Catalyst design for synthesis, Final Exam

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

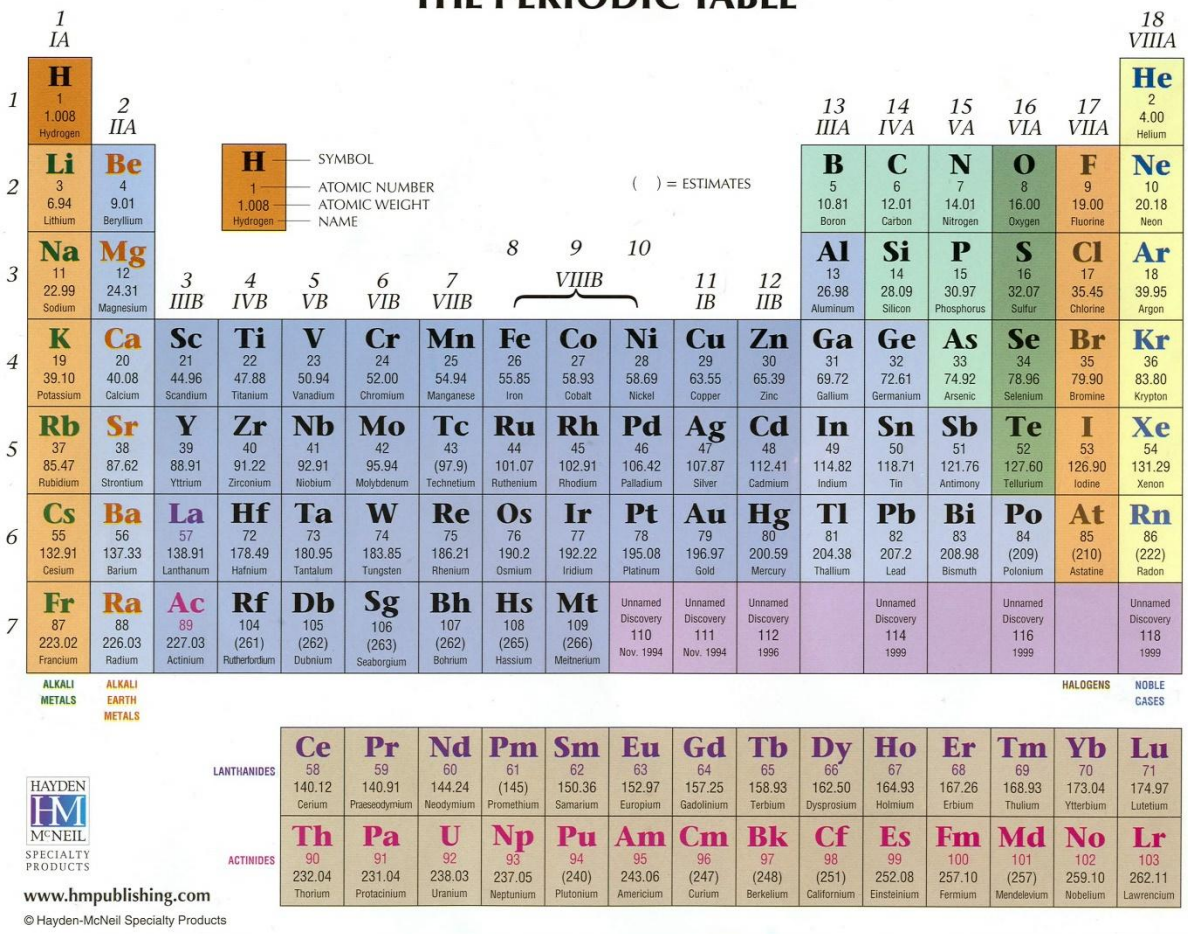
PCs must not be used. No material other than the exam paper is permitted.

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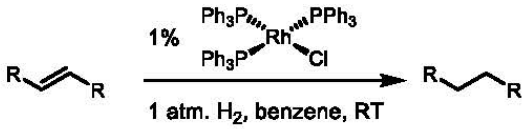
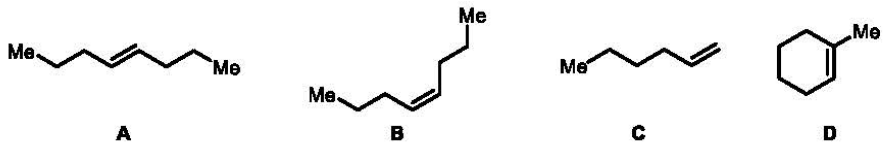
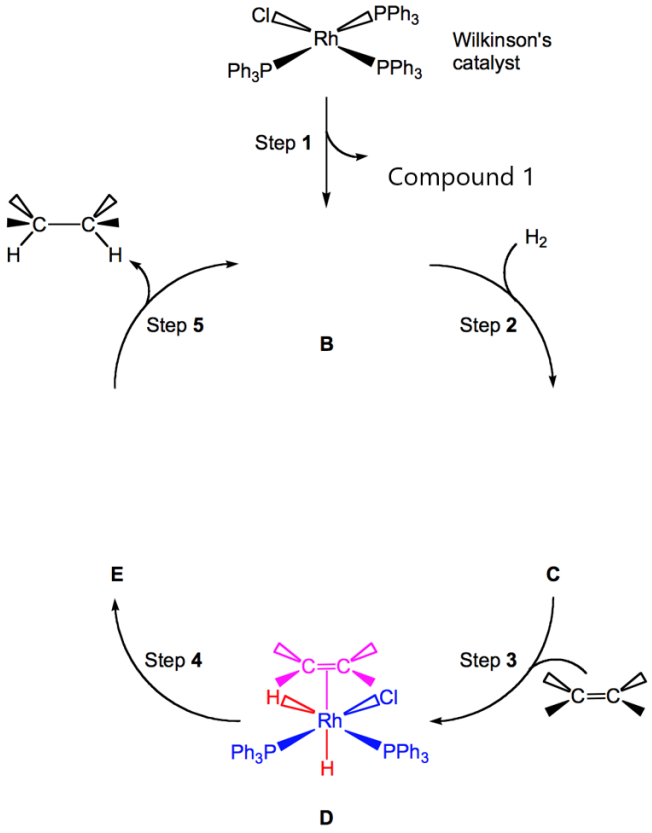
1. For the following hydrogenation reaction, rank the substrates in increasing rate of reaction. (4 points)

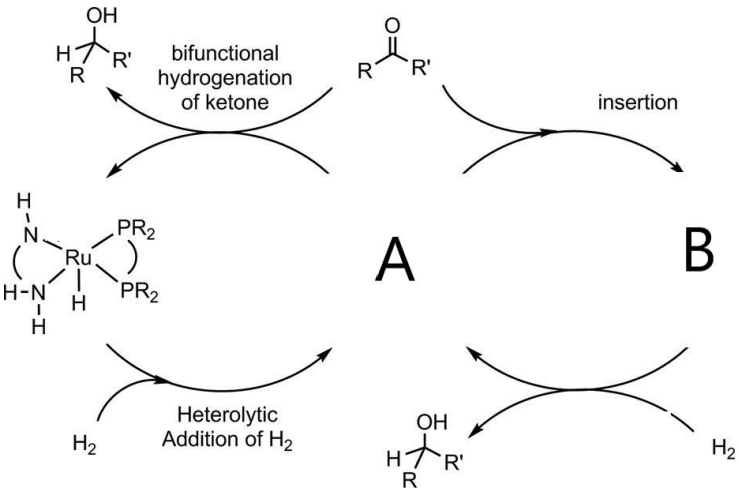




2. (4 points) Please complete the following mechanistic cycle for Wilkinson's catalyst. (1) What is compound 1. (2) Draw the structures of compounds B, C, and E.



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.

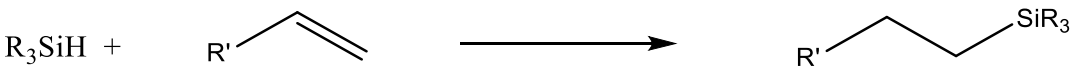


(1) What is the oxidation state of the Ru catalyst in the left. (2 points)

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

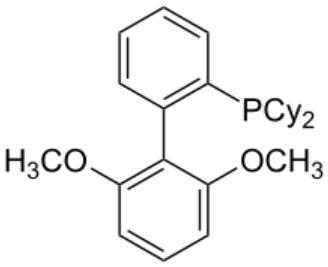
(3) What is the oxidation state of Ru in A and B? (2 points)

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

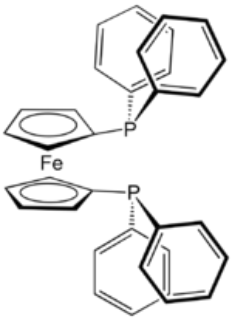


An Ir(I) complex is known to catalyze this reaction. In the catalytic cycle, the first step is oxidative addition of silane (R_3Si-H) on the Ir(I) complex. The last step is the C-Si reductive elimination. Based on this information, draw the catalytic cycle of this Ir-catalyzed hydrosilylation. Label the oxidation state of Ir intermediates. You can use "Ir(I)" to present the initial catalyst.

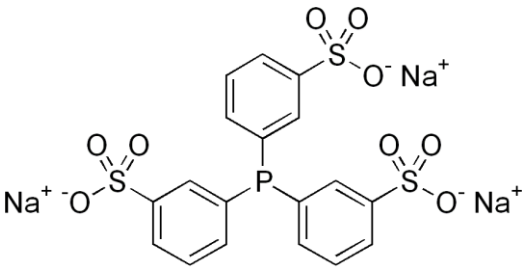
5. (6 points) (a) Associate the most suitable phosphine ligands below for the following Pd-catalyzed cross-coupling reaction. (b) Give a brief explanation for each of your choice.



A, S-Phos



B, DPPF



C, TPPTS

Reactions:

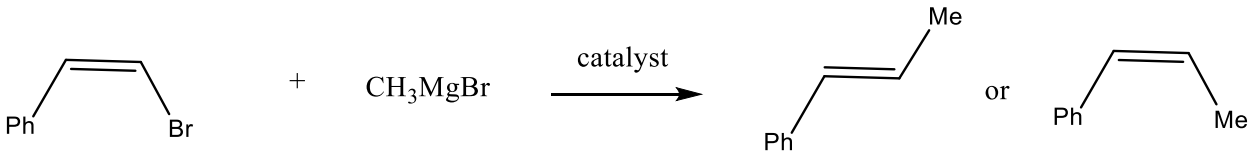
(i) Suzuki coupling of sterically hindered aryl chlorides; why?

(ii) Suzuki coupling in water medium; why?

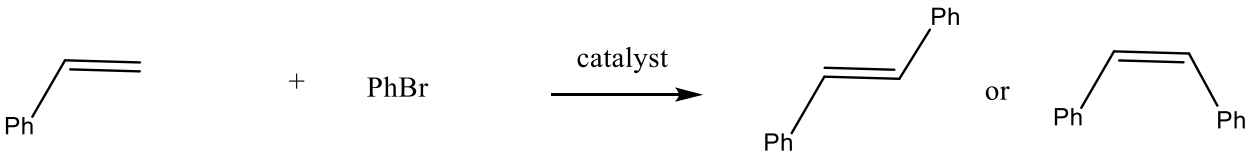
(iii) Kumada and Suzuki coupling of alkyl nucleophiles; why?

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

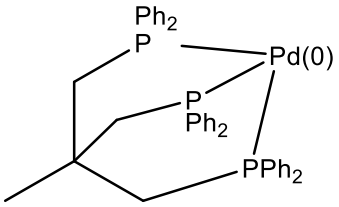
(1)



(2)



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



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)