

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

	1 IA																					18 VIIIA
1	H 1 1.008 Hydrogen															He 2 4.00 Helium						
2	Li 3 6.94 Lithium	Be 4 9.01 Beryllium											B 5 10.81 Boron	C 6 12.01 Carbon	N 7 14.01 Nitrogen	O 8 16.00 Oxygen	F 9 19.00 Fluorine	Ne 10 20.18 Neon				
3	Na 11 22.99 Sodium	Mg 12 24.31 Magnesium	3 IIIB	4 IVB	5 VB	6 VIB	7 VII B	8 9 10 VIIIB			11 IB	12 IIB	Al 13 26.98 Aluminum	Si 14 28.09 Silicon	P 15 30.97 Phosphorus	S 16 32.07 Sulfur	Cl 17 35.45 Chlorine	Ar 18 39.95 Argon				
4	K 19 39.10 Potassium	Ca 20 40.08 Calcium	Sc 21 44.96 Scandium	Ti 22 47.88 Titanium	V 23 50.94 Vanadium	Cr 24 52.00 Chromium	Mn 25 54.94 Manganese	Fe 26 55.85 Iron	Co 27 58.93 Cobalt	Ni 28 58.69 Nickel	Cu 29 63.55 Copper	Zn 30 65.39 Zinc	Ga 31 69.72 Gallium	Ge 32 72.61 Germanium	As 33 74.92 Arsenic	Se 34 78.96 Selenium	Br 35 79.90 Bromine	Kr 36 83.80 Krypton				
5	Rb 37 85.47 Rubidium	Sr 38 87.62 Strontium	Y 39 88.91 Yttrium	Zr 40 91.22 Zirconium	Nb 41 92.91 Niobium	Mo 42 95.94 Molybdenum	Tc 43 (97.9) Technetium	Ru 44 101.07 Ruthenium	Rh 45 102.91 Rhodium	Pd 46 106.42 Palladium	Ag 47 107.87 Silver	Cd 48 112.41 Cadmium	In 49 114.82 Indium	Sn 50 118.71 Tin	Sb 51 121.76 Antimony	Te 52 127.60 Tellurium	I 53 126.90 Iodine	Xe 54 131.29 Xenon				
6	Cs 55 132.91 Cesium	Ba 56 137.33 Barium	La 57 138.91 Lanthanum	Hf 72 178.49 Hafnium	Ta 73 180.95 Tantalum	W 74 183.85 Tungsten	Re 75 186.21 Rhenium	Os 76 190.2 Osmium	Ir 77 192.22 Iridium	Pt 78 195.08 Platinum	Au 79 196.97 Gold	Hg 80 200.59 Mercury	Tl 81 204.38 Thallium	Pb 82 207.2 Lead	Bi 83 208.98 Bismuth	Po 84 (209) Polonium	At 85 (210) Astatine	Rn 86 (222) Radon				
7	Fr 87 223.02 Francium	Ra 88 226.03 Radium	Ac 89 227.03 Actinium	Rf 104 (261) Rutherfordium	Db 105 (262) Dubnium	Sg 106 (263) Seaborgium	Bh 107 (262) Bohrium	Hs 108 (265) Hassium	Mt 109 (266) Meitnerium	Unnamed Discovery 110 Nov. 1994	Unnamed Discovery 111 Nov. 1994	Unnamed Discovery 112 1996	Unnamed Discovery 114 1999	Unnamed Discovery 116 1999	Unnamed Discovery 118 1999	Unnamed Discovery 118 1999	Unnamed Discovery 118 1999	Unnamed Discovery 118 1999				
	ALKALI METALS		ALKALI EARTH METALS														HALOGENS		NOBLE GASES			

LANTHANIDES													
Ce 58 140.12 Cerium	Pr 59 140.91 Praseodymium	Nd 60 144.24 Neodymium	Pm 61 (145) Promethium	Sm 62 150.36 Samarium	Eu 63 152.97 Europium	Gd 64 157.25 Gadolinium	Tb 65 158.93 Terbium	Dy 66 162.50 Dysprosium	Ho 67 164.93 Holmium	Er 68 167.26 Erbium	Tm 69 168.93 Thulium	Yb 70 173.04 Ytterbium	Lu 71 174.97 Lutetium
ACTINIDES													
Th 90 232.04 Thorium	Pa 91 231.04 Protactinium	U 92 238.03 Uranium	Np 93 237.05 Neptunium	Pu 94 (240) Plutonium	Am 95 243.06 Americium	Cm 96 (247) Curium	Bk 97 (248) Berkelium	Cf 98 (251) Californium	Es 99 252.08 Einsteinium	Fm 100 257.10 Fermium	Md 101 (257) Mendelevium	No 102 259.10 Nobelium	Lr 103 262.11 Lawrencium



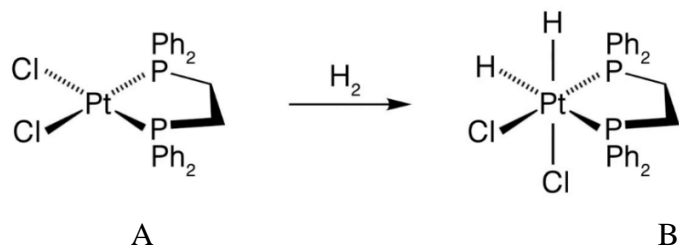
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1. (6 points)

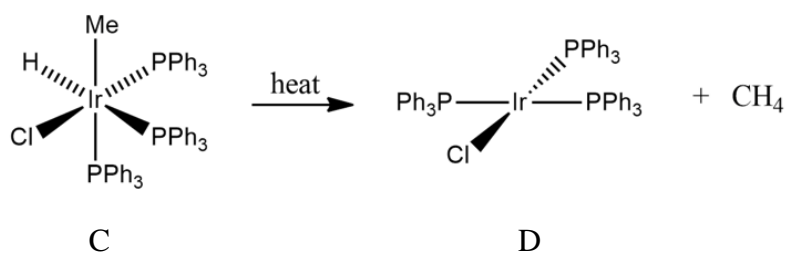
Describe the oxidation state of the metal and the number of total valence electrons including those from the ligands for the following species (A-F).

(a)



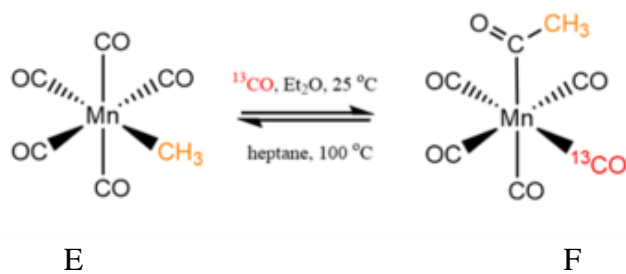
A: Pt +2 or II; 16 electrons. B: Pt +4 or IV. 18 electrons (0.5 point each)

(b)



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

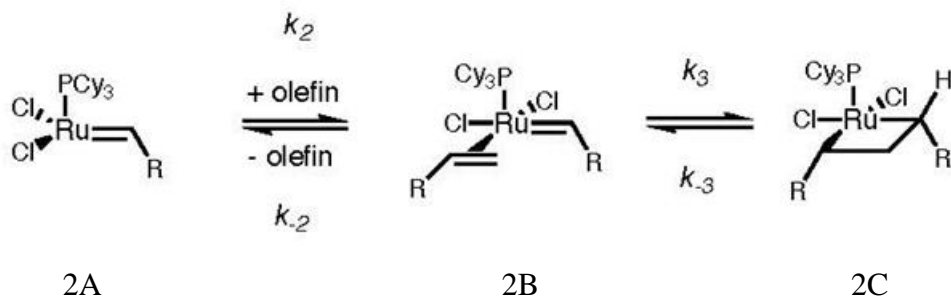
(c)



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.



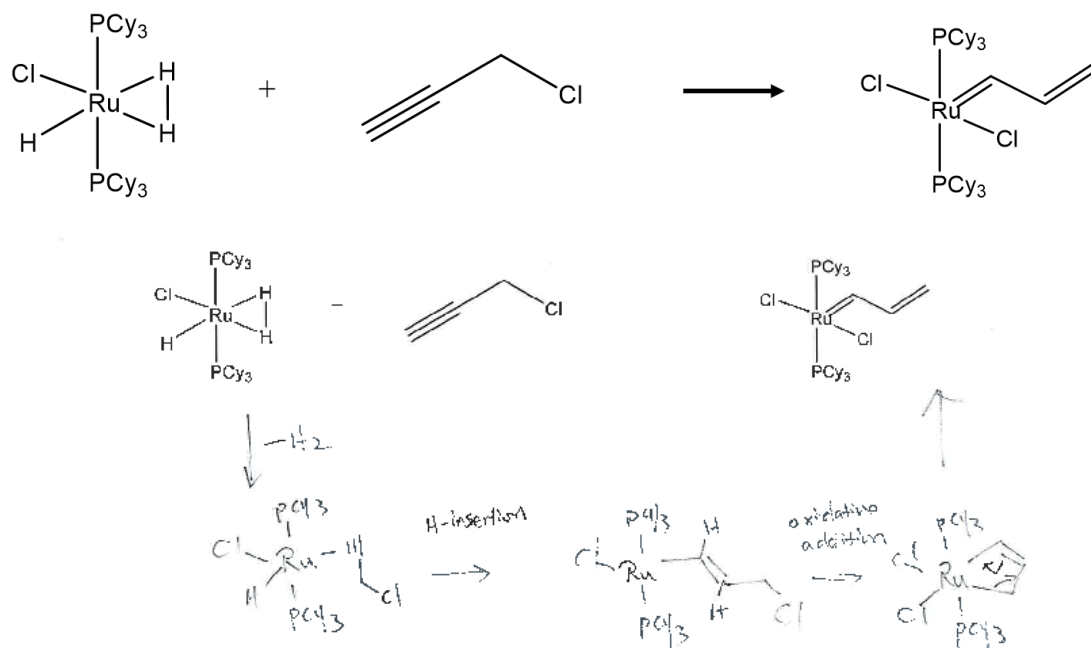
2A: Ru +4 or Ru (IV); 14 electrons

2B: Ru +4 or Ru (IV); 16 electrons

2C: Ru +4 or Ru (IV); 14 electrons

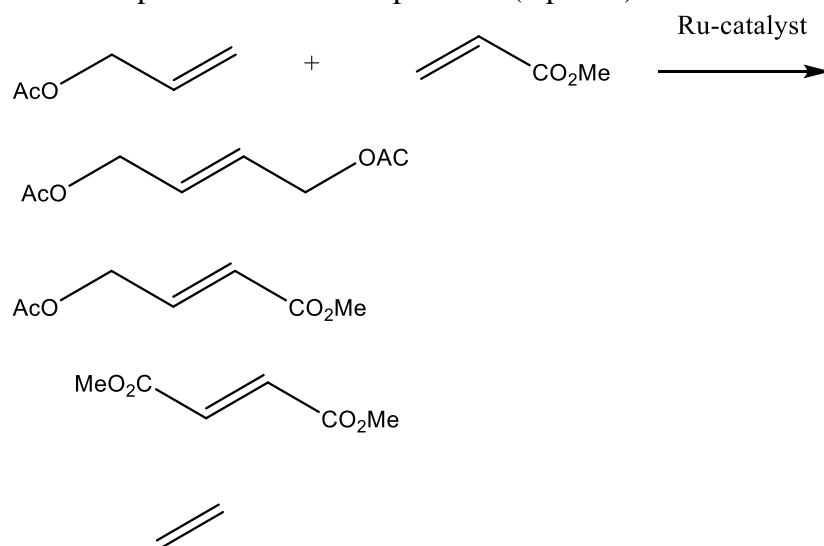
0.5 point each

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



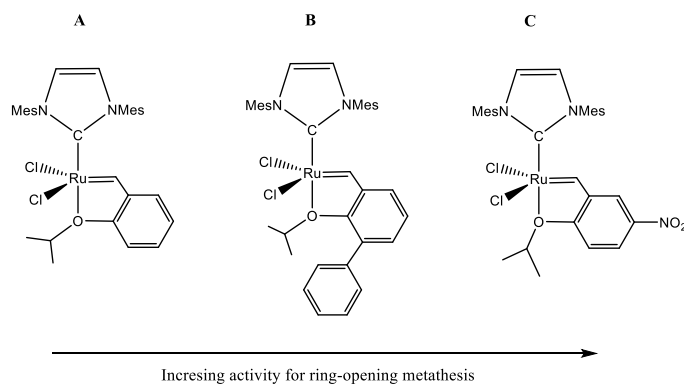
Coordination, H-insertion, oxidative addition, re-arrangement, each 1 point

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)

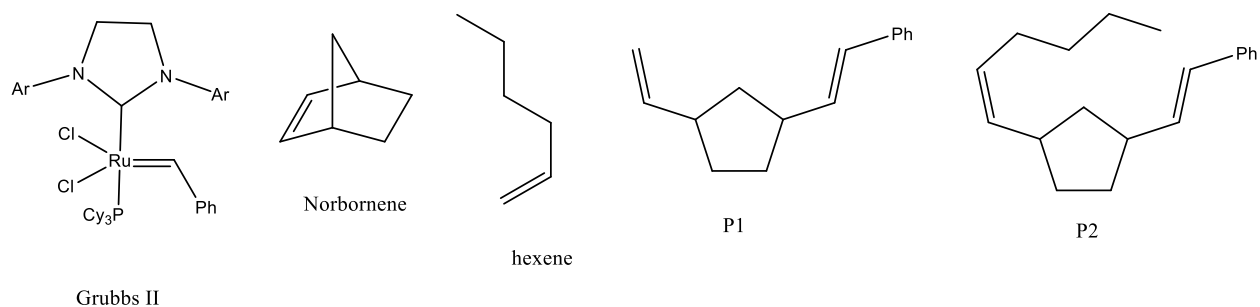
(b) Give a potential benefit of these catalysts compared to the classic Grubbs II catalyst. Explain why.

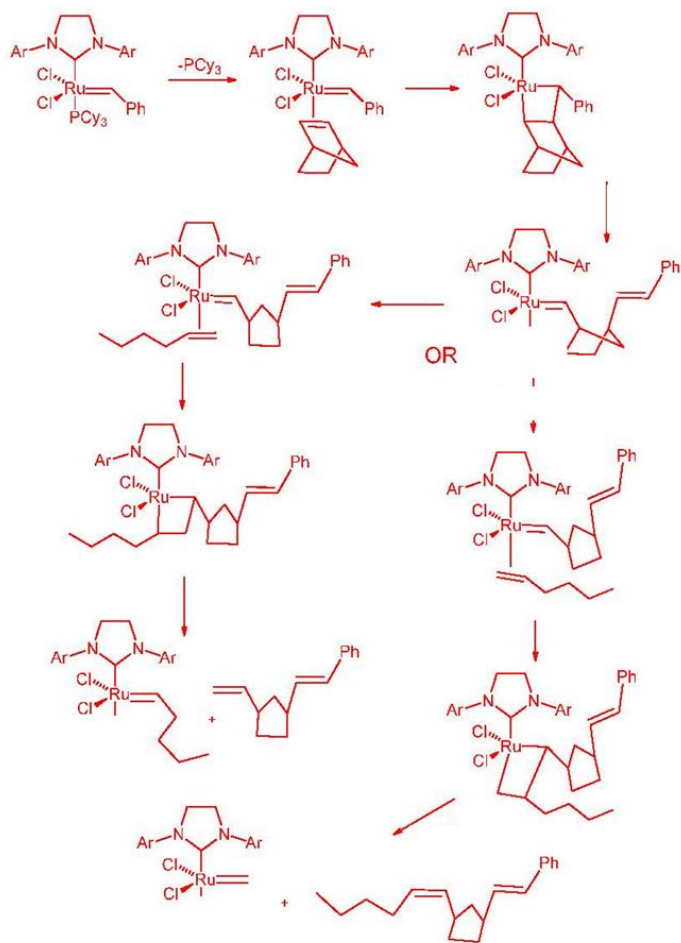
The aryl ether bond to Ru is weaker than a Ru-Phosphine bond, so we expect a faster initiation of the catalysts (dissociation of the ether ligand) shown here compared to classic Grubbs catalysts.

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.

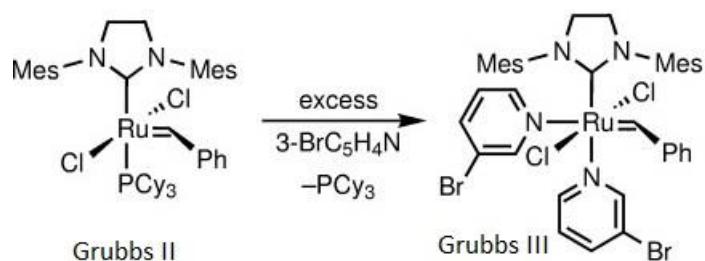
(5 points)





Each step 0.5 point

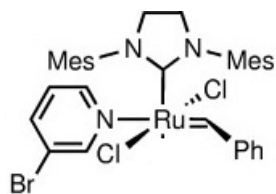
7. The following reaction describes the synthesis of Grubbs III (3) catalyst from Grubbs II (2) catalyst. Grubbs 3 catalyst is found to be a better catalyst than Grubbs 2 catalyst for making monodispersed ring-opening-metathesis polymerization because Grubbs 3 is faster in initiating the catalysis. (4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



(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 bromopyridine is gone, then give 1 point.