

Chemistry 652

Organometallic Chemistry

Midterm Examination, April 7, 2020 (the year of Covid-19!)

- In a deviation from normal procedure, this is an open book/notes exam. Specifically, you are welcome to look at a periodic table of the elements. During the exam, you may not discuss your work with anybody else!
- If you have a printer, you can print the exam and put your answers right on it. Alternatively, just write them on a piece of paper (organized by problem no., and put your name on it!). Send a copy/photo of your answers to: theopold@udel.edu
- The exam is timed. I must receive your answers - electronically - by the end of class (i.e. 3:15 PM on April 7, 2020). I will subtract points for answers submitted late. Allow some time (~ 5 mins?) at the end to send me your answers!

Name: Key

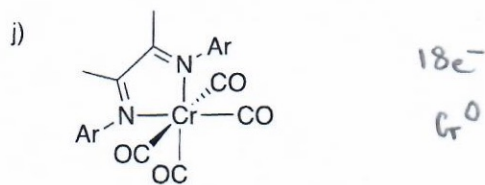
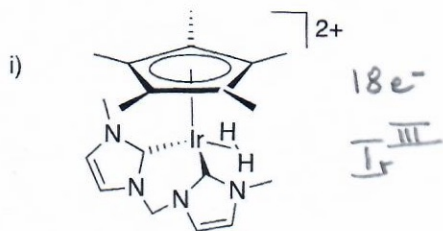
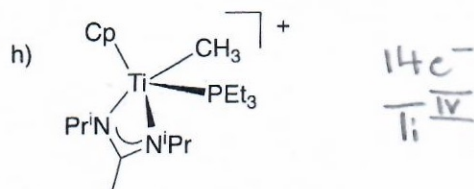
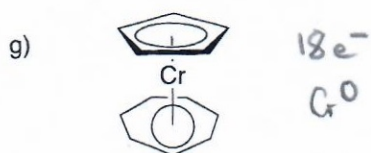
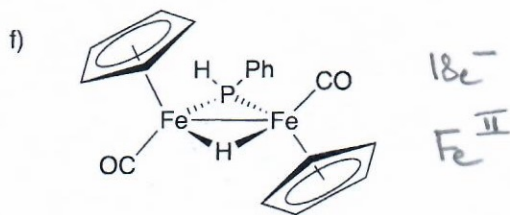
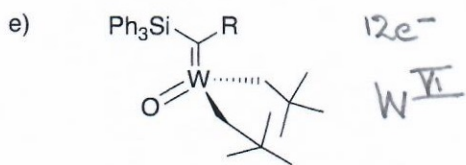
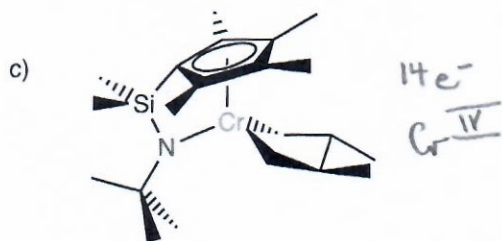
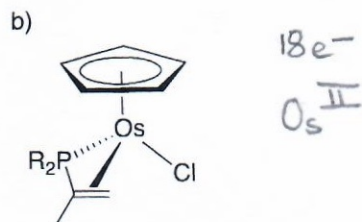
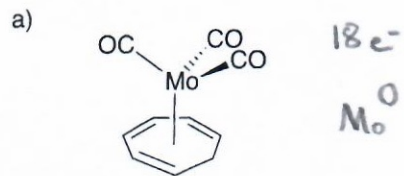
1:

2:

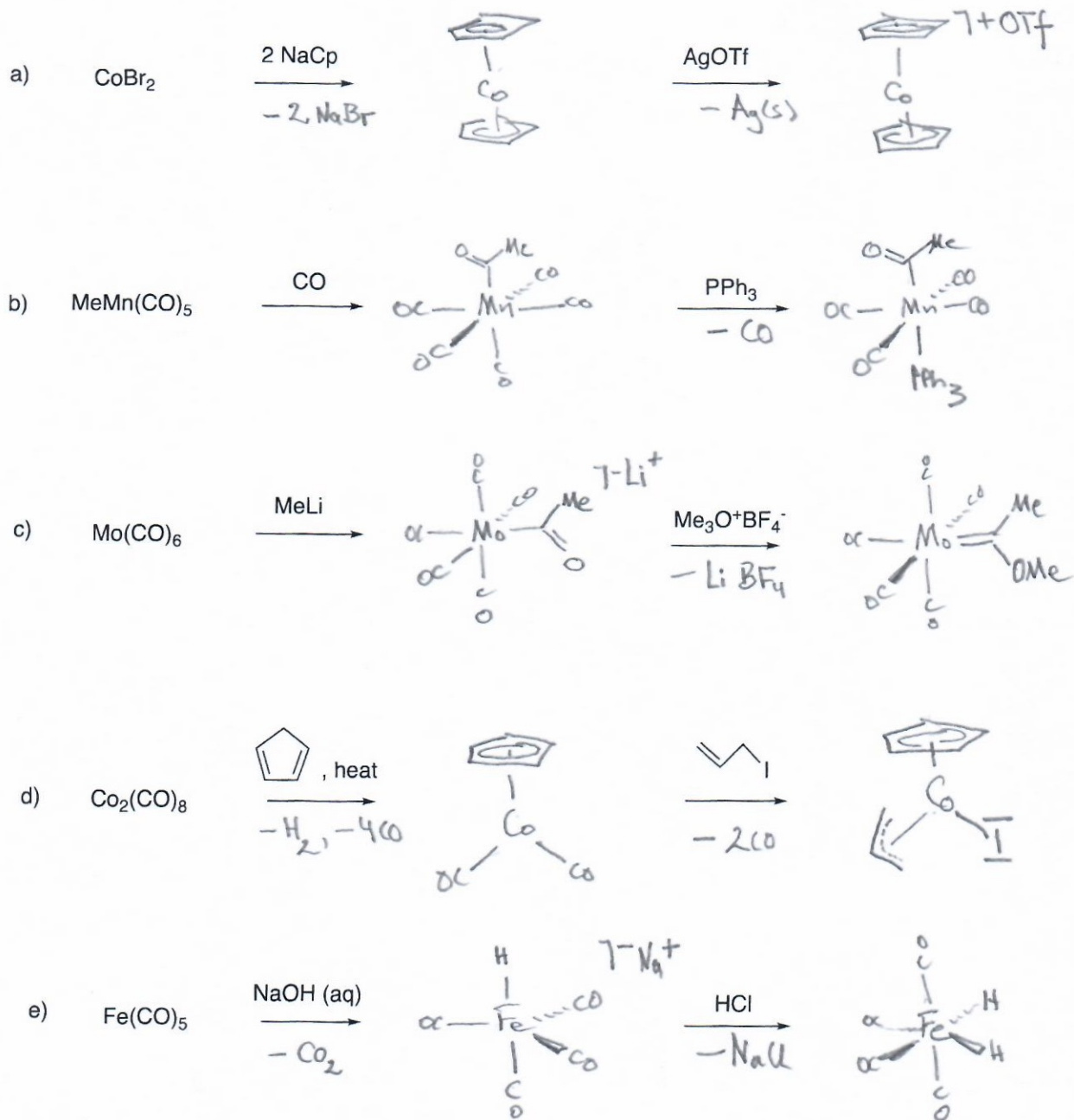
3:

4:

1. (20 pts.) For the following molecules, give the valence electron count and the formal oxidation state of the metal.

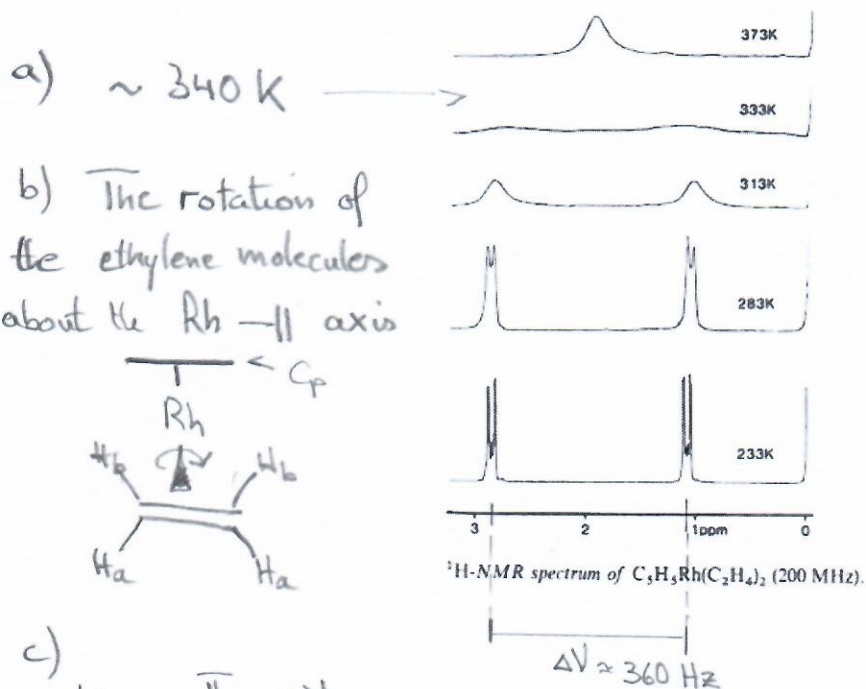


2. (30 pts.) For the 2-step syntheses shown below, list all(!) products (i.e., I am looking for balanced equations) and draw structures of the organometallic ones



3. (25 pts.) Shown below are variable temperature ^1H NMR spectra of $\text{CpRh}(\text{C}_2\text{H}_4)_2$, showing the ethylene resonances only.

- Estimate the temperature of coalescence (T_c)
- What dynamic process gives rise to the coalescence phenomenon.
- Based on these data, estimate the rate constant (units!) for the process at T_c .
- Estimate ΔG^\ddagger (the free energy of activation) for the process.
- Estimate T_c when measured in a 600 MHz spectrometer.
- ΔG^\ddagger is an approximate measure of what?
- How many resonances does the full ^{13}C NMR of $\text{CpRh}(\text{C}_2\text{H}_4)_2$ at 20°C exhibit?



c)

$$k_c = \frac{\pi}{\sqrt{2}} \cdot \Delta\nu$$

$$= 2.22 \cdot 360\text{ s}^{-1}$$

$$\approx 800\text{ s}^{-1}$$

d)

$$\Delta G^\ddagger = 50 \cdot T_c (\text{cal/mol})$$

$$= 17.0\text{ kcal/mol}$$

e) at 600 MHz, $\Delta\nu \approx 3 \times 360$
 $= 1080\text{ Hz}$

$k_c \approx 2400\text{ s}^{-1}$, which requires a higher temperature

Using Eyring eq. ($k = \frac{kT}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$)

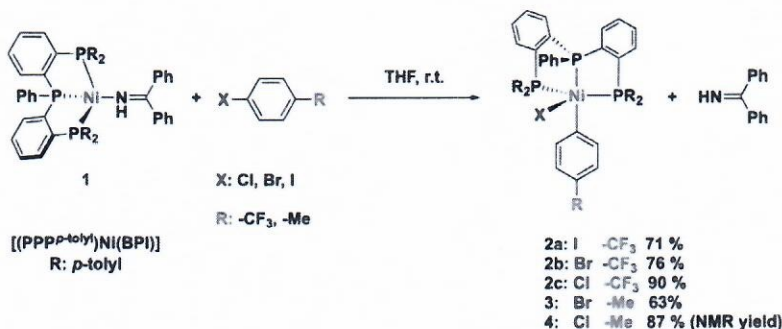
get $T_c (@600\text{ MHz}) = 356\text{ K}$

f) ΔG^\ddagger is a measure of the strength of the π -backbonding between Rh and C_2H_4

g) All the ethylene carbons are equivalent, thus
 2 resonances, 1 for Cp
 & 1 for C_2H_4

See P.M. Perez-Garcia et al.
Organometallics 2020 ASAP
DOI: 10.1021/acs.organomet.0c0060

4. (25 pts.) Consider the reaction shown below.



Its rate law has been determined by kinetic measurements. It is:

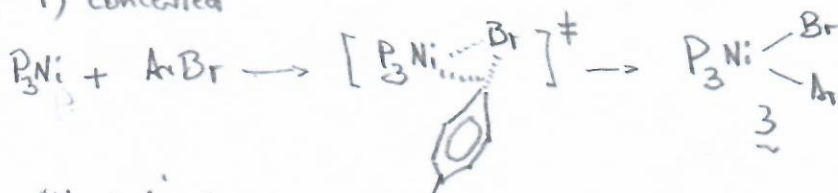
$$-d[\mathbf{1}]/dt = k [\text{ArBr}][\mathbf{1}]/[\text{BPI}]$$

- What type of reaction is this?
- What does the rate law suggest about the mechanism?
- Suggest two different possible reaction mechanisms. Draw intermediates/transition states as needed, to identify the significant differences.
- As the PI, what would you suggest to determine the actual mechanism?

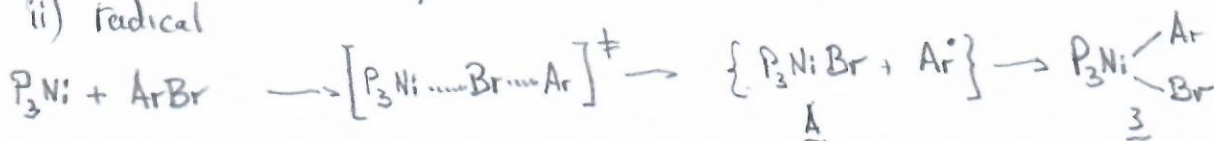
a) an 'oxidative addition'

b) The inverse order in [BPI] suggest a pre-equilibrium dissociation of the BPI ligand to liberate a 'P₃Ni' fragment
The orders in [1] and [ArBr] suggest a bimolecular encounter of 'P₃Ni' and ArBr in the transition state

c) i) concerted



ii) radical



d)

kinetics:

- compare rates of ArI, ArBr, ArCl
- do a Hammett type correlation

experiments:

- radical traps?
- make Ni(I) complex

computation:

- Calculation of energies of transition states