

# CHEM 3331 (Richardson) Second Hour Exam – October 18, 2016

Your Name \_\_\_\_\_

Student ID \_\_\_\_\_

- Recitation  1:00 Monday w/ Thomas Carey  
 (check one)  2:00 Monday w/ Thomas Carey  
 3:00 Monday w/ Matthew Farmer  
 9:00 Tuesday w/ Ryan McCaffrey  
 11:00 Tuesday w/ Ryan McCaffrey  
 1:00 Tuesday w/ Ryan McCaffrey  
 2:00 Tuesday w/ Patrick Nordeen  
 3:00 Tuesday w/ Matthew Farmer

Question	Score	Out of
1		30
2		25
3		30
4		15
5		10 e.c.
Total		100

This is a closed-book exam. The use of notes, calculators, or cell phones will not be allowed during the exam. You may use models sets brought in a clear ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states.

1 <b>H</b> 1.008																	2 <b>He</b> 4.0026
3 <b>Li</b> 6.94	4 <b>Be</b> 9.0122											5 <b>B</b> 10.81	6 <b>C</b> 12.011	7 <b>N</b> 14.007	8 <b>O</b> 15.999	9 <b>F</b> 18.998	10 <b>Ne</b> 20.180
11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305	13 <b>Al</b> 26.982	14 <b>Si</b> 28.085	15 <b>P</b> 30.974	16 <b>S</b> 32.06	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.948										
19 <b>K</b> 39.098	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.956	22 <b>Ti</b> 47.867	23 <b>V</b> 50.942	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.938	26 <b>Fe</b> 55.845	27 <b>Co</b> 58.933	28 <b>Ni</b> 58.693	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.38	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.630	33 <b>As</b> 74.922	34 <b>Se</b> 78.97	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.798
37 <b>Rb</b> 85.468	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.906	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.906	42 <b>Mo</b> 95.95	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53 <b>I</b> 126.90	54 <b>Xe</b> 131.29
55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.33	57-71 *	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.95	74 <b>W</b> 183.84	75 <b>Re</b> 186.21	76 <b>Os</b> 190.23	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.97	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.38	82 <b>Pb</b> 207.2	83 <b>Bi</b> 208.98	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)
87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89-103 #	104 <b>Rf</b> (265)	105 <b>Db</b> (268)	106 <b>Sg</b> (271)	107 <b>Bh</b> (270)	108 <b>Hs</b> (277)	109 <b>Mt</b> (276)	110 <b>Ds</b> (281)	111 <b>Rg</b> (280)	112 <b>Cn</b> (285)	113 <b>Nh</b> (286)	114 <b>Fl</b> (289)	115 <b>Mc</b> (289)	116 <b>Lv</b> (293)	117 <b>Ts</b> (294)	118 <b>Og</b> (294)

\* Lanthanide series

57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.96	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.93	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.93	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.93	70 <b>Yb</b> 173.05	71 <b>Lu</b> 174.97
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# Actinide series

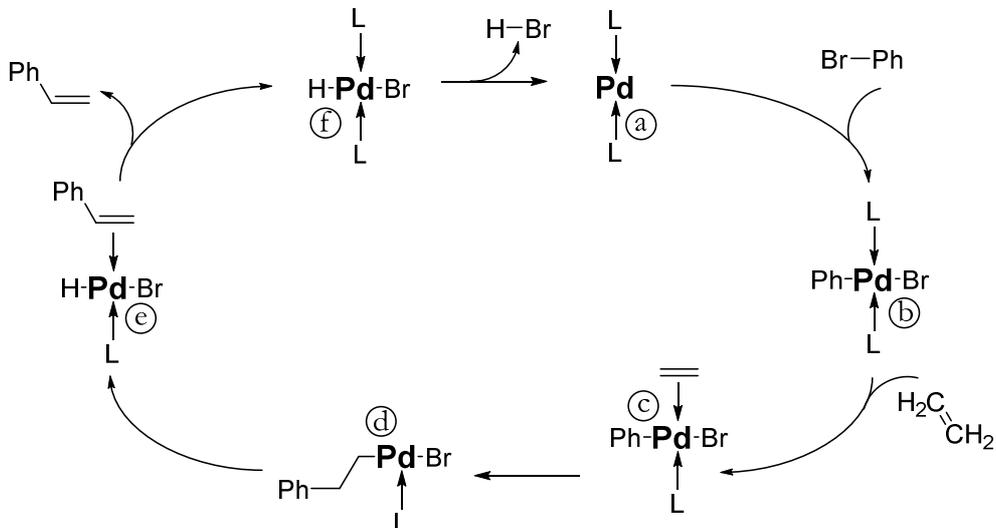
89 <b>Ac</b> (227)	90 <b>Th</b> 232.04	91 <b>Pa</b> 231.04	92 <b>U</b> 238.03	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)
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## pKa Values

HI	-10	CH <sub>3</sub> COOH	4.7	Phenol	10	H <sub>2</sub>	35
HBr	-8	HN <sub>3</sub>	4.7	RSH	10-12	NH <sub>3</sub>	36
HCl	-6	H <sub>2</sub> S	7.0	H <sub>2</sub> O	15.7	H <sub>2</sub> C=CH <sub>2</sub>	45
H <sub>3</sub> O <sup>+</sup>	-1.7	NH <sub>4</sub> <sup>+</sup>	9.3	Alcohol (ROH)	16-18	CH <sub>4</sub>	60
HF	3.2	HCN	9.4	HC≡CH	26		



2) The mechanism for the Heck reaction is shown below. (25 pts total)



- Label each arrow with the name for the step occurring at the transition metal. (6 pts)
- For each Pd species (a through f) list the oxidation state, unshared electrons, and electron count at the transition metal. (9 pts)

These formulas may help you:

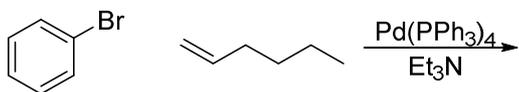
$$\text{Oxidation state of metal atom} = \# \text{ of X-type ligands} + \text{charge on metal}$$

$$n = \# \text{ of unshared electrons} = \text{valence electrons in neutral metal} - \text{oxidation state}$$

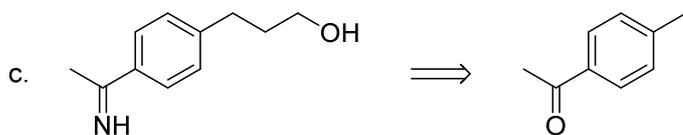
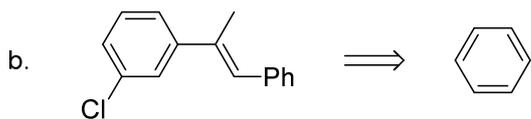
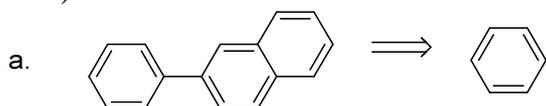
$$\text{Electron count} = \# \text{ of valence electrons in neutral metal} - \text{charge on metal} + \# \text{ of X-type ligands} + 2 \cdot (\# \text{ of L-type ligands})$$

- |                          |                          |
|--------------------------|--------------------------|
| Oxidation state =        | Oxidation state =        |
| (a) Unshared electrons = | (d) Unshared electrons = |
| Electron count =         | Electron count =         |
| Oxidation state =        | Oxidation state =        |
| (b) Unshared electrons = | (e) Unshared electrons = |
| Electron count =         | Electron count =         |
| Oxidation state =        | Oxidation state =        |
| (c) Unshared electrons = | (f) Unshared electrons = |
| Electron count =         | Electron count =         |

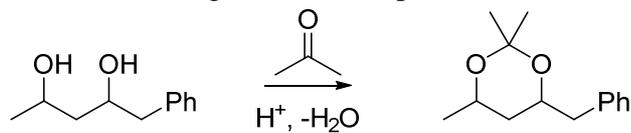
c. Show the product(s) of the following reactions. (10 pts)



- 3) Find a way to synthesize the desired product from the given starting material plus any other reagents. If more than one step is necessary, show the product of each step. You do not need to show mechanisms or the specific structure of transition metal catalysts. (30 pts; 10 pts each)



4) Provide a mechanism for the following reaction. (15 pts)



5) Extra credit! Arrange each of the following groups of compounds in order of decreasing reactivity (1 = fastest, 5 = slowest) towards nucleophilic aromatic substitution with NaOMe. For the fastest reactant, show all the resonance forms in the intermediate and point out which ones are particularly stable. (10 pts e.c.)

