Scripps
Research

Organometallic Chemistry 2019 Exam 1
May 1st, 2019; 10:00 AM PST

Directions: This is a closed notes exam. Answer the following questions to the best of your ability. There are **10 questions**, 15 pages, and the exam is **130 points total.** There is one bonus question worth 10 points. You have **3 hours** to complete this exam. All answers must be written on the pages provided. Please write legibly.

NAME:____

1____________________________/13

2____________________________/10

3____________________________/10

4____________________________/16

5____________________________/15

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7____________________________/15

8_____________________________/9

9____________________________/10

10____________________________/10

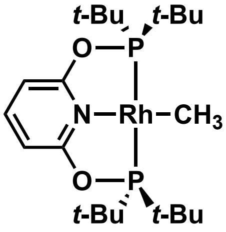
11 (BONUS)___________________/10

TOTAL:________________/130 (+10 bonus)

1. 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). Each element is worth 0.5 points (**13 points total**). Please ignore Lanthanum and Actinium.

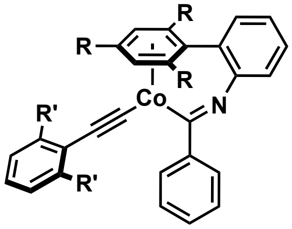
3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B
									30 **Zn** Zinc 65.39
									48 **Cd** Cadmium 112.411
57-71									80 **Hg** Mercury 200.59
89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108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

2. Electron counting. Provide the (i) coordination number, (ii) oxidation state, (iii) *d*-electron count, (iv) total electron count of the following complexes **(10 points, 2 points each)**.



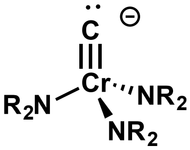
A.

Coordination Number	Oxidation state	*d*-electron count	Total electron count



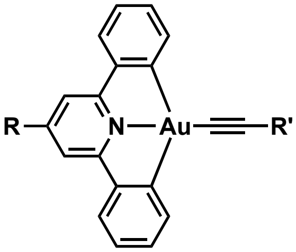
B.

Coordination Number	Oxidation state	*d*-electron count	Total electron count



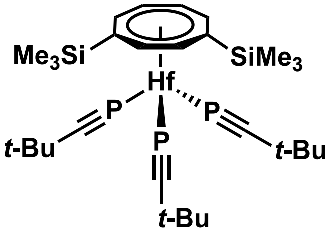
C.

Coordination Number	Oxidation state	*d*-electron count	Total electron count



D.

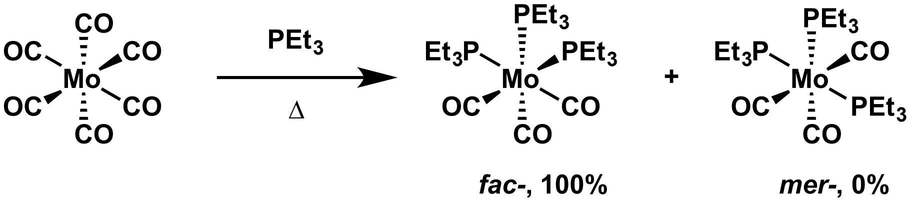
Coordination Number	Oxidation state	*d*-electron count	Total electron count



E. **HINT**: the cyclooctateraene ligand is planar

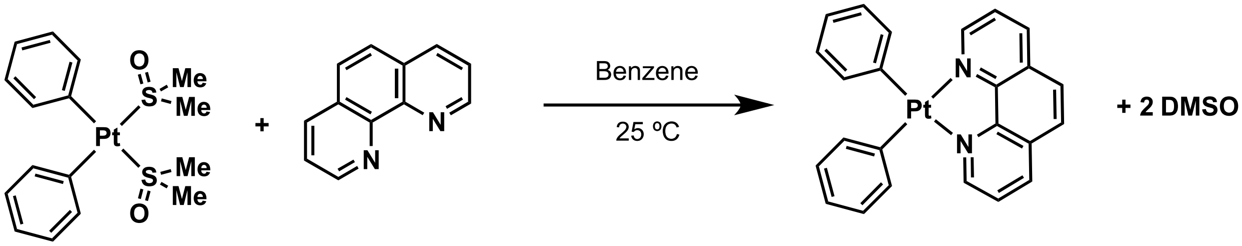
Coordination Number	Oxidation state	*d*-electron count	Total electron count

3. Part A. When $Mo(CO)_6$ is refluxed with excess PEt_3 in toluene, the final product is *fac*-$Mo(CO)_3(PEt)_3$ rather than *mer*-$Mo(CO)_3(PEt)_3$ (Note: *fac* indicates that each ligand type resides on one face of the octahedron*; mer* indicates that each ligand type [*i.e.* CO's or PEt_3's] resides in a plane with the metal):

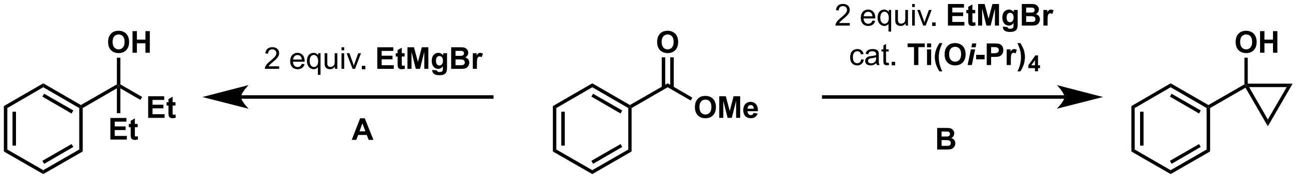


Please briefly explain why (i) the substitution stops at the tris-phosphine complex and (ii) why *mer*-$Mo(CO)_3(PEt)_3$ is not observed (**5 points**).

3. Part B. Although we've seen in lecture that 16-electron square planar complexes tend to undergo associative substitution, there have been several reports of such complexes undergoing dissociative substitution. One case is shown below. Why should dissociative substitution be preferred in this case over associative substitution? In your explanation, please propose structures for the reaction intermediates (**5 points**).



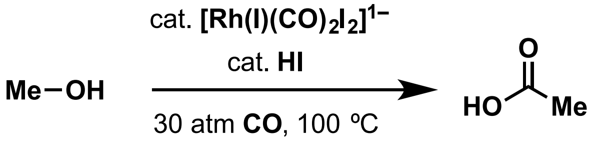
4. The addition of two equivalents of ethyl magnesium bromide to methyl benzoate forms the corresponding diethyl alcohol; however, addition of catalytic Ti(O*i*-Pr)$_4$ forms the corresponding cyclopropyl alcohol:



4. Part A. Provide a reasonable mechanism for reaction B **(10 points total**)

4. Part B. Based off of your knowledge on the Schlenck equilibrium, explain how it precludes the formation of α-chiral Grignard reagents. Draw the presumed transition state that accounts for the racemization of such reagents (**6 points**).

5. Part A. The industrial synthesis of acetic acid from methanol, carbon monoxide, and hydrogen iodide is carried out by Rh(I) catalysis in the **Monsanto Acetic Acid synthesis:**



Please provide a reasonable catalytic cycle for the above reaction (**15 points**).

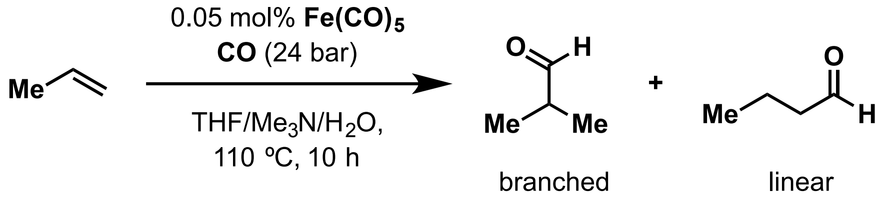
6. Part A. The Monsanto process has been replaced with an Ir(I) catalyst in what is known as the **Cativa process**. Despite the greater cost of Iridium, the Ir(I) catalyst requires less water; less water suppresses a side reaction known as the **Water-Gas Shift Reaction** (WGSR) and is more environmentally friendly.

Many transition metal carbonyl complexes catalyze the WGSR under basic conditions:

$$\mathbf{CO} + \mathbf{H_2O} \xrightleftharpoons{\substack{\text{cat. } \mathbf{Fe(CO)_5} \\ \text{cat. } \mathbf{NaOH}}} \mathbf{CO_2} + \mathbf{H_2} \qquad \textbf{(WGSR)}$$

Please draw the catalytic cycle for the above reaction. *Only consider the forward reaction* (**5 points**).

6. Part B. Because the WGSR produces hydrogen directly from carbon monoxide in water, it has been proposed as an environmentally friendly means of performing hydrogenations and hydroformylation. Industrially it is used in **Reppe-type hydroformylation:**

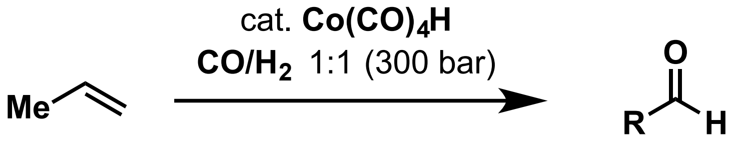


Please draw a catalytic cycle for the above reaction (**4 points**). What ligand would you add to the reaction for improved linear:branched selectivity? (**1 point**).

6. Part C. If a polynuclear cluster such as $Ru_3(CO)_{12}$ is used instead of a mononuclear complex there is higher linear:branched selectivity. Why? (**2 points**)

Linear:Branched: $Ru_3(CO)_{12}$ = 11.5:1, $Fe(CO)_5$ = 1:1

6. Part D. Breslow and Heck elucidated the mechanism of hydroformylation of olefins using syngas (H_2/CO) catalyzed by cobalt tetracarbonyl hydride ($Co(CO)_4H$). This is the oldest homogeneous catalysis process still in use (**Oxo process**):

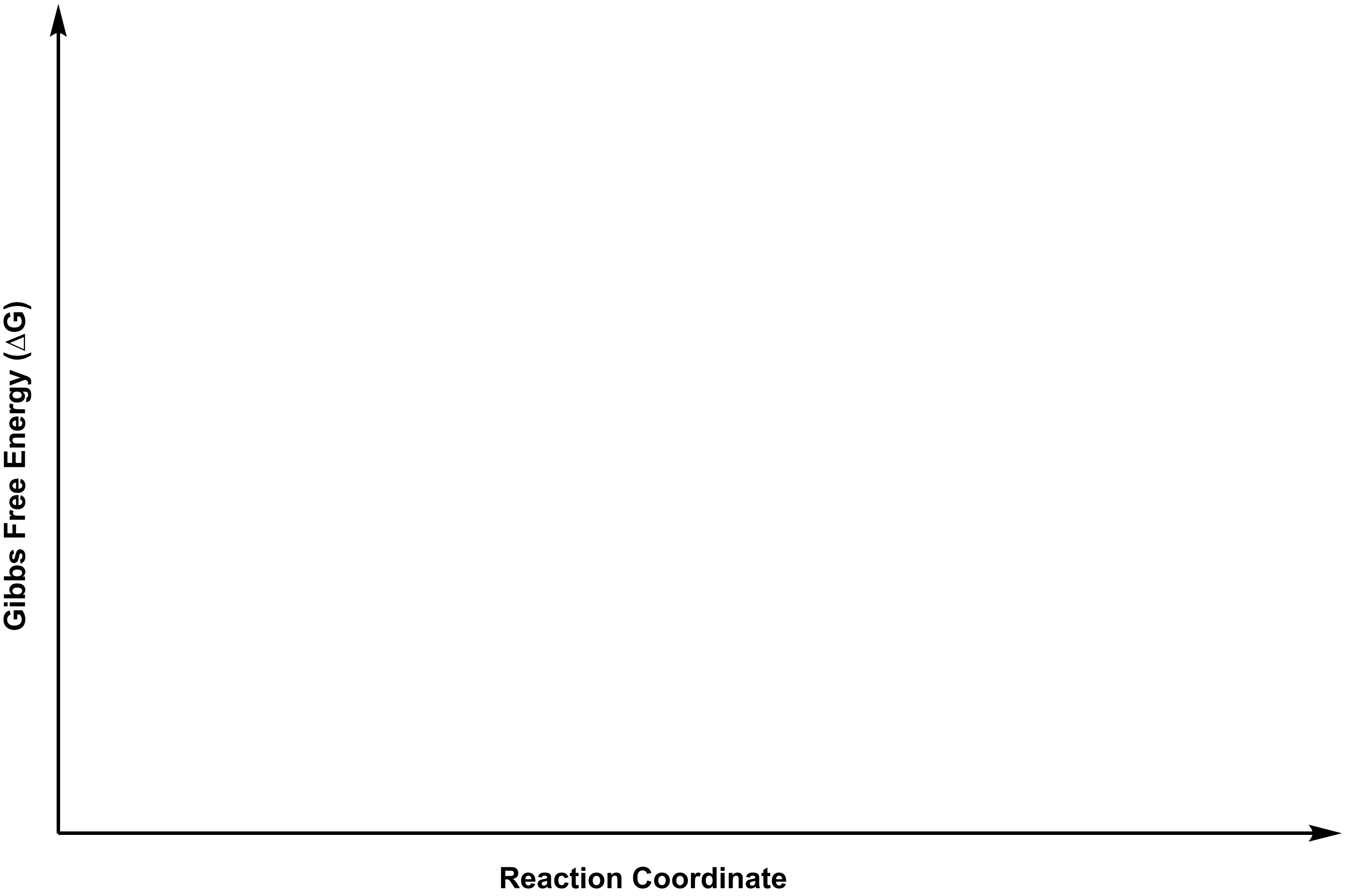


$$\boxed{\frac{\partial(\text{aldehyde})}{\partial t} = \frac{k[\text{alkene}][\text{Co cat}][H_2]}{[\text{CO}]}}$$

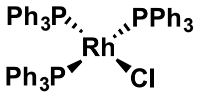
linear (R = *n*-Pr): branched (R = *i*-Pr): 4:1

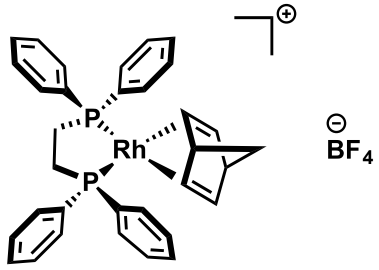
Based off of your understanding of elementary steps in organometallic chemistry, please (i) propose a catalytic cycle for this reaction (**5 points**) and indicate the *d*-electron count and total electron count for each intermediate (**2 points**). (ii) What is the major difference in the Oxo-process to Reppe-type hydroformylation (*i.e.* what is the major difference in elementary steps, **1 point**). (iii) The rate equation is shown above and kinetic experiments revealed that the rate of aldehyde formation is inversely proportional to the concentration of CO. Why? (**2 points**) (**10 points total**).

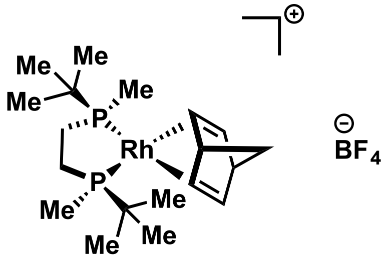
7. Part A. The Curtin–Hammett principle can be used to explain the high enantioselectivity observed in many asymmetric hydrogenation reactions. Pick an example of this reaction class (*e.g.* Noyori asymmetric hydrogenation [beta-keto-esters, ketones], Knowles asymmetric hydrogenation of olefins to make L–DOPA, *etc.*) Please explain this observation using the theory (**3 points**). Draw the energy diagram for the reaction of your choice (**3 points**) (**6 points total**).



7. Part B. Extensive studies by Osborn and Halpern have elucidated the mechanistic differences between directed homogeneous hydrogenation of olefins between neutral Wilkinson’s catalyst Rh(PPh_3)$_3$Cl, **1**, and cationic [Rh(NBD)(DIPHOS)][BF_4], **2**.


Wilkinson's Catalyst
1

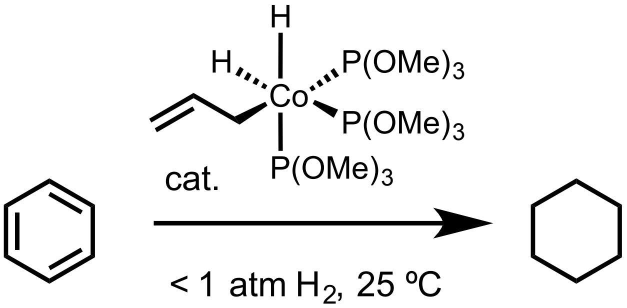

[Rh(NBD)(DIPHOS)][BF_4]
2


3

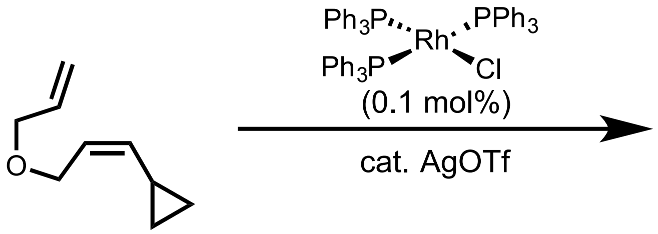
In lecture we discussed two major mechanistic regimes for homogeneous hydrogenation (*i.e.* “hydrogen first”, “olefin-first”). What mechanisms do catalysts **1** and **2** follow (**5 points**)?

List the properties of **3** that would be advantageous for both mechanisms. What mechanism would you expect complex **3** to undergo? State your reasoning (**4 points**).

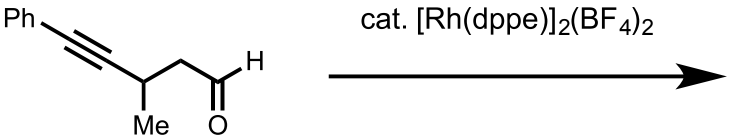
8. Hydrogenation of benzene to cyclohexane can be achieved under mild conditions using a cobalt catalyst. Propose a detailed catalytic cycle – including the oxidation state of cobalt and total electron-count for each intermediate – for both (1) monohydride and (2) dihydride mechanisms (Hint: Both will go through an η^4-benzene intermediate) (**4 points each, 8 points**). Design an experiment that would support one mechanism over the other (**2 points**) (**10 points total**).



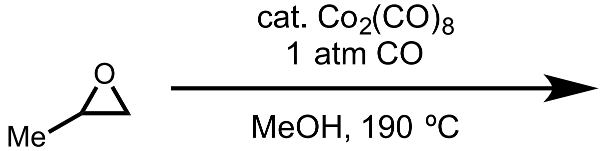
9. Predict the products/starting materials **(2 points each; 10 points total)**.



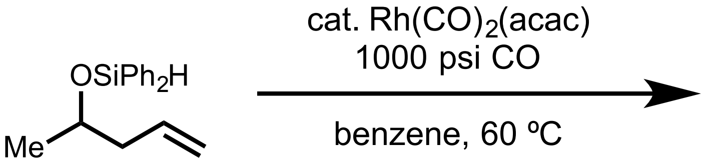
a.



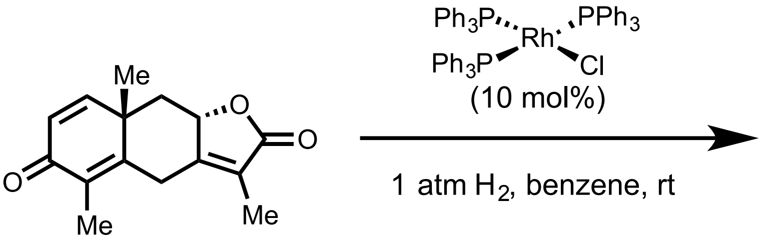
b.



c.

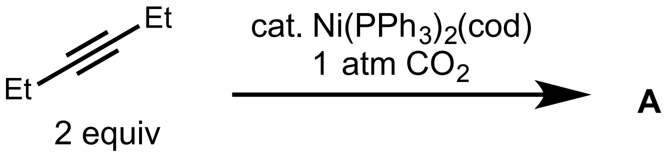


d.

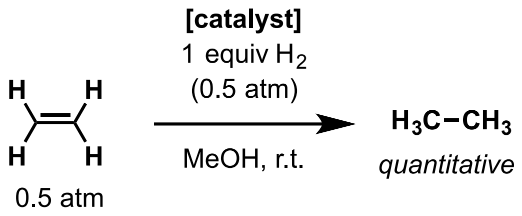


e.

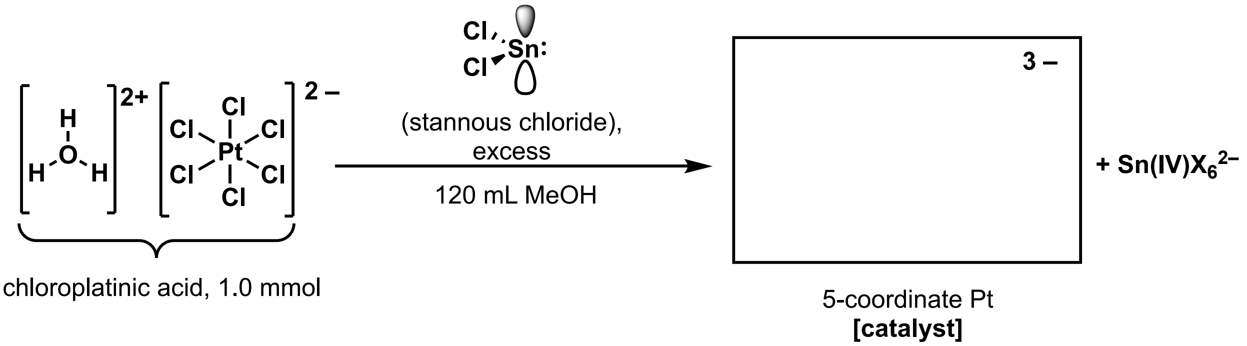
10. Provide the product of the following reaction, A, **(5 points)** along with a reasonable catalytic cycle (**5 points**) **(10 points total)**.



11. (BONUS, 10 points). In 1963, Cramer, Lenner, and Stolberg reported the homogeneous hydrogenation of ethylene and acetylene with platinum-tin complexes at room temperature and atmospheric pressure of hydrogen:

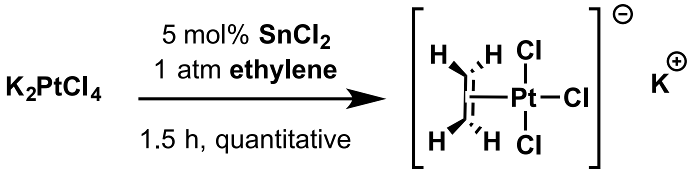


The catalyst for this reaction was prepared by the following:



The following observations were made:

1. Hydrogenation of ethylene was first order in Pt
2. At constant Pt concentration, maximum hydrogenation rates are observed in a 5:1 molar ratio of Sn:Pt
3.



, without $SnCl_2$, Zeise's salt does not form

4. Exposure of K_2PtCl_4 to H_2 in MeOH generates colloidal nanoparticles, addition of $SnCl_2$ prevents this process

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(a) Draw the structure of the catalyst in the box above **(2.5 points)**
(b) Draw the mechanism for formation of Zeise's salt with catalytic stannous chloride (**2.5 points**)
(c) Based on your answer to 11a. What are the **two** reasons stannous chloride enables the above reaction(s)? (**5 points; 2.5 points each**)