** is generated during the catalyst initiation. Propose the structure of **X**. (**1 point**)

b) Complete the catalytic cycle by filling in structures of intermediates **A–D**, abbreviating the ligand as $\overset{\frown}{\text{P}\quad\text{P}}$ and coordinating solvent as solv. (Hint: The amide carbonyl of the substrate serves as a directing group) (**8 points**)

c) This catalytic system is a classical case where the enantioselectivity is under Curtin-Hammett control. Under low H_2 pressures, it was observed that the more stable intermediate $\mathbf{B}_{\boldsymbol{R}}$ (formed from **A** through $\mathbf{TS}_{\mathbf{1}\boldsymbol{R}}$) leads to the minor ***R*** enantiomer, while the less stable intermediate $\mathbf{B}_{\boldsymbol{S}}$ (formed from **A** through $\mathbf{TS}_{\mathbf{1}\boldsymbol{S}}$) leads to the major ***S*** enantiomer. Kinetic data suggests that the elementary step from **B** to **C** via $\mathbf{TS}_{\mathbf{2}}$ is rate determining and irreversible. In the reaction coordinate profile map below, draw out the reaction energy diagram that reflects the relative energies of **A**, $\mathbf{TS}_{\mathbf{1}\boldsymbol{R}\mathbf{\&1}\boldsymbol{S}}$, $\mathbf{B}_{\boldsymbol{R}\mathbf{\&}\boldsymbol{S}}$, $\mathbf{TS}_{\mathbf{2}\boldsymbol{R}\mathbf{\&2}\boldsymbol{S}}$ **and** $\mathbf{C}_{\boldsymbol{R}\mathbf{\&}\boldsymbol{S}}$**.** (No need to consider elementary steps after formation of **C**) (**3 points**)



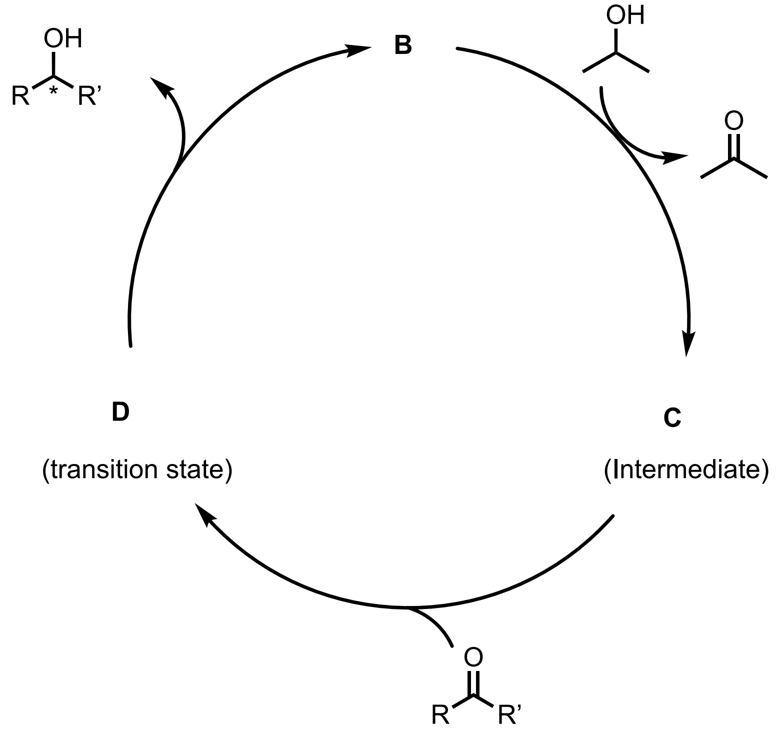
12. (**8 points total**) Asymmetric transfer hydrogenation of ketones using a Ruthenium catalyst system was studied in detail by Noyori and co-workers.



While **A** is known as Noyori catalyst and is commercially available, **B** is the catalytically active species.

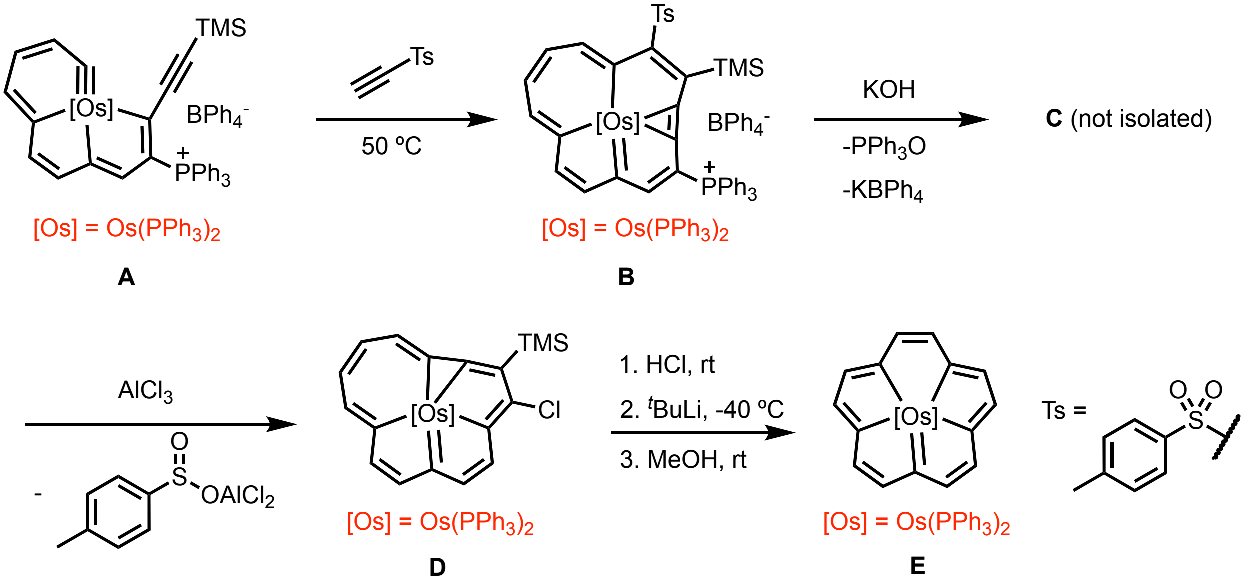
a) Propose the structures of **A** and **B**. (**4 points**)

b) Provide the structures of intermediate **C** and transition state **D** in the catalytic cycle shown below. (**4 points**)



(Please provide your answers in the following page)

Bonus: (**7 points total**) Very recently, the first metal-centered planar [15]annulene was synthesized by Xia and co-workers:



a) Provide the Os oxidation state, electron count and total electron count for **A** and **E**, considering the carbyne/carbene species as Fischer carbyne/carbenes. (**2 points**)

b) Propose the structure of intermediate **C**. (**2 points**)

c) Propose a reasonable mechanism for transformation **C**–**D**. You may abbreviate parts of the structure if needed. (**3 points**)