Worksheet 5. In class. 462 2017

I. Consider the following two structures and answer the questions relating to them:

a) Label them according to the type of divalent carbon atom ligands: Fischer Carbene or Schrock Alkylidene

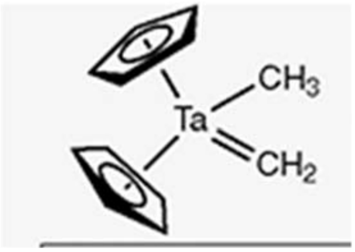
b) Choose the correct label for the divalent carbons: neutral, 2-electron donor; anionic, 2-electron donor; dianionic, 4-electron donor; neutral, 4-electron donor.

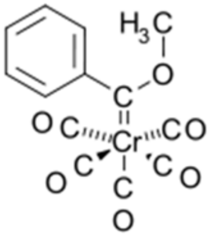
c) According to your assignment for the divalent carbon ligand, give the oxidation state of the metal and the d-electron count in each case.

d) Which divalent carbon ligand is most likely to react with PhLi? What is the product?

e) Which divalent carbon ligand is most likely to have resulted from an α-H elimination?

f) Which complex is more likely to react with BX_3 to yield a carbide?





a) ____________________ ____________________

b) ____________________ ____________________

c) ____________________ ____________________

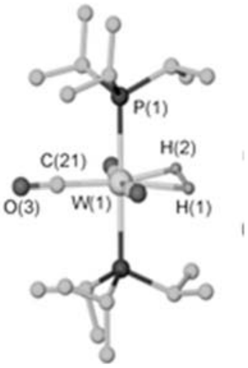
d) ____________________ ____________________

e) ____________________ ____________________

f) ____________________ ____________________

g) Exchange of a CO by PMe_3 in the $Cr(PhC(OCH_3))(CO)_5$ complex is expected to proceed by a (dissociative or associate) mechanism and generate the (cis or trans) isomer? At right, sketch the expected reaction coordinate and the structures of the transition state and any intermediate.

II. Consider Kubas' η^2-dihydrogen complex shown right.
A) Give the oxidation state and electron count about tungsten.

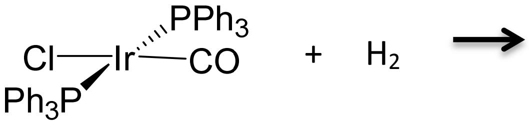


B) Two types of π-backbonding are in the tungsten complex, to CO and to the η^2-H_2 ligand. Give drawings to illustrate the orbital overlap between W and CO and between W and H_2.

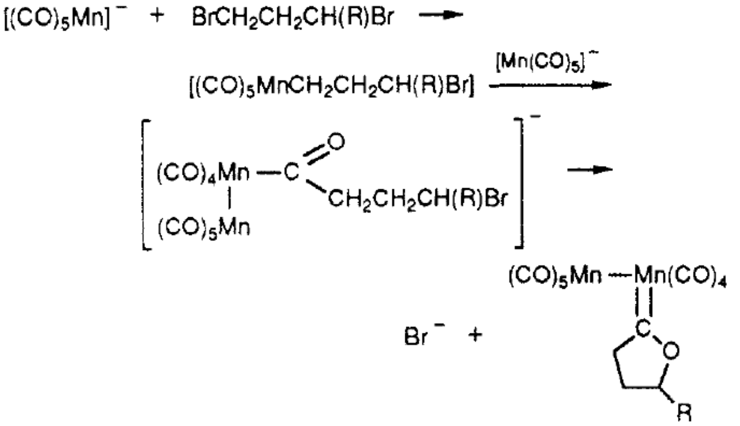
C) Discuss the orientation of ligands in this complex. That is, which orientation of the P(i-Pr)$_3$ ligand, cis or trans to the W- η^2-H_2, should give the "better" interaction? Explain your reasoning and why the solid state structure is the same or different from your conclusion.

D) The following list of physical or spectroscopic techniques were used to characterize the Kubas complex. Choose 3 and describe what could be or was learned from the results: i) Infrared spectroscopy in diatomic (CO) ligand region. ii) ^{1}H NMR spectroscopy iii) ^{31}P NMR spectroscopy iv) X-ray diffraction v) Neutron diffraction (use the back of the page for your descriptions).

E) Attempts to prepare a Kubas-type dihydrogen complex with the iridium complex shown below resulted in a 6-coordinate complex. A) Sketch the structure of the product. B) Give the oxidation states and electron counts about Ir in both reactant and product. C) Discuss why should this result be different from the Kubas study?



III. Consider the reaction pathway at right. Give the oxidation state of Mn in each of the manganese-containing products. Give the 3-dimensional structure/geometry of all products. How many C-13 NMR resonances attributable to carbonyl carbons do you expect the final product might have? What is the local symmetry about each manganese in the final product?



(1)

1, R = H
2, R = CH_3

IV. Give the electron count for each Mn derivative in the following equation. Show how you derived each overall count (by giving oxidation state of Mn and d-count).

$$[Mn(CO)_5]^- + C_3H_5Cl \longrightarrow \underset{+\ Cl^-}{(\eta^1\text{–}C_3H_5)Mn(CO)_5} \xrightarrow{\Delta \text{ or } h\nu} \underset{+\ CO}{(\eta^3\text{–}C_3H_5)Mn(CO)_4}$$