Catalyst design for synthesis, Final Exam

December 20, 2023
Name (First name, Last name):
Student ID number:

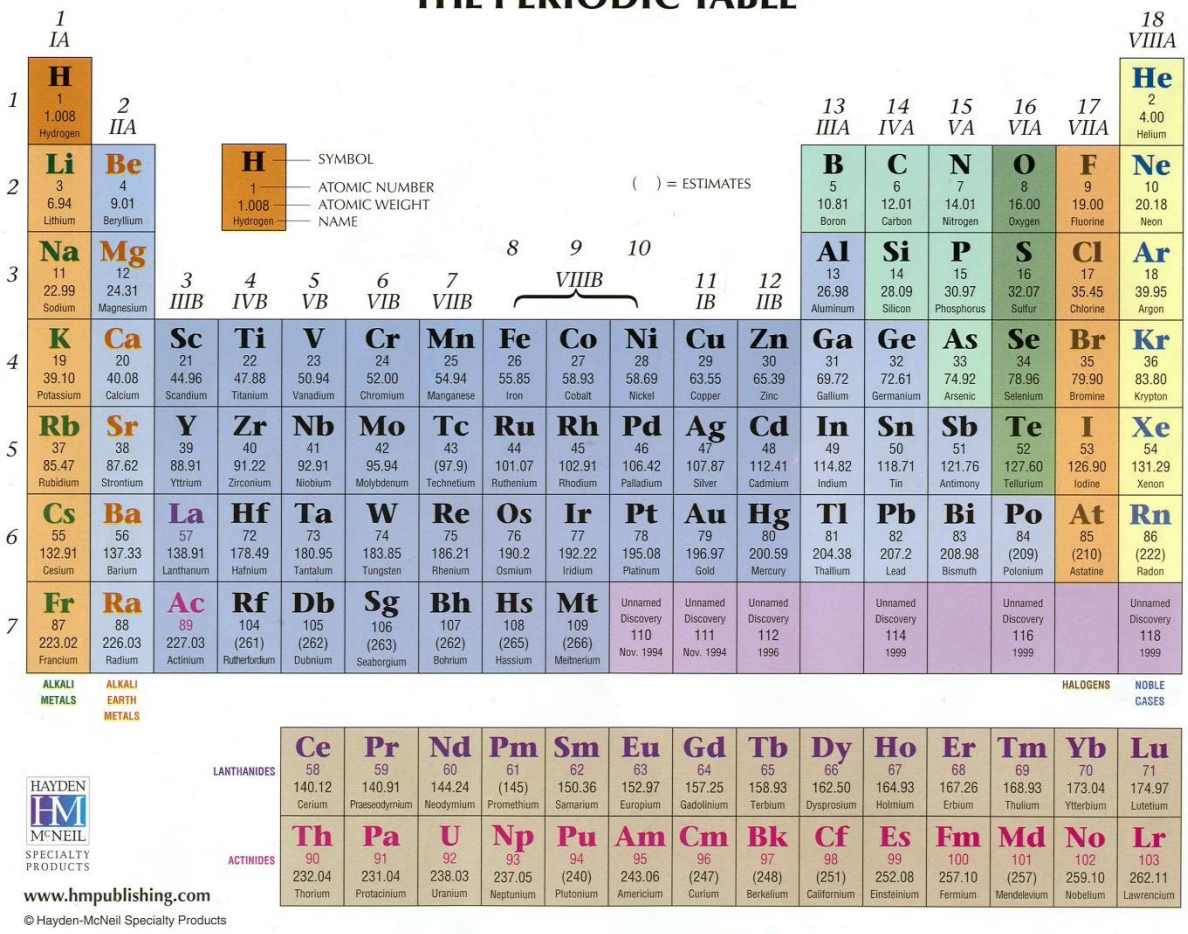
PCs must not be used. No material other than the exam paper is permitted.

Overall 38 points.

You can also write the answer on the back of the exam paper if you run out of space; if you choose to do so, make a clear indication in the exam paper.

You have a maximum of **105 minutes** to finish the exam.

THE PERIODIC TABLE



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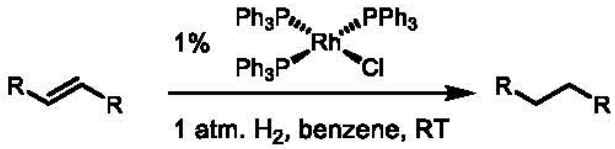
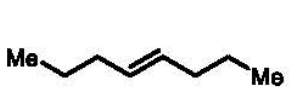
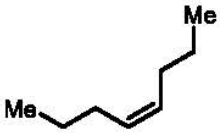
1. For the following hydrogenation reaction, rank the substrates in increasing rate of reaction. (4 points)



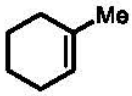


A



B

C



D

D < A < B < C (or C > B > A > D)

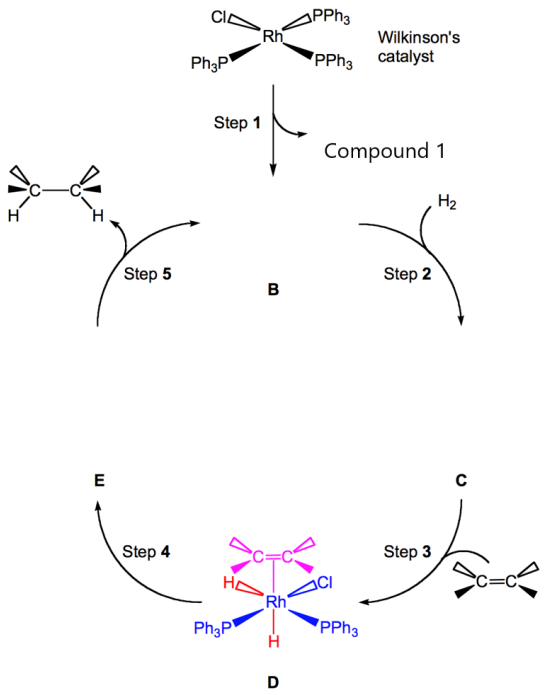
All correct, 4 points

If D is slowest, 1 point;

If C is fastest, 1 point.

If B faster than A, 1 point.

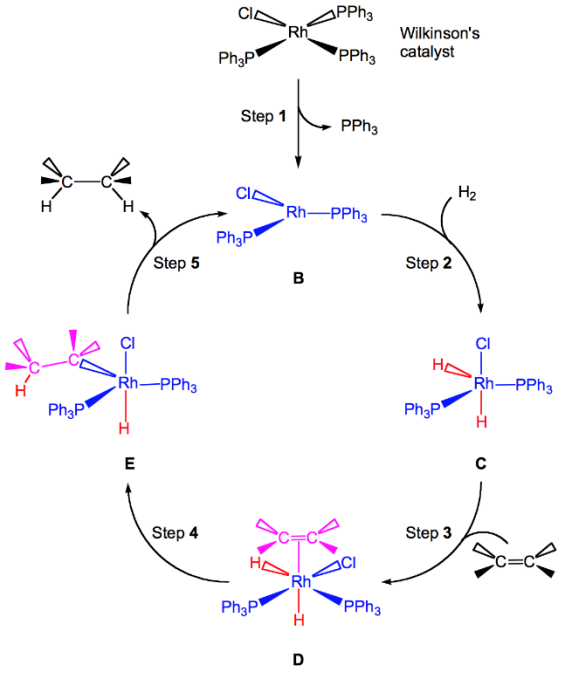
2. (4 points) Please complete the following mechanistic cycle for Wilkinson's catalyst. (1) What is compound 1. (2) Draw the structures of compounds B, C, and E.



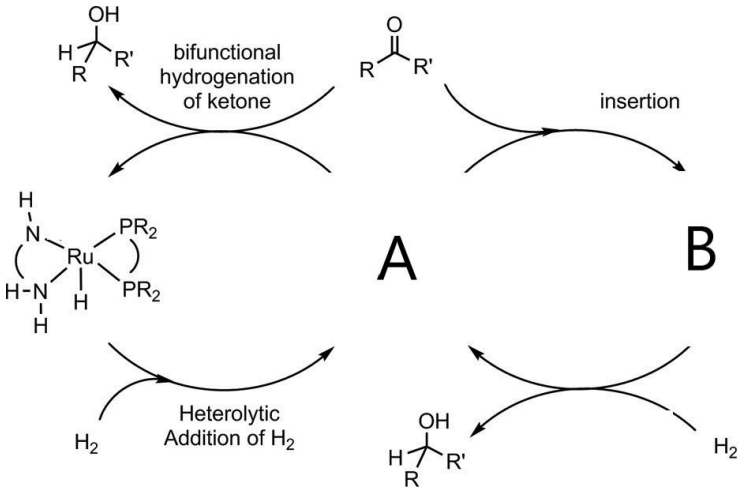
A:

1. Compound 1: PPh3

2: see this:



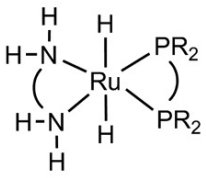
3. (8 points) For the following Ru-catalyzed hydrogenation. Two possible mechanisms are known: a bifunctional mechanism and a step-wise mechanism. Please complete the following questions.

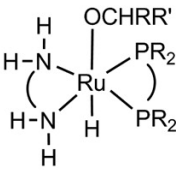


(1) What is the oxidation state of the Ru catalyst in the left. (2 points)

+2

(2) Draw the structure of intermediates A and B. (4 points)

A: Sth like: 

B: sth like 

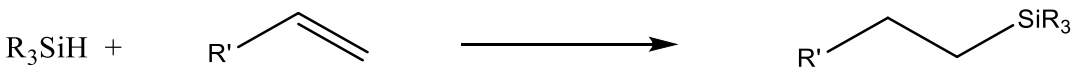
2 points each. For A, key is to protonate the N=Ru; for B, key is insertion of ketone to H. Can be on the top or on the bottom.

(3) What is the oxidation state of Ru in A and B? (2 points)

Both +2. One point each.

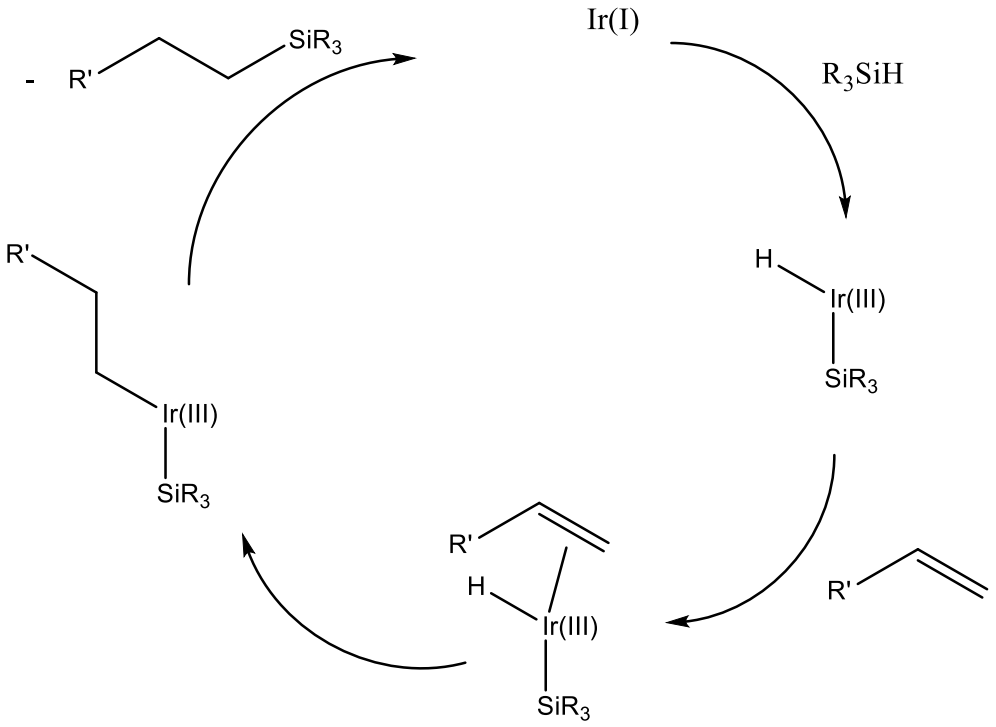
If the same as answer 1, but not +2, then get 1 point.

4. (6 points) Hydrosilylation of alkene is similar to hydrogenation of alkene. The reaction is shown below:



An Ir(I) complex is known to catalyze this reaction. In the catalytic cycle, the first step is oxidative addition of silane on the Ir(I) complex. The last step is the C-Si reductive elimination. Based on this information, draw the catalytic cycle of this Ir-catalyzed hydrosilylation. Label the oxidation state of Ir intermediates. You can use "Ir(I)" to present the initial catalyst.

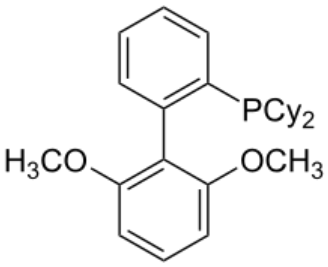
A:



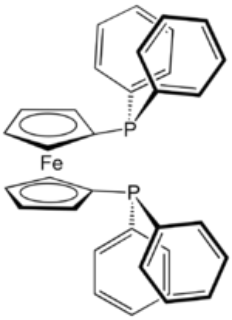
Oxidation state, 0.5 point each.

Each step : 1 point each.

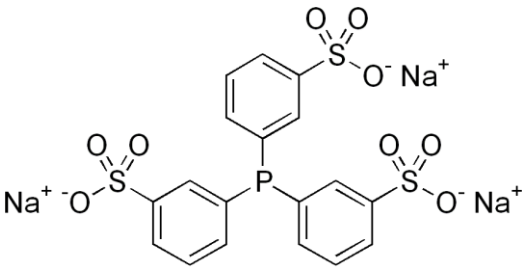
5. (6 points) (a) Associate the most suitable phosphine ligands below for the following Pd-catalyzed cross-coupling reaction. (b) Give a brief explanation for each of your choice.



A, S-Phos



B, DPPF



C, TPPTS

Reactions:

(i) Suzuki coupling of sterically hindered aryl chlorides; why?

A: S-Phos. Because this ligand can stabilize one-coordinate Pd(0) species (along this line)

(ii) Suzuki coupling in water medium; why?

C: TPPTS. Because this ligand is water soluble (charged).

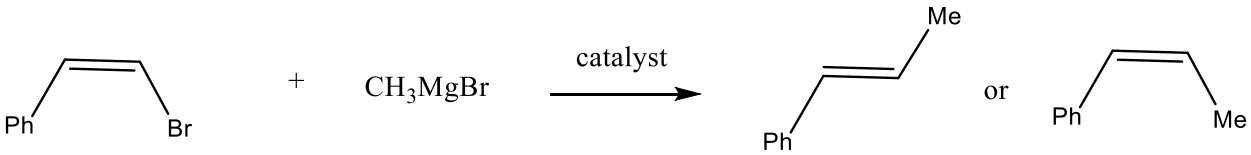
(iii) Kumada and Suzuki coupling of alkyl nucleophiles; why?

B: DPPF. Because this ligand is bidentate and suppress β-elimination. (second answer, promote reductive elimination)

1 point each for the right choice. One point each for the right answer.

6. (4 points) Choose the correct major product in the following cross-coupling reactions. Explain why.

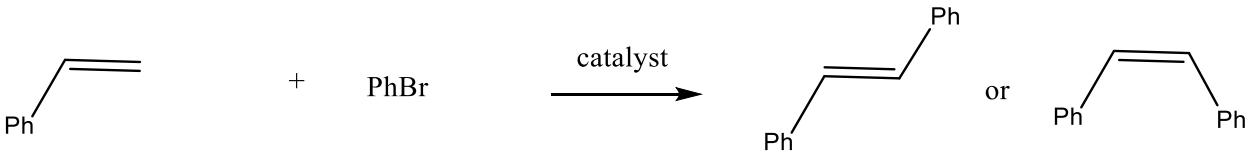
(1)

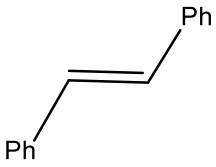


A: 

. Because cross coupling is stereospecific, or because the cis/trans configuration is conserved.

(2)

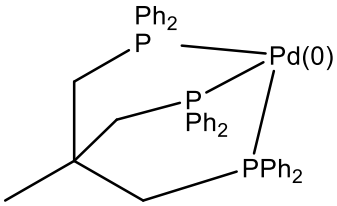


A: 

. Because heck reaction gives the trans isomer as the major product (due to the syn-elimination).

1 point each correct choice; 1 point each correct answer.

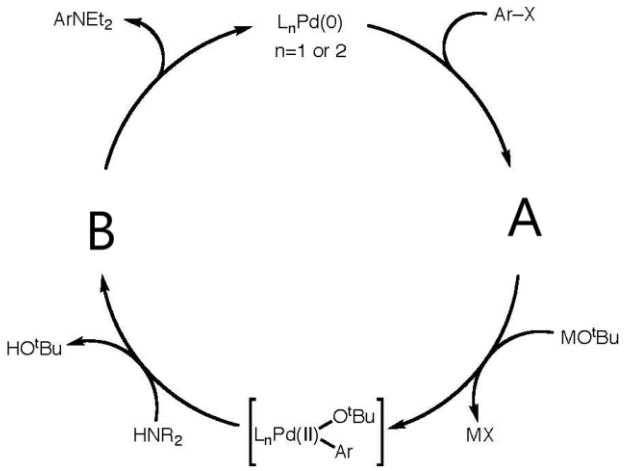
7. (2 points) Do you expect the following complex to be a very active catalyst for Suzuki coupling? Why or why not?

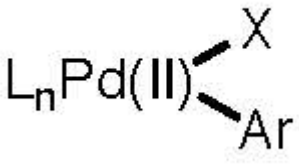


A : Not very active. (1 point)

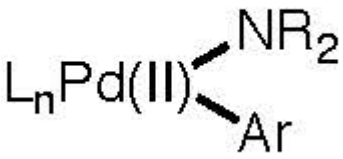
Because it has a tridentate ligand. Normally a bi or mono-dentate Pd(0) complex is active for Suzuki coupling. This compound has a tridentate ligand. (1 point)

8. Pd-catalyzed C-N cross-coupling is similar to C-C cross coupling. Below is a catalytic cycle for Pd-catalyzed C-N coupling. Please draw the structures of intermediates A and B. And label their oxidation states. (4 points)





A:



B:

Structure 1 point each; oxidation state 1 point each. If Ln is not written, OK.