Chemistry 652
Organometallic Chemistry

Midterm Examination, April 5, 2016

Please write your answers directly in the spaces provided.

Name: key

1: 
2: 
3: 
4: 
5: ____
1. (18 points) For the following compounds give the valence electron count and the formal oxidation state of the metal.

a) \[15e, \text{Cu}(III)\]

b) \[18e, \text{W}(IV)\]

c) \[Tsi = C(SiMe_3)_3\]

d) \[18e, \text{Rh}(III)\]

e) \[14e, \text{Cu}(II)\]

f) \[16e, \text{Au}(III)\]

g) \[12e, \text{Ti}(IV)\]

h) \[18e, \text{Fe}(0)\]

i) \[18e, \text{Fe}(I)\]
2. (16 points) Using readily available starting materials (i.e. metal halides or carbonyls and commercially available organic reagents), propose syntheses for the following molecules.

a) 
\[
\begin{align*}
\text{CoCl}_2 & \xrightarrow{Na} \text{Na} \left[ \text{Co} \left( \text{P(OMe)}_3 \right)_4 \right] & \xrightarrow{\text{MeI}} & \text{CH}_3\text{Co(}[\text{P(OMe)}_3]_4 \\
- \text{NaCl} & & - \text{NaI}
\end{align*}
\]

b) 
\[
\begin{align*}
\text{Mo} \left( \text{CO} \right)_6 & \xrightarrow{\text{CH}_3\text{CN}, \Delta} \text{Mo} \left( \text{CO} \right)_3 \left( \text{NCMe} \right)_3 & \xrightarrow{\text{C}_{\text{SH}}_2, \Delta} & \left[ \text{CpMo} \left( \text{CO} \right)_3 \right]_2 \\
- 3 \text{CO} & & - \mu_2
\end{align*}
\]

c) 
\[
\begin{align*}
\text{PtCl}_2 & \xrightarrow{2 \text{PPh}_3} \left( \text{PPh}_3 \right)_2 \text{PtCl}_2 & \xrightarrow{2 \text{MeI}, X} & \left( \text{PPh}_3 \right)_2 \text{PtMe}_2 & \xrightarrow{\text{MeOTf}} & \left( \text{PPh}_3 \right)_2 \text{PtMe}_3(\text{OTf}) \\
- \text{CO} & & & & &
\end{align*}
\]

d) 
\[
\begin{align*}
\text{V} \left( \text{CO} \right)_6 & \xrightarrow{\text{PPh}_2} \text{V} \left( \text{PPh}_2 \right) \left( \text{CO} \right)_5 & \xrightarrow{\text{Na}} & \text{Na} \left[ \text{V} \left( \text{PPh}_2 \right) \left( \text{CO} \right)_5 \right] & \xrightarrow{\text{HCl}} & \text{HV(} \text{PPh}_2 \text{)(CO)}_5 \\
- \text{CO} & & & & - \text{NaX}
\end{align*}
\]
3. (26 points) Consider the molecule shown below – it may well seem familiar.

![Molecule Diagram]

a) Draw structure of the products of the reaction of this molecule with
   i) pyridine  
   ii) BuNC  
   iii) O₂

b) What is the nature of the interaction between the phenyl C-H bond shown and the metal, and how does this interaction affect the physical properties (spectroscopy) of the molecule?
   - This is an *agostic* interaction, i.e., a 3-center-2-electron bond between C-H₂O. 
   - It is a kind of η-complex.
   - Both the H and the C are shielded upfield in NMR (¹H-NMR: 2.03(1), ¹³C-NMR: 62.0 ppm)
   - J₇ Hz coupling is low: 102.0 Hz (normal is ~160Hz)
   - Bond distances in X-ray structure: Co-H, 1.72(1)Å; Co-C, 2.2237(6)Å
   - DFT calculations support weak Co-H and Co-C bonds

c) How many ν₃ CO bands would you expect in the IR spectrum of this molecule? How many carbonyl CO resonances in its ¹³C NMR spectrum? If these numbers were different, how might you explain the difference?

2 CO's which are inequivalent → 2 νCO's, 2 ¹³C-NMR resonances

One could imagine a dynamic (flurional) process, in which the agostic C-H bond flip from top to bottom. C-C = C-H. If this happens 'fast on the ¹³C NMR timescale', the 2 CO resonances would coalesce to 1
4. (20 points) Using real (i.e. know to exist) molecules*, give one example each of:

*Note: Be specific – i.e. do not use general placeholders like M, L, or R; ‘impossible’ molecules will result in subtraction of points.

a) an oxidative addition

\[
\text{e.g.} \quad \begin{array}{c}
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{Me}
\end{array} \quad \text{OC} \quad \begin{array}{c}
\text{PR}_3
\end{array}
\]

b) a reductive elimination

\[
\text{e.g.} \quad \begin{array}{c}
\text{Ph}_3\text{P} \quad \text{Ir} \quad \text{PR}_3
\end{array} \quad \text{Me} \quad \text{H}
\]

\[
\xrightarrow{\text{PR}_3} \quad \begin{array}{c}
\text{Pt(Ph}_3\text{)}_3
\end{array} \quad \text{+ Me-H}
\]

c) a migratory insertion

\[
\text{e.g.} \quad \begin{array}{c}
\text{PR}_3
\end{array} \quad \text{OC} \quad \text{Mn} \quad \text{CO}
\]

\[
\xrightarrow{\text{PR}_3} \quad \begin{array}{c}
\text{OC} \quad \text{Mn} \quad \text{CO} \quad \text{PR}_3
\end{array}
\]

d) a β-elimination

\[
\text{e.g.} \quad \begin{array}{c}
\text{C}_6\text{P}_2\text{Nb} \quad \text{Ph}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{C}_6\text{P}_2 \quad \text{Nb} \quad \text{Ph}
\end{array}
\]
5. (20 points) Alkynes bind to transition metals. a) Discuss the nature of the bonding between the metal and the C-C triple bond in terms of the orbitals involved. Draw diagram showing the topology (shape) of the orbitals involved and label the various interactions with the appropriate terms describing the contribution to the bonding. b) How many electrons can an alkyne donate to the metal’s valence electron count? c) How does the structure of an alkyne change upon coordination to a metal.

a) The bonding is an extended version of the Dewar-Chatt-Duncanson model for alkynes, keeping in mind that alkynes have 2 orthogonal π-bonds (and associated π* levels)

1) [Diagram showing bonding interactions]
2) [Diagram showing bonding interactions]
3) [Diagram showing bonding interactions]
4) [Diagram showing bonding interactions]

b) If both 1) and 3) contribute to bonding, an alkyne can donate up to 4 electrons.

c) C≡C triple bond is lengthened beyond the usual (1.20 Å)
   - the alkyne is no longer linear, as the substituents are bent back (see ‘metallacyclopropene’ resonance structure)