Catalyst design for synthesis, Midterm Exam

October 17, 2024
Name (First name, Last name):
Student ID number:

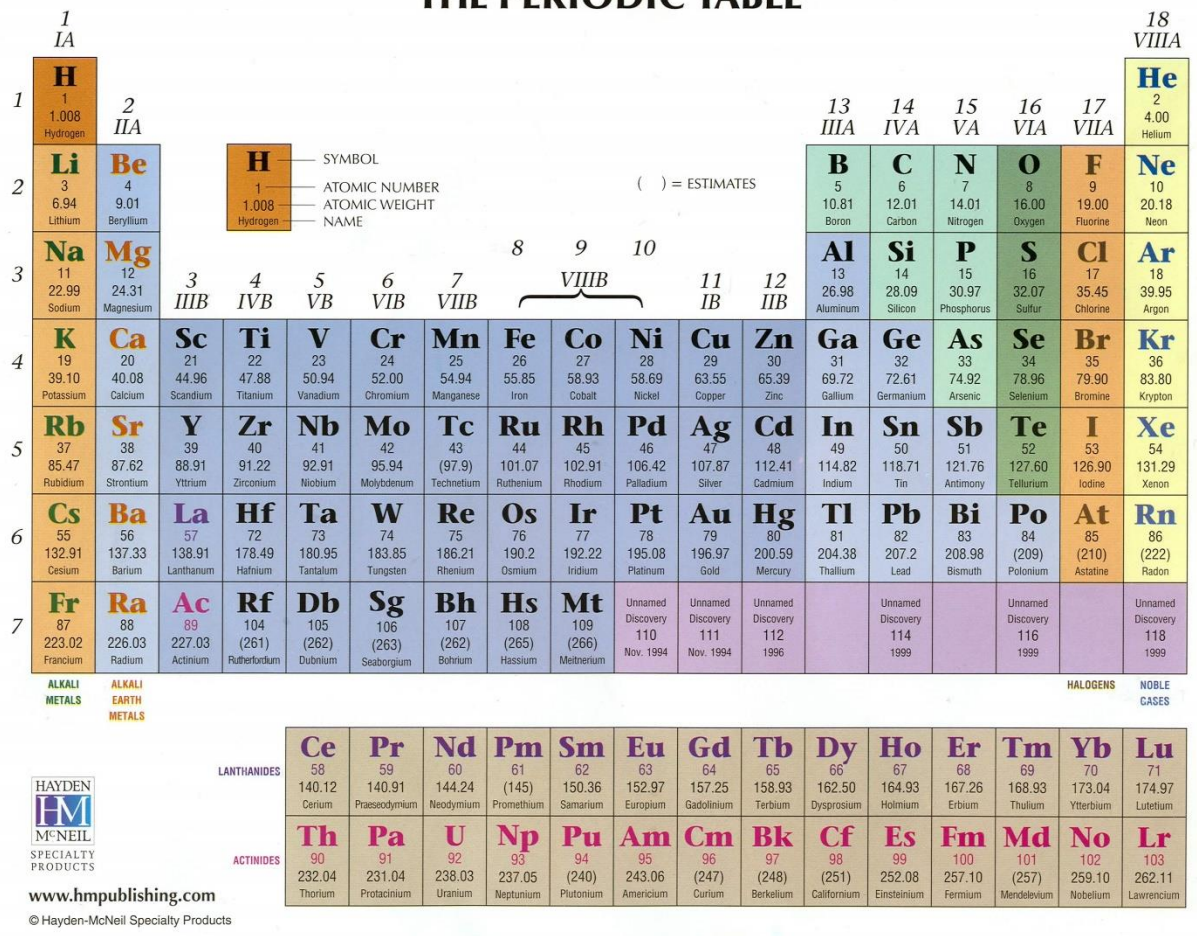
PCs must not be used. No material other than the exam paper is permitted.

Overall 30 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 **90 minutes** to finish the exam.

THE PERIODIC TABLE



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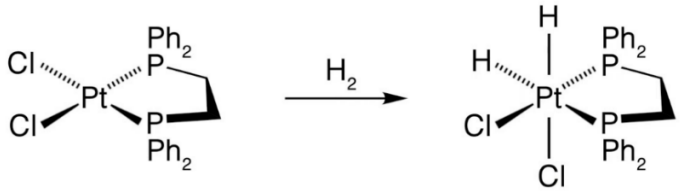
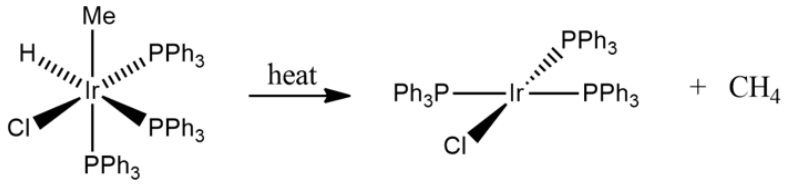
1. (6 points)
Describe the oxidation state of the metal and the number of total valence electrons including those from the ligands for the following species (A-F).
(a)



A B

A: Pt +2 or II; 16 electrons. B: Pt +4 or IV. 18 electrons (0.5 point each)

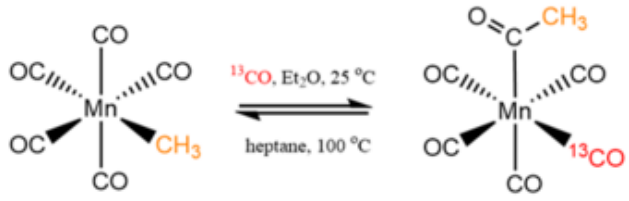
(b)



C D

C: Ir +3 or +III. 18 electrons. D. Ir +1 or I. 16 electrons. (0.5 point each)

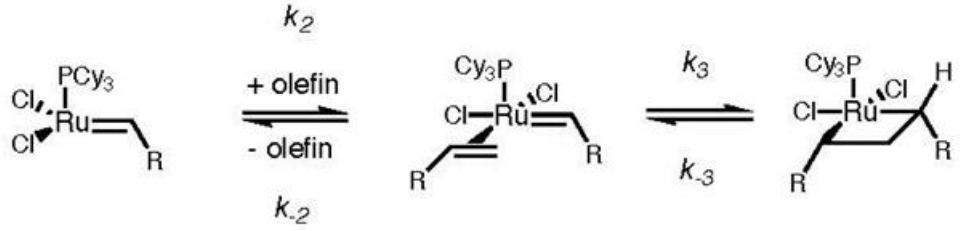
(c)



E F

E: Mn +1 or +I. 18 electrons. F. Mn +1 or I. 18 electrons. (0.5 point each)

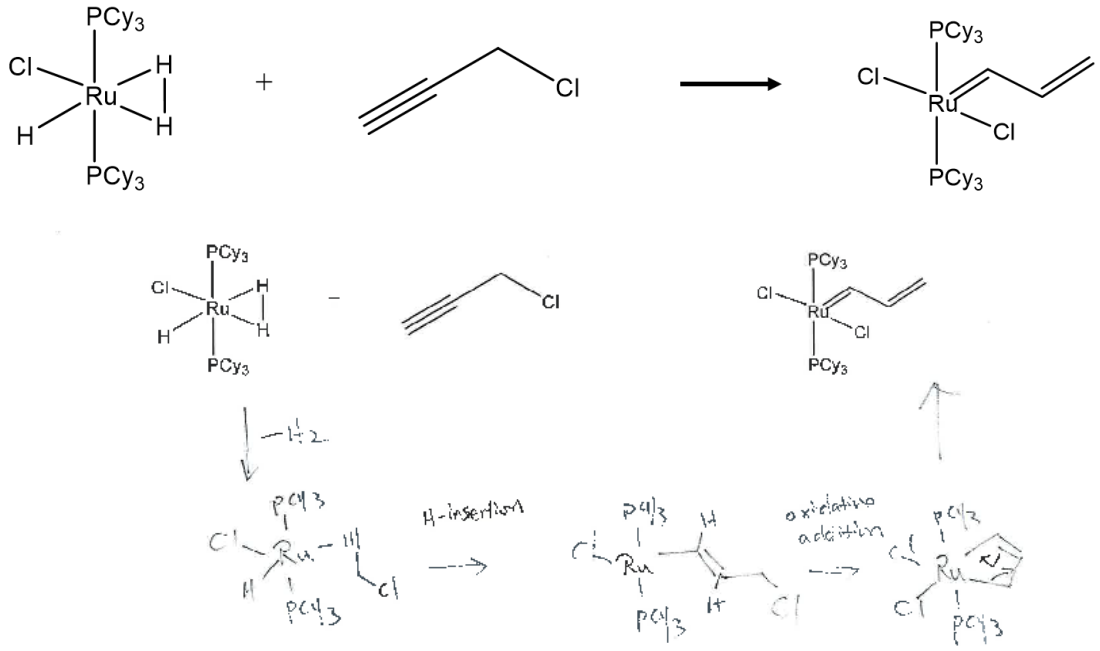
2. (3 points)
Describe the oxidation state of the Ru and the number of total valence electrons (including from ligands) for the following three Ru species.



2A 2B 2C

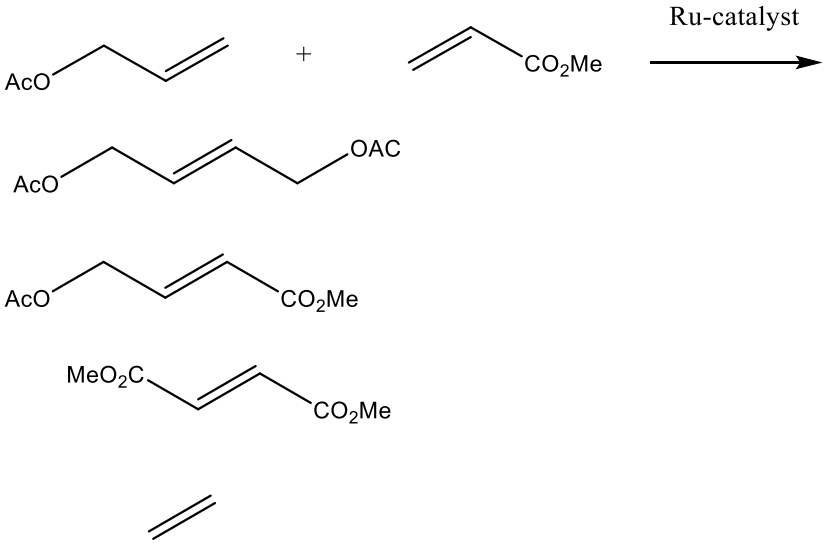
2A: Ru +4 or Ru (IV); 14 electrons
2B: Ru +4 or Ru (IV); 16 electrons
2C: Ru +4 or Ru (IV); 14 electrons
0.5 point each

3. The following reaction produced a Ru carbene complex that is active for olefin metathesis. Please propose a mechanism for its formation. (4 points)



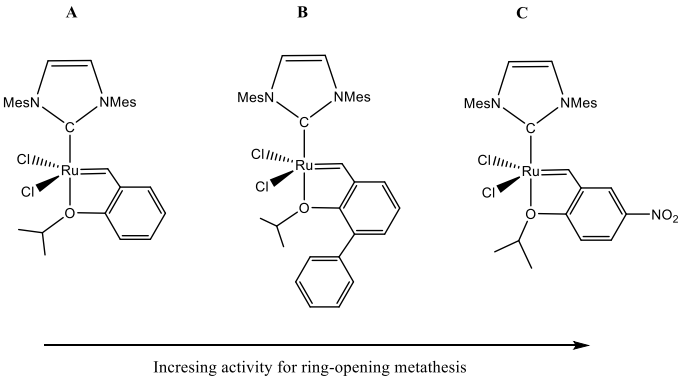
Coordination, H-insertion, oxidative addition, re-arrangement, each 1 point

4. List all possible metathesis products (4 points)



One point each

5. For the following Ru based catalysts, the trend of reactivity is observed. (4 points)



(a) Give possible explanations of the observed activity trend.

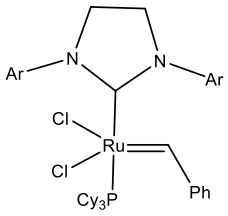
From electronic point of view, the NO2 group in C is most electron-withdrawing, the second aryl group in B is also electron withdrawing, but less so than NO2. So the activity is related to the electronic properties of the group next to the ether O atom. The more electron poor, the weaker the Ru-O bond, the faster the dissociation of the ligand opposite to the NHC, and the higher the activity.

(3 points)

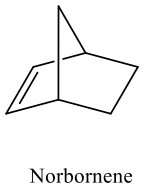
(b) Give a potential benefit of these catalysts compared to the classic Grubbs II catalyst. Explain why.

The aryl ether bond to Ru is weaker than a Ru-Phoshine bond, so we expect a faster initiation of the catalysts (dissociation of the ether ligand) shown here compared to classic Grubbs catalysts. 1 point

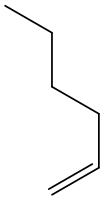
6. The reaction of Grubbs II catalyst with one equivalent of norbornene, followed by reaction with hexene, gives compounds P1 and P2. Draw a mechanism for the reaction sequences. (5 points)



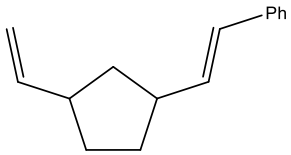
Grubbs II



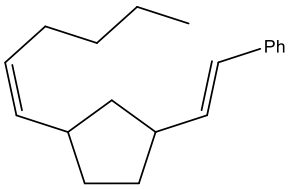
Norbornene



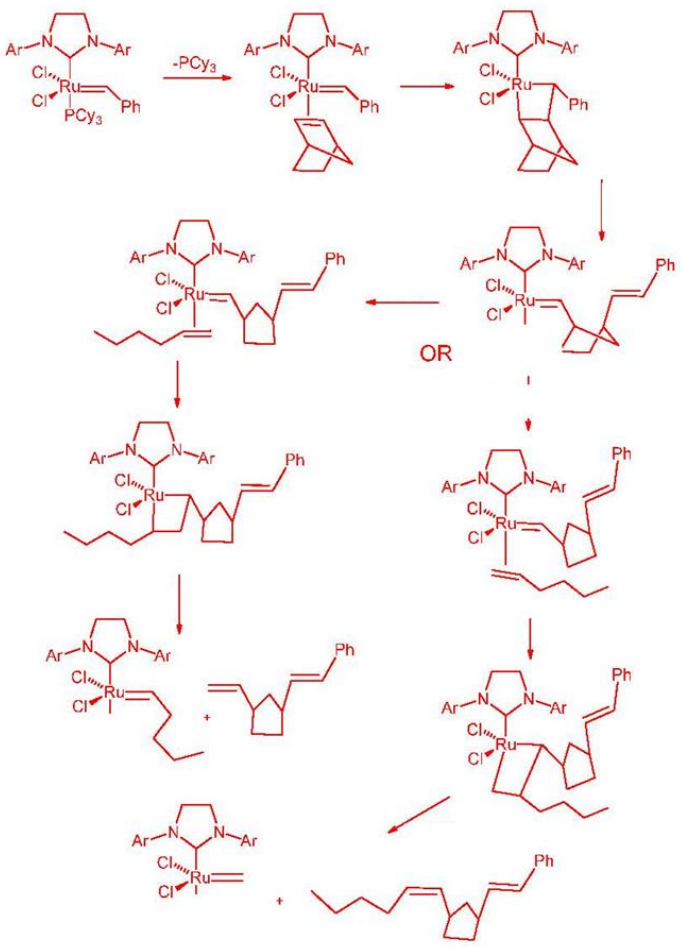
hexene



P1

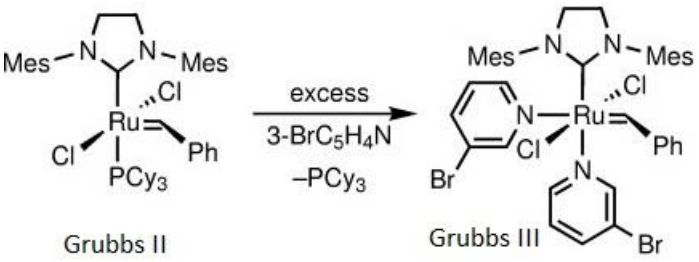


P2



Each step 0.5 point

7. The following reaction describes the synthesis of Grubbs III (3) catalyst from Grubbs II (2) catalyst. Grubbs 3 catalyst is found to be a better catalyst than Grubbs 2 catalyst for making monodispersed ring-opening-metathesis polymerization because Grubbs 3 is faster in initiating the catalysis. (4 points)

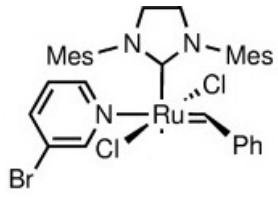


Grubbs II

(a) Explain why Grubbs 3 is faster in initiation.

The 3-bromopyridine ligand is a weak ligand, and it dissociates faster than a PCy3 ligand from the Ru. (2 points)

(b) Draw the active species from Grubbs 3 catalyst.



2 points. If the other bormopyridine is gone, then give 1 point.