

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

THE PERIODIC TABLE																		18 VIIIA						
1 IA																								
1 H 1 1.008 Hydrogen																	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	2 He 4.00 Helium		
2 IIA	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						
			H 1 1.008 Hydrogen																	() = ESTIMATES				
3	Na 11 22.99 Sodium	Mg 12 24.31 Magnesium	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 9 10 VIII			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						
	ALKALI METALS			ALKALI EARTH METALS										HALOGENS					NOBLE GASES					



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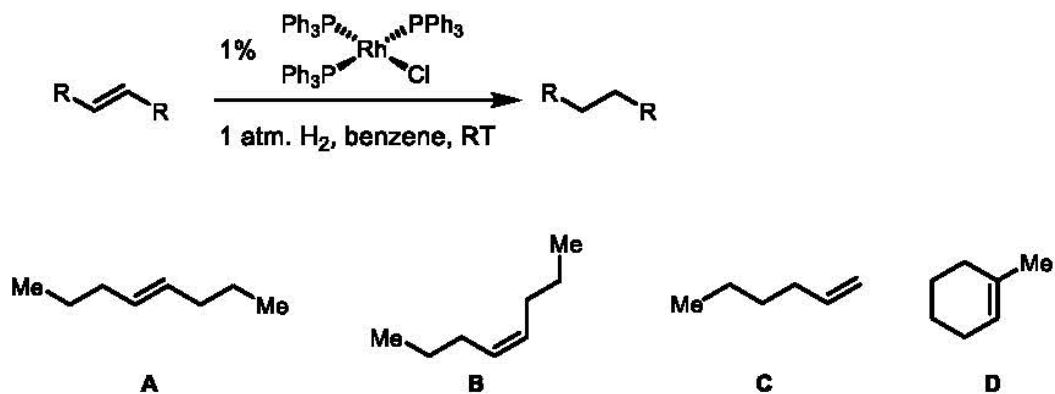
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LANTHANIDES

ACTINIDES

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
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

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



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

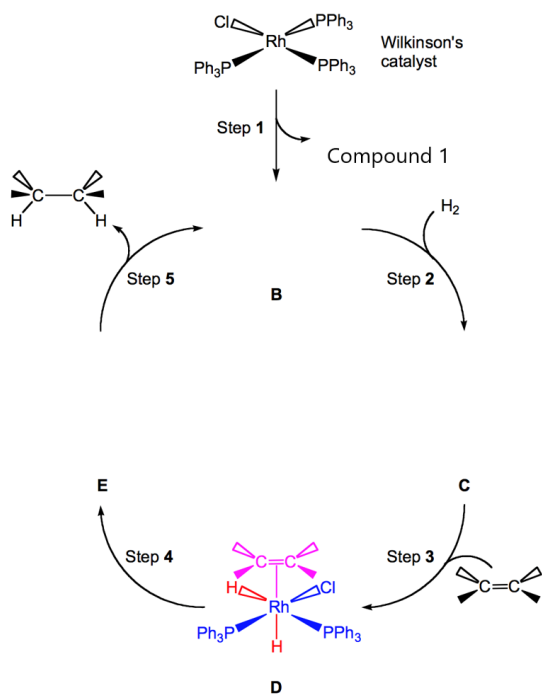
All correct, 4 points

If D is slowest, 1 point;

If C is fastest, 1 point.

If B faster than A, 1 point.

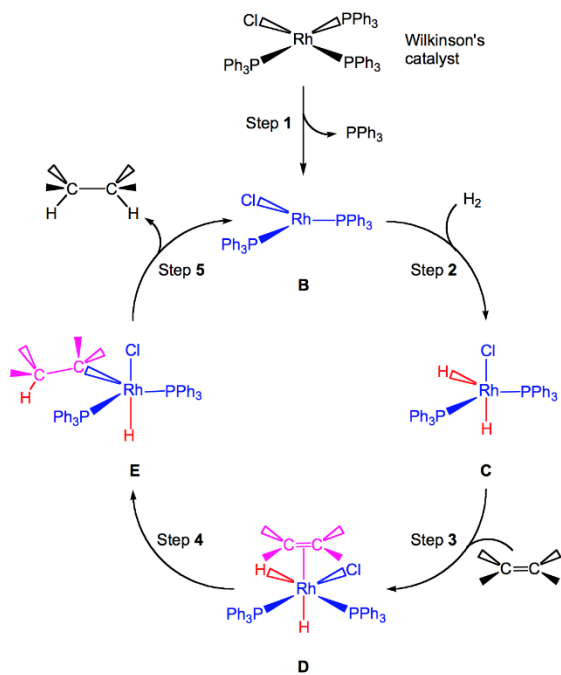
2. (4 points) Please complete the following mechanistic cycle for Wilkinson's catalyst. (1) What is compound 1. (2) Draw the structures of compounds B, C, and E.



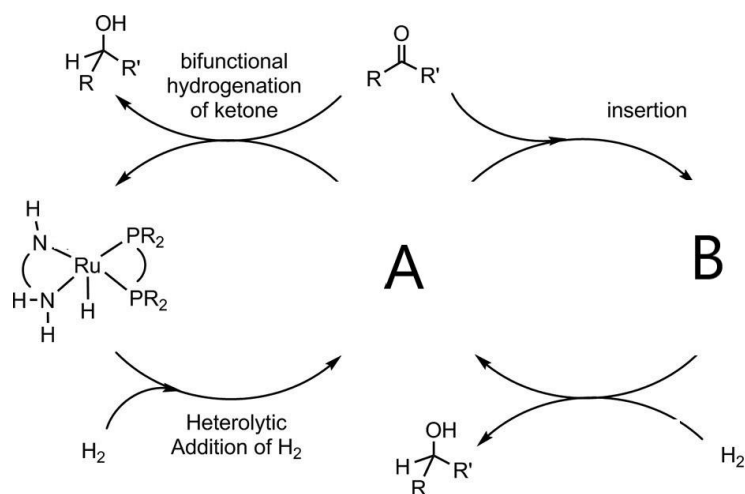
A:

1. Compound 1: PPh₃

2: see this:



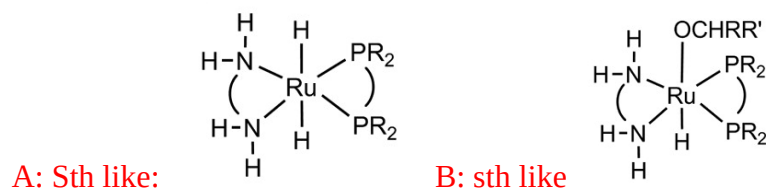
3. (8 points) For the following Ru-catalyzed hydrogenation. Two possible mechanisms are known: a bifunctional mechanism and a step-wise mechanism. Please complete the following questions.



(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)



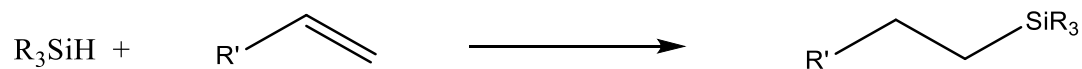
2 points each. For A, key is to protonate the N=Ru; for B, key is insertion of ketone to H. Can be on the top or on the bottom.

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

Both +2. One point each.

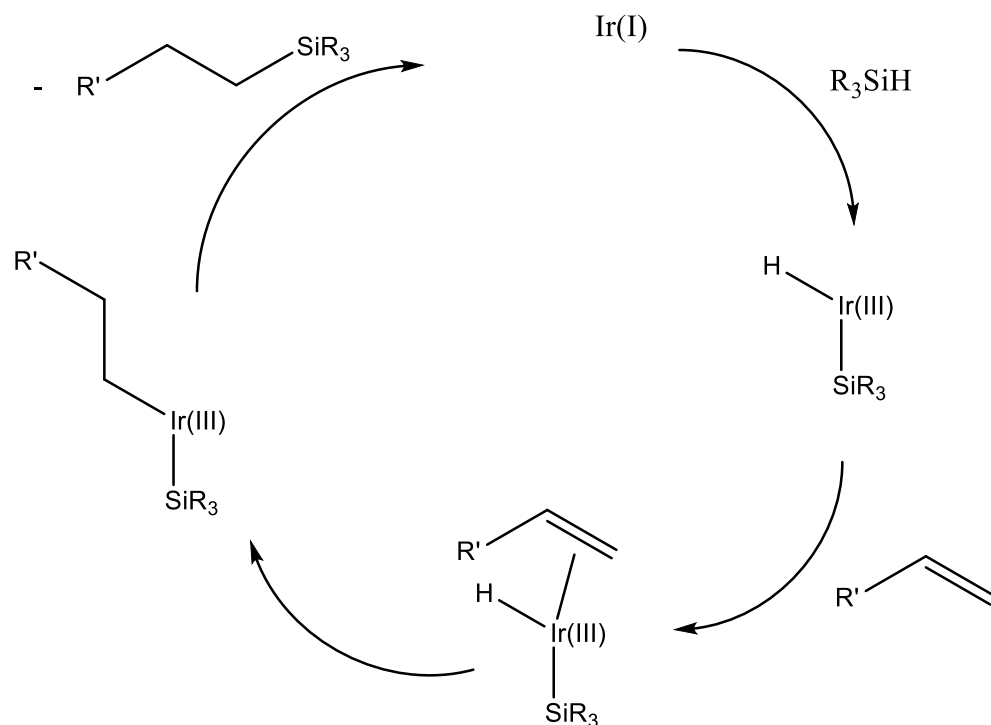
If the same as answer 1, but not +2, then get 1 point.

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.

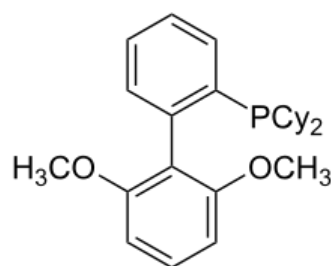
A:



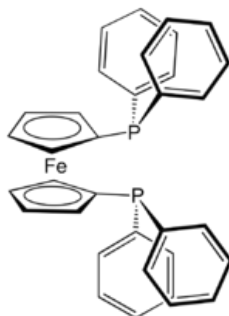
Oxidation state, 0.5 point each.

Each step : 1 point each.

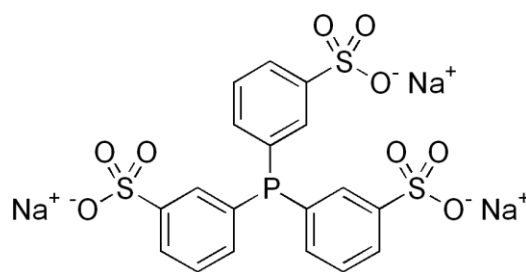
5. (6 points) (a) Associate the most suitable phosphine ligands below for the following Pd-catalyzed cross-coupling reaction. (b) Give a brief explanation for each of your choice.



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).

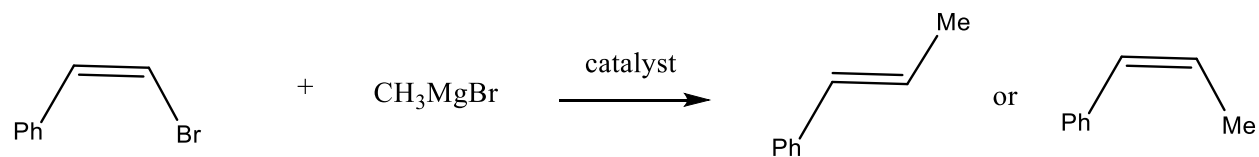
(iii) Kumada and Suzuki coupling of alkyl nucleophiles; why?

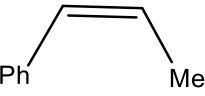
B: DPPF. Because this ligand is bidentate and suppress β -elimination. (second answer, promote reductive elimination)

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

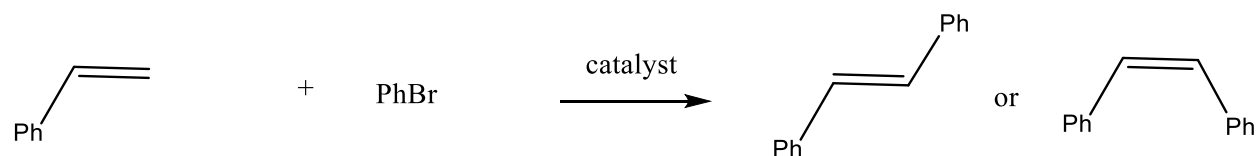
6. (4 points) Choose the correct major product in the following cross-coupling reactions. Explain why.

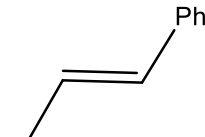
(1)



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

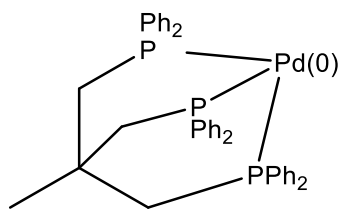
(2)



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.

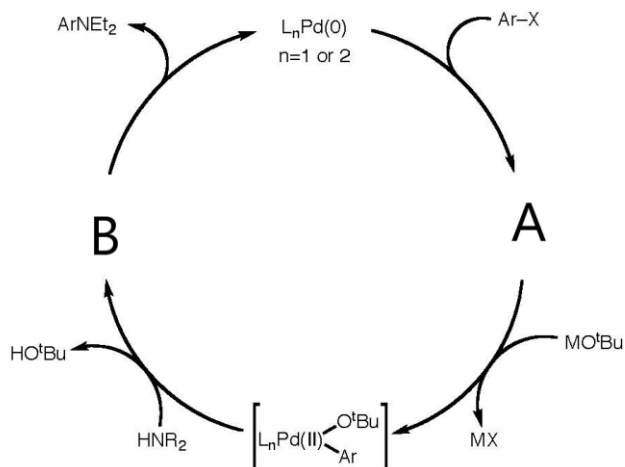
7. (2 points) Do you expect the following complex to be a very active catalyst for Suzuki coupling? Why or why not?

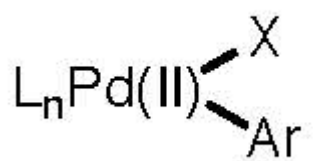


A : Not very active. (1 point)

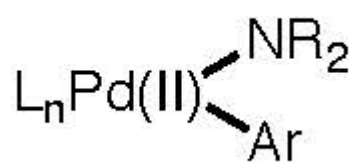
Because it has a tridentate ligand. Normally a bi or mono-dentate Pd(0) complex is active for Suzuki coupling. This compound has a tridentate ligand. (1 point)

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.