

Chemistry 652

Organometallic Chemistry

Midterm Examination, April 11, 2019

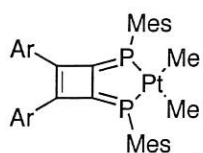
Please write your answers directly in the spaces provided.

Name: \_\_\_\_\_

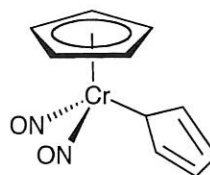


- 1:
- 2:
- 3:
- 4:
- 5: \_\_\_\_\_

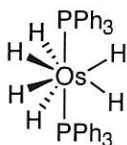
1. (20 pts.) For the following molecules, give the valence electron count and the formal oxidation state of the metal.



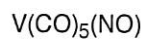
16e<sup>-</sup>  
Pt<sup>II</sup>



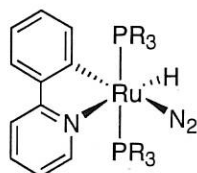
18e<sup>-</sup>  
Cr<sup>0</sup>



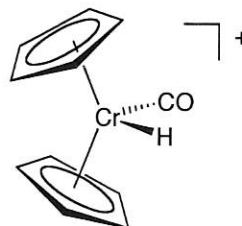
18e<sup>-</sup>  
Os<sup>VI</sup>



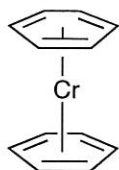
18e<sup>-</sup>  
V<sup>-I</sup>



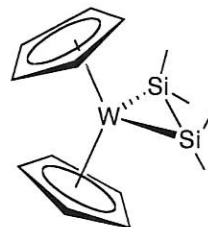
18e<sup>-</sup>  
Ru<sup>II</sup>



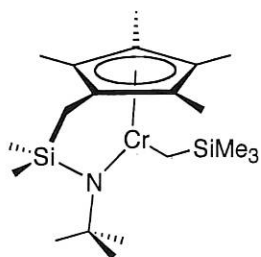
18e<sup>-</sup>  
Cr<sup>IV</sup>



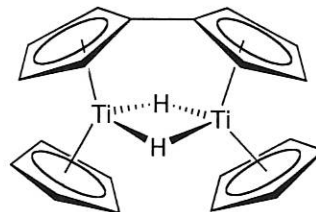
18e<sup>-</sup>  
Cr<sup>0</sup>



18e<sup>-</sup>  
W<sup>IV</sup>

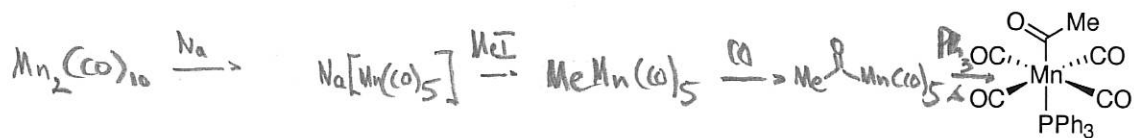
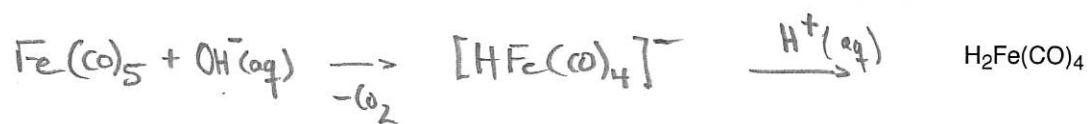
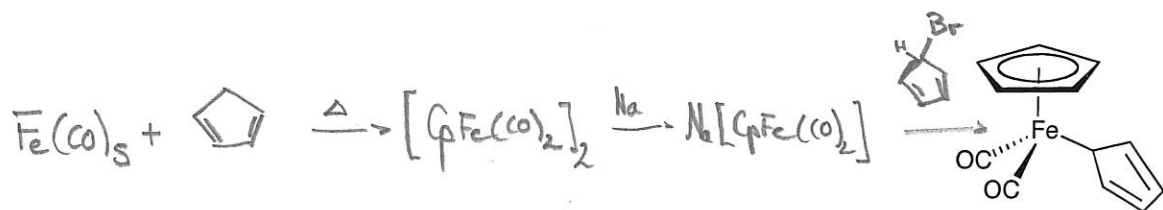


13e<sup>-</sup>  
Cr<sup>III</sup>

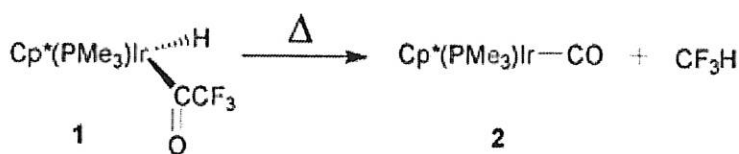


15e<sup>-</sup>  
Ti<sup>III</sup>

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:

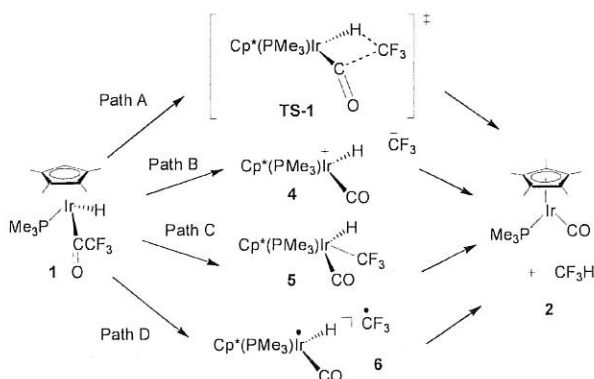


- What spectroscopic methods could be used to identify compound **1**? List them and give an indication of the expected spectroscopic features.
- Write all possible mechanisms that you would consider for this reaction (draw structures of intermediates).
- Here are some experimental observations: a) the reaction has first order kinetics in [**1**]; b) it exhibits a pronounced solvent effect – i. e. it proceeds 32 times faster in CD<sub>3</sub>OD and 180 times faster in DMSO-d<sub>6</sub> than in C<sub>6</sub>D<sub>6</sub>; substitution of H with D in **1** did not cause a measurable kinetic isotope effect; when the reaction was carried out in CD<sub>3</sub>OD or CH<sub>3</sub>OD, the product was CF<sub>3</sub>D rather than CF<sub>3</sub>H. Based on these facts choose which of the mechanisms listed under ii) is the most likely one.

i) <sup>1</sup>H-NMR : 3 resonances, coupling (J<sub>PH</sub>) to <sup>31</sup>P  
<sup>13</sup>C-NMR : 5 resonances, coupling to <sup>31</sup>P, <sup>19</sup>F  
<sup>31</sup>P-NMR : 1 resonance  
<sup>19</sup>F-NMR : 1 resonance  
 IR : ν<sub>CO</sub> ~ 1650-1700 cm<sup>-1</sup>  
 -mass spectrum

ii)

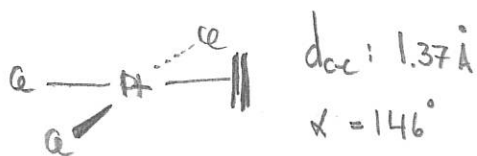
Scheme 1. Possible Mechanisms for Observed Reaction



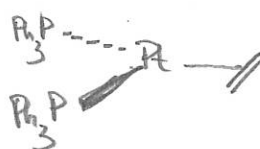
iii) Path B

- polar solvents stabilize ion pair
- Ir-H bond breaking is not rate-determining (no kinetic isotope effect!)
- CF<sub>3</sub><sup>-</sup> anion gives CF<sub>3</sub>D in MeOD

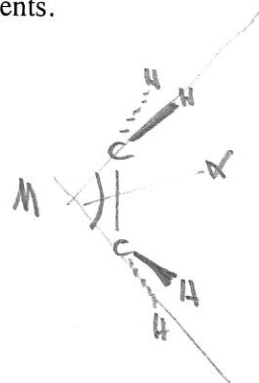
4. (20 pts.) Compare and contrast the structures of the two ethylene complexes [Pt(C<sub>2</sub>H<sub>4</sub>)Cl<sub>2</sub>] and (C<sub>2</sub>H<sub>4</sub>)Pt(PPh<sub>3</sub>)<sub>2</sub>. Begin by drawing three-dimensional pictures of both molecules, and giving relevant estimated bond distances and 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.



square planar, C<sub>2</sub>H<sub>4</sub> perpendicular to plane

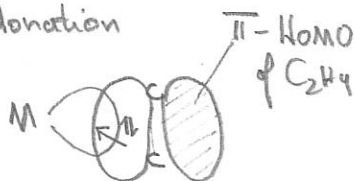


trigonal planar  
C<sub>2</sub>H<sub>4</sub> in plane

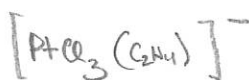


Bonding interactions:

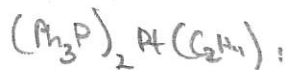
a)  $\sigma$ -donation



b)  $\pi$ -backbonding



Pt<sup>II</sup> ox. state and e-withdrawing Cl<sup>-</sup> ligands  $\rightarrow$   $\sigma$ -bonding more important the  $\pi$ -bonding  $\Rightarrow$  short C-C bond, little rehybridization  
Perpendicular geometry is steric in origin



Pt<sup>0</sup> ox. state and strong donor phosphines  $\rightarrow$   $\pi$ -backbonding is major interaction  $\rightarrow$  longer C-C bond and more rehybridization to 'metallacyclopropane'

In plane geometry due to  $d_{\pi}-p_{\pi}$  interaction

Pt<sup>0</sup>, d<sup>10</sup>

$d_{xy}, d_{x^2-y^2} \uparrow \uparrow$

$d_{z^2}, d_{xz}, d_{yz} \uparrow \uparrow$



$\pi^*(C_2H_4)$  - interacts w/ d-orbital closest in energy.

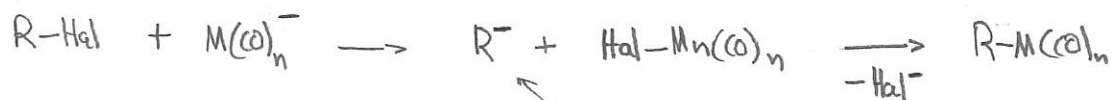
trigonal planar  
d-orbital splitting diagram

5. (20 pts.) Reproduced below is the abstract of a paper by K. Sazonov et al.:

**Abstract.** The mechanism of reactions of metal carbonyl anions,  $[\text{CpFe}(\text{CO})_2]^-$ ,  $[\text{Re}(\text{CO})_5]^-$  and  $[\text{Mn}(\text{CO})_5]^-$  with various halogenated (Hal = Br, I) aryl and alkenyl halides has been examined with the help of anion trapping experiments. Reactions discussed in this communication are shown to proceed *via* the initial attack of metal carbonyl anion on halogen. The **halogen-metal exchange mechanism** is demonstrated by the trapping of the intermediate aryl (alkenyl) carbanion and by the formation of halo(acyl)metallate anions *cis*- $[\text{R}(\text{CO})\text{M}(\text{CO})_4\text{Hal}]^-$  instead of  $\text{RM}(\text{CO})_5$  complexes (M=Re, Mn) in the reactions with  $[\text{Re}(\text{CO})_5]^-$  and  $[\text{Mn}(\text{CO})_5]^-$ . The yield of nucleophilic substitution products varies widely from trace in certain reactions with  $[\text{CpFe}(\text{CO})_2]^-$ , which give the  $[\text{CpFe}(\text{CO})_2]_2$  dimer, to quantitative in reactions with  $[\text{Re}(\text{CO})_5]^-$ .

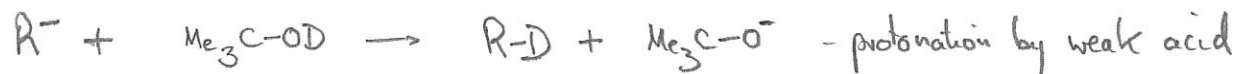
- What is that 'halogen-metal exchange mechanism' referred to? Write a series of elementary steps comprising it. Propose an 'anion trapping experiment'.
- Draw the structure of that 'halo(acyl)metallate anion'. How is it formed?
- How is the  $\text{Fp}_2$  dimer formed, and how does it limit the formation of the products of nucleophilic substitution?

i)

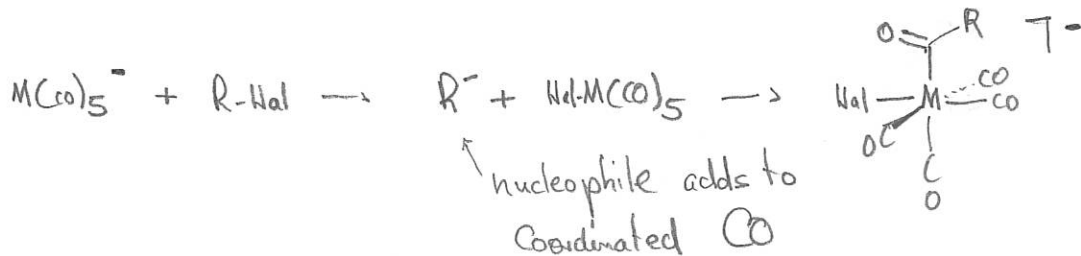


the first step is the halogen-metal exchange, followed by a nucleophilic subst.

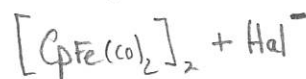
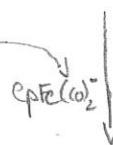
The 'anion trapping experiment traps'  $\text{R}^-$ ; e.g.



ii)



iii)



This coupling reaction removes the metal carbonyl which is no longer available for bonding to  $\text{R}^-$