

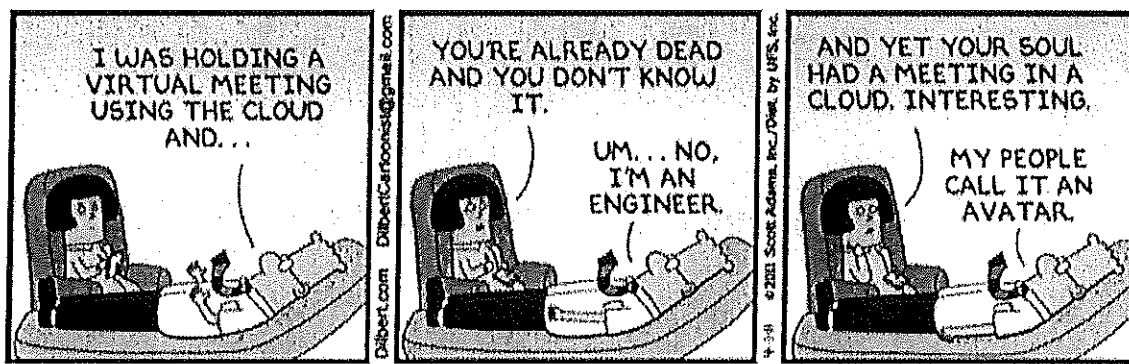
Chemistry 652

Organometallic Chemistry

Midterm Examination, April 7, 2011

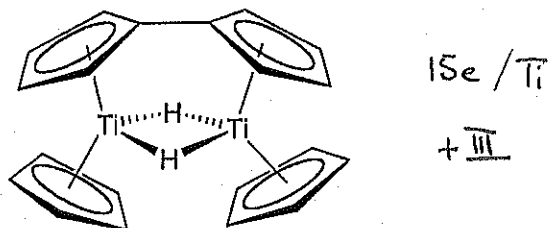
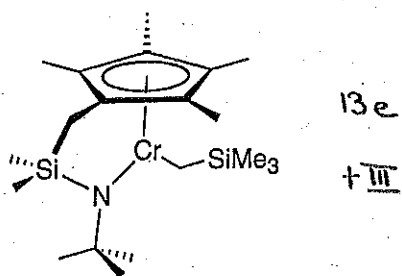
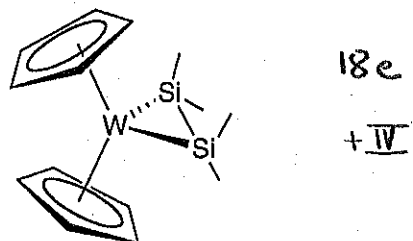
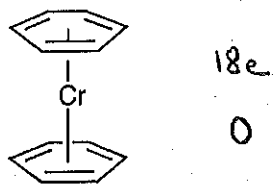
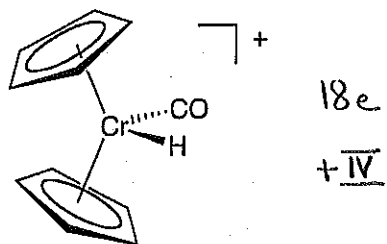
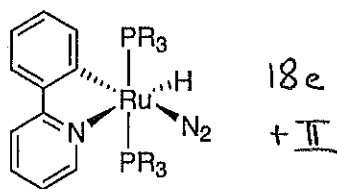
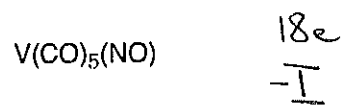
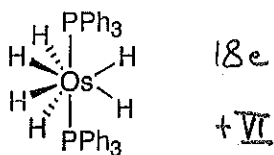
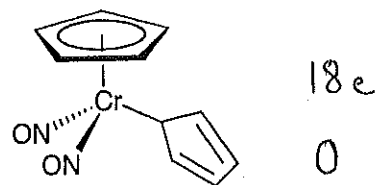
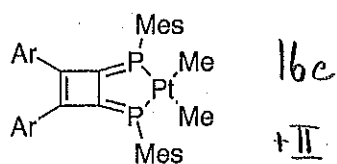
Please write your answers directly in the spaces provided.

Name: Key

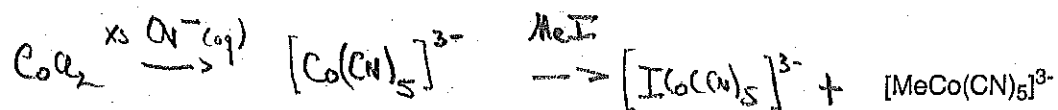
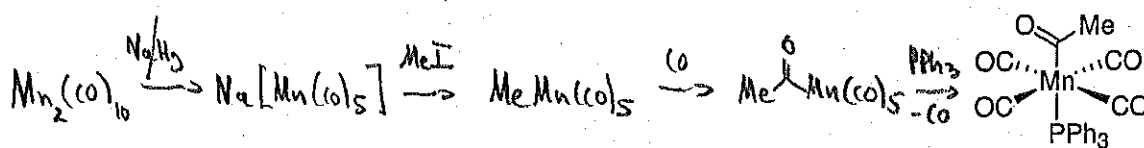
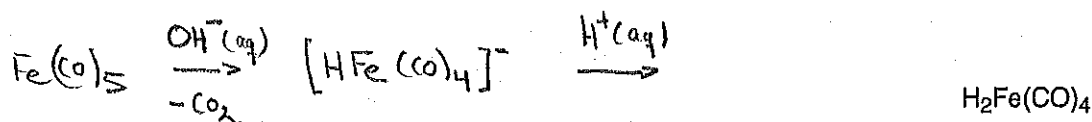
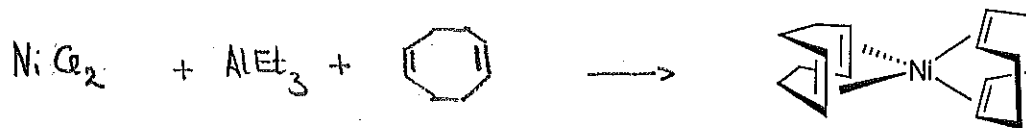
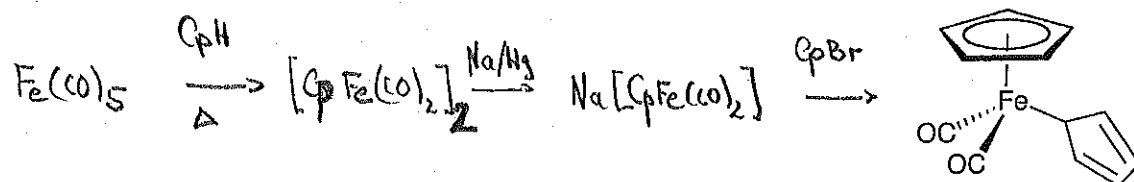


- 1:
- 2:
- 3:
- 4:
- 5: _____

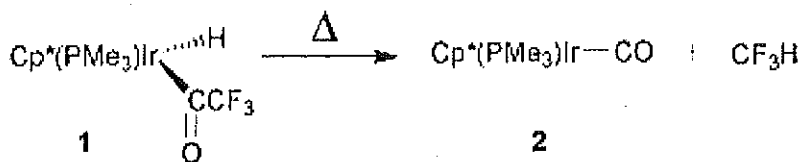
1. (20 pts.) For the following molecules, give the valence electron count and the formal oxidation state of the metal.



2. (20 pts.) Using only readily available starting materials (i.e. metals, metal halides, or homoleptic carbonyls, as well as organic molecules (including lithium alkyls etc.), give plausible synthetic routes to the following organometallic molecules.



3. (20 pts.) Cordaro and Bergman have recently published on the reaction shown below:



- What spectroscopic methods could be used to identify compound **1**? List them and give an indication of the expected spectroscopic features.
- Write all possible mechanisms that you would consider for this reaction (draw structures of intermediates).
- Here are some experimental observations: a) the reaction has first order kinetics in [**1**]; b) it exhibits a pronounced solvent effect – i. e. it proceeds 32 times faster in CD_3OD and 180 times faster in DMSO-d_6 than in C_6D_6 ; substitution of H with D in **1** did not cause a measurable kinetic isotope effect; when the reaction was carried out in CD_3OD or CH_3OD , the product was CF_3D rather than CF_3H . Based on these facts choose which of the mechanisms listed under i) is the most likely one

i) $^1\text{H-NMR}$: 3 resonances, coupling to ^{31}P (J_{PH})

$^{13}\text{C-NMR}$: 5 resonances, coupling to P, F

$^{31}\text{P-NMR}$: 1 resonance

$^{19}\text{F-NMR}$: 1 resonance

IR: $\nu_{\text{CO}} \sim 1650-1700 \text{ cm}^{-1}$

mass spectroscopy

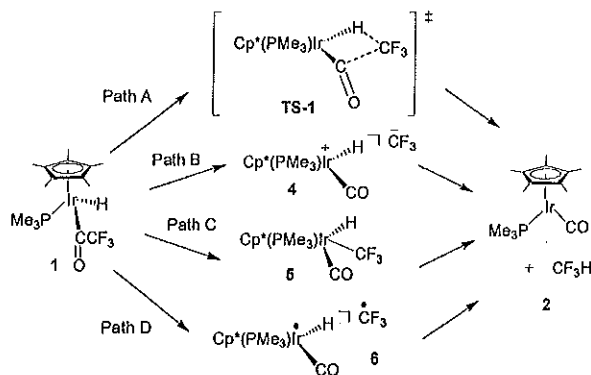
ii)

iii)

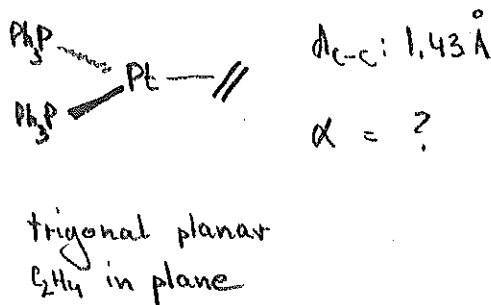
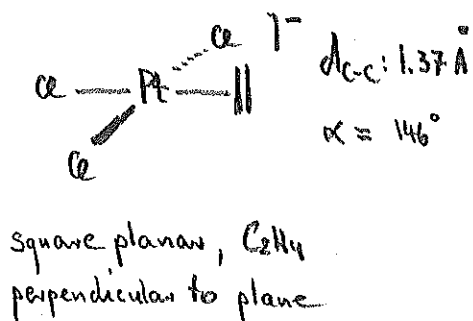
Path B!

- polar solvent stabilizes ion pair
- Ir-H bond breaking is not rate determining (no isotope effect)
- CF_3^- anion gives CF_3D in MeOD

Scheme 1. Possible Mechanisms for Observed Reaction



4. (20 pts.) Compare and contrast the structures of the two ethylene complexes $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^-$ and $(\text{C}_2\text{H}_4)\text{Pt}(\text{PPh}_3)_2$. Begin by drawing three-dimensional pictures of both molecules, and giving estimated bond distances and angles. Outline the major bonding interactions between the olefin and the metal, and describe how the structural details are related to them. Draw MO diagrams as necessary to support your arguments.

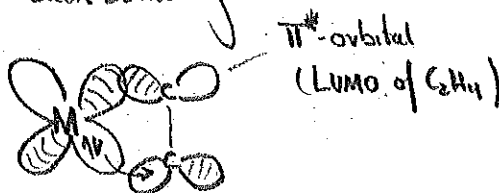


bonding interactions:

a) σ -donation

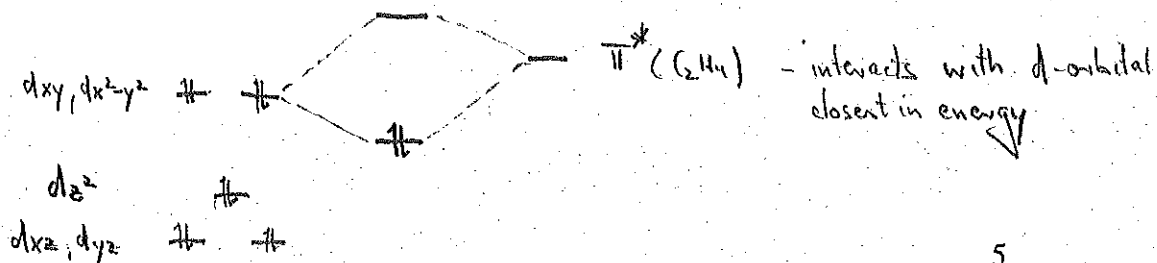


b) π -backbonding

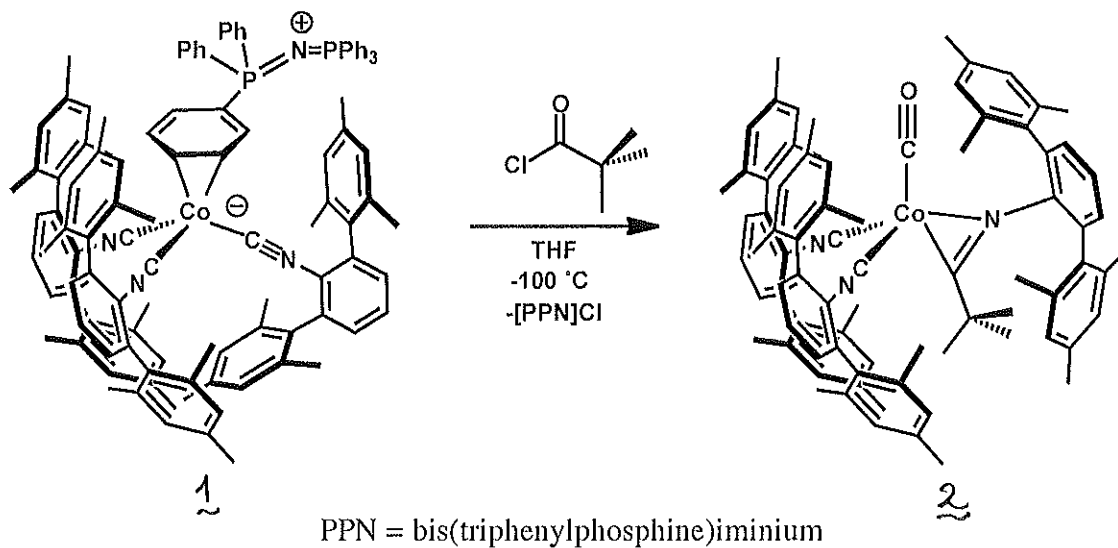


$[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$: Pt^{II} and electron withdrawing Cl^- ligands \rightarrow σ -donation more important than π -backbonding \rightarrow relatively short C-C bond, little rehybridization perpendicular geometry is steric in origin

$(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$: Pt^0 and strong donor phosphines \rightarrow π -backbonding is major interaction \rightarrow longer C-C bond and more rehybridization toward 'metallacyclopropane' in-plane geometry - due to π -interaction (see below)



5. (20 pts.) J. Figueroa described the reaction below at the recent Anaheim ACS meeting:



- i) Draw the most probable mechanism of this reaction (you may want to use ArNC to denote the ligands).
- ii) Indicate formal oxidation state and electron count for all organometallic species.
- iii) Name the fundamental organometallic reaction types involved?

