Chemistry 652
Organometallic Chemistry
Final Examination, May 26, 2015

Please write your answers directly in the spaces provided.

Name: __________

1)

2)

3)

4)

5)

6)

7)

8)

Total: __________

Have a productive summer!
1) (20 points) For each of the following organometallic compounds, give the electron count, the formal oxidation state of the metal, and the $d^n$ configuration.

![Chemical structures](image)

- $18e$, $+\text{III}$, $d^6$
- $16e$, $+\text{VI}$, $d^0$
- $16e$, $+\text{II}$, $d^8$
- $17e$, $+\text{III}$, $d^5$
- $18e$, $0$, $d^6$
- $16e$, $+\text{VI}$, $d^0$
- $18e$, $+\text{IV}$, $d^{10}$
2) (15 pts). Using only simple starting materials (i.e. metals, stable metal halides, homoleptic metal carbonyls, and commercially available organic reagents), design and outline synthetic procedures for the synthesis of the following compounds:

a) \([\text{CpCo}(\eta^3-\text{C}_3\text{H}_5)]\text{PF}_6\)

\[
\text{Co}_2((\text{O})_8 + 2\text{CpH} \rightarrow \text{Co}_2\text{Co}(\text{O})_2 \rightarrow \text{Co}_2\text{Co}(\eta^3-\text{C}_3\text{H}_5)\text{I} \rightarrow \text{Co}_2\text{Co}(\eta^3-\text{C}_3\text{H}_5)\text{I} \rightarrow [\text{CpCo}(\eta^3-\text{C}_3\text{H}_5)]\text{PF}_6
\]

b) \([\text{Cp}^*\text{Zr}(\text{CO})_2\]

\[
\text{ZrC}_{12+} + 2\text{Cp}^*\text{Li} \rightarrow \text{ZrC}_{22+} \rightarrow \text{ZrC}_{22+} \rightarrow \text{ZrC}_{22+} \rightarrow \text{ZrC}_{22+}
\]

c) \((\text{OC})_2\text{W}=\text{C}(\text{OMe})\text{Ph}\)

\[
\text{W}((\text{O})_6 \rightarrow (\text{OC})_5 \text{W} \rightarrow (\text{OC})_5 \text{W} \rightarrow (\text{OC})_5 \text{W}
\]

d) \([\text{CpFe}(\text{PPh}_3)(\text{CO})(\text{C}=(\text{OMe})\text{Me})]

\[
\text{Fe}((\text{CO})_2 + \text{CpH} \rightarrow [\text{CpFe}(\text{CO})_2]_2 \rightarrow [\text{CpFe}(\text{CO})_2] \rightarrow [\text{CpFe}(\text{CO})_2] \rightarrow [\text{CpFe}(\text{CO})_2]
\]

e) \([\text{Cp}^*(\text{Me})\text{Rh}(\mu-\text{CH}_2)_2\text{Rh}(\text{Me})\text{Cp}^*]

\[
\text{Rh}((\text{C})_2 + \text{Cp}^*\text{Li} \rightarrow [\text{Cp}^*\text{Rh}(\text{C})_2]_2 \rightarrow [\text{Cp}^*\text{Rh}(\text{C})_2]_2 \rightarrow [\text{Cp}^*\text{Rh}(\text{C})_2]_2
\]
3) (10 points) Draw reaction mechanisms for the two transformations shown below. Show structures of proposed intermediates. Keep track of unusual charges, oxidation states and electron counts, to avoid mistakes.
4) (10 points) The compound Cp*Nb(η²-3-hexyne)Cl₂ is an example of an electron deficient early metal organometallic. The alkyne in this complex is best considered to be a 4-electron donor. Discuss – and draw pictures of the relevant orbitals – of all interactions between niobium and 3-hexyne that contribute to the chemical bonding.

a) σ-donation

b) τi - backbonding

c) τi - donation

d) 8 - backbonding
5) (15 points) Consider the mechanism of the reductive elimination of mercury dialkyls, RHgR'. The following observations provide relevant information:

i) "When a solution of isobutyl(neopentyl)mercury in CCl₄ is heated, metallic mercury is formed as a shiny globule along with equimolar amounts of chloroform and neopentylchloride (NpCl). In addition, isobutene is observed.

ii) Only traces of isobutylchloride are formed and neither isobutyl- nor neopentyl-mercuric chloride is found.

iii) Decomposition of mercurycycloheptane yields discrete amounts of cyclopentylmethylchloride.

iv) The reaction is markedly accelerated by the addition of small amounts of AIBN (i.e., azobisisobutynitrile), and it is inhibited by galvinoxyl or o,o'-di-tert-butyl-p-cresol.

Identify the mechanism of this reductive elimination. Write a series of reaction steps rationalizing the observed products, and explain how observations i) – iv) support your mechanistic assignment.

This reductive elimination proceeds by a 'free radical chain mechanism'.

![Chemical reaction diagram]

This mechanism explains the formation of all products listed in i) – see boxes. The tertiary C-H of iBu is the weakest C-H bond in the molecule, leading to elimination. The mercurycycloheptane forms a hexenyl radical, which rearranges to . The effect of known radical initiators and radical traps indicates the occurrence of a radical chain reaction.
6) (10 points) Shown below are the $^1$H NMR spectra (note: shifts given on the $\tau$ scale) of ($\eta^5$-C$_5$H$_5$)Fe(CO)$_2$(H$_2$)$_2$($\eta^1$-C$_3$H$_3$)$_2$ (I) in CS$_2$ at various temperatures. The position and width of the ($\eta^5$-C$_5$H$_5$)-resonance at $\tau \sim 5.6$ are essentially invariant.

   ![NMR spectra diagram]

   a)

   i) Draw the structure of I, and assign the resonances observed in the low temperature spectrum.

   ii) What process is responsible for the temperature dependence of the spectra?

   iii) Estimate the free energy of activation for this process.

   ![Structure diagram]

   b)

   i) The process is a series of 1,5-shifts of the Fe around the $\eta^1$-bound Cp which eventually equilibrates all its H-atoms on the NMR time scale.

   $\Rightarrow$ a fluxional process, thus a coalescence phenomenon

   ii) $\Delta G^\neq = 50 \cdot Tc$

   $= 50 \cdot 250 = 12,500$

   $\Delta G^\neq \approx 12.5 \text{ kcal/mol}$
7) (10 points) One of the largest scale homogeneous catalytic processes in the chemical industry is the ‘hydroformylation’ of olefins.

i) Write a balanced reaction equation for the hydroformylation of 2-butene, showing all possible products. Over the reaction arrow indicate the catalyst (or catalyst precursor) and typical reaction conditions.

ii) Draw a catalytic cycle showing the elementary reaction steps and structures of intermediates, which – in aggregate – explain the formation of all products you listed in i).
8) (10 pts) Yves Chauvin received 1/3 of the 2005 Nobel Prize in Chemistry for his proposal regarding the mechanism of the olefin metathesis reaction. Using the example of the 'ring opening metathesis polymerization' (ROMP) of norbornene, show how his mechanism yields a polymer, and what its structure is. Draw critical intermediates, using either a Grubbs- or Schrock-type catalyst.

\[ \text{poly-norbornene} \]