

Catalyst design for synthesis, Midterm Exam

October 17, 2025

Name (First name, Last name):

Student ID number:

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

Overall 35 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																18				
	IA																VIIIA				
1	H 1 1.008 Hydrogen											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				
2	Li 3 6.94 Lithium	Be 4 9.01 Beryllium											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			
3	Na 11 22.99 Sodium	Mg 12 24.31 Magnesium	3 IIB	4 IVB	5 VB	6 VIB	7 VIIB	8 9 10 VIII B			11 IB	12 IIB	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			
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

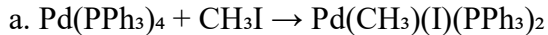
LANTHANIDES													
Ce 58 140.12 Cerium	Pr 59 140.91 Praseodymium	Nd 60 144.24 Neodymium	Pm 61 (145) Promethium	Sm 62 150.36 Samarium	Eu 63 152.97 Europium	Gd 64 157.25 Gadolinium	Tb 65 158.93 Terbium	Dy 66 162.50 Dysprosium	Ho 67 164.93 Holmium	Er 68 167.26 Erbium	Tm 69 168.93 Thulium	Yb 70 173.04 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



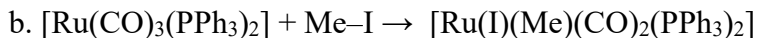
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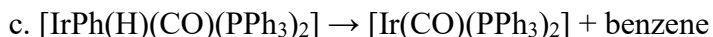
1. (8 points) Write the oxidation state and electron count (total valence electrons) before and after the reaction for the following complexes:



Before: Pd(0), 18 electrons. After, Pd(II), 16 electrons.
(each answer 0.5 points, same below)



Before, Ru(0), 18 electrons; after, Ru(II), 18 electrons.



Before, Ir(II), 17 electrons, After, Ir(0), 15 electrons.



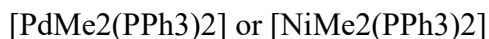
Before, Mn(I), 18 electrons; After, Mn(I), 16 electrons.

2. (1 point) Which of the following would undergo reductive elimination more rapidly? Why?
 $[\text{Pd}(\text{Ar})(\text{Me})(\text{PPh}_3)_2]$ or $[\text{Pd}(\text{Ar})(\text{Me})(\text{PMe}_3)_2]$

Hint: Consider the role of electron-rich vs electron-poor phosphines.

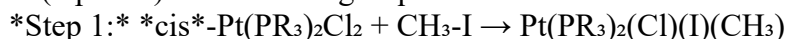
$[\text{Pd}(\text{Ar})(\text{Me})(\text{PPh}_3)_2]$. Because PPh₃ is more electron poor ligand, so $[\text{Pd}(\text{Ar})(\text{Me})(\text{PPh}_3)_2]$ is more electron poor complex. It is better for reductive elimination.

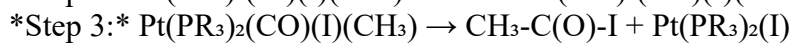
3 (1 point) Compare the tendency for reductive elimination in the following complexes. Why?



$[\text{NiMe}_2(\text{PPh}_3)_2]$ because Ni(II) is more electron poor than Pd(II), so better for reductive elimination.

4. (3 points) The following sequence of reactions is observed for a platinum complex:





a) Classify each step (1, 2, and 3) as an oxidative addition, substitution, migratory insertion, reductive elimination, or β -hydride elimination, or combination of them.

Step 1: Oxidative Addition. Step 2: Substitution. Step 3: Migratory insertion and Reductive Elimination.

(each name 0.5 point; total 2 points)

b) Step 3 is an unusual step. Propose a mechanism for this step, explaining what makes it possible. (Hint: Consider the properties of the CO ligand).

Mechanism for Step 3: The CO ligand inserts into the Pt-CH₃ bond, forming an acyl intermediate [Pt(PR₃)₂(I)(C(O)CH₃)]. This acyl ligand can then undergo RE with the adjacent iodide ligand.

(0.5 point for each step; total 1 point)

5. (8 points) The Chauvin mechanism is the accepted pathway for olefin metathesis.

a) Draw a complete catalytic cycle for the self-metathesis of propene (2 CH₂=CH-CH₃) using a generic metal alkylidene catalyst, **M=CH₂**. Show all intermediates and indicate the distribution of products.

The cycle should show: **M=CH₂** + CH₂=CH-CH₃ → [2+2] → Metallacyclobutane → Cycloreversion → **M=CH-CH₃** + CH₂=CH₂. The new metal alkylidene (**M=CH-CH₃**) then reacts with another propene: **M=CH-CH₃** + CH₂=CH-CH₃ → [2+2] → Metallacyclobutane → Cycloreversion → **M=CH₂** + CH₃-CH=CH-CH₃.

(3 points)

b) Based on your cycle, explain why the self-metathesis of propene produces both ethene and but-2-ene in a statistically predictable ratio.

The mechanism is a statistically random exchange. Every time a metal alkylidene reacts with propene, there is an equal probability of forming either ethene (**M=CH-CH₃**) or the original methylidene (**M=CH₂**).

(1 point)

c) What would be the statistically predictable ratio of ethene, propene, and but-2-ene, ignoring any other factors such as thermodynamics. Explain why. (Hard question!)

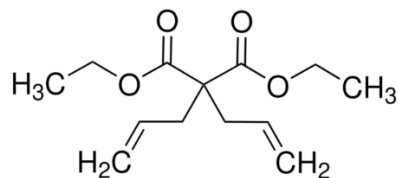
This leads to an equilibrium mixture with ethene, propene, and but-2-ene in a 1:2:1 ratio.
Ratio: 2 points (correct ethene to but-ene, 1 point; correct ethene to propene, 1 point).

Why: In equilibrium, the ratio of $M=CH_2$ and $M=CH-CH_3$ is 1:1. Each $M=CH_2$ can give equal ratio of $CH_2=CH_2$ and $CH_2=CH-CH_3$; each $M=CH-CH_3$ can give equal ratio of $CH_2=CH-CH_3$ and $CH_3-CH=CH-CH_3$.

Reason: 2 points.

6. (9 points) For each of the following reactions, draw a simplified catalytic cycle (starting from the metal methylene, $M=CH_2$) and show the products:

a) **Ring-Closing Metathesis (RCM)** of diethyl diallylmalonate. The reaction is performed under high dilution conditions. Why is this necessary for high-yielding RCM?



The diene coordinates to $M=CH_2$, and the cycle proceeds to form a ring and release $CH_2=CH_2$.

4 points

Dilution To avoid cross metathesis.

1 point

b) **Cross Metathesis (CM)** between ethylene and 2-decene. Why is ethylene often used as a reactant in CM?



b) Application in Tandem Catalysis: In one pot, a sequence requires a metathesis step after a Pd-catalyzed cross-coupling reaction. Knowing that the metathesis catalyst must be tolerant to a variety of functional groups and residual phosphines from the cross-coupling step, indicate which catalyst between the original Grubbs II or HG-II is better suited for this application, and why.

HG-II. Because the Ru center is protected by the O group, so phosphine cannot attack.

One point for choice. One point for reason. Total 2 point.

c) What is the primary kinetic trade-off of this chelating design?

Slow initiation.

1 point