Chemistry 652
Organometallic Chemistry
Midterm Examination, April 10, 2018

Please write your answers directly in the spaces provided.

Name:

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

\[
\text{Rh(I)} \quad 16e^- \\
\text{Cr} \quad 16e^- \\
\text{SiMe}_3 \\
\text{Mo(III)} \quad 17e^- \\
\text{Co(III)} \quad 18e^- \\
\text{Re(II)} \quad 18e^- \\
\text{Fe(II)} \quad 18e^- \\
\text{W(0)} \quad 18e^- \\
\text{Cr(VI)} \quad 11e^- \\
\text{Co(II)} \quad 18e^- \\
\text{W(II)} \quad 18e^-
\]
2. (20 pts.) Using only readily available starting materials (i.e. metals, stable metal halides, or homoletic carbonyls, as well as organic molecules (including common lithium alkyls), give plausible synthetic routes to the following organometallic molecules.

The syntheses shown below work. Other routes are possible.

\[ \text{Mo}(	ext{CO})_6 \xrightarrow{\Delta} \text{Mo}(	ext{CO})_3(\text{NMe}_3) \xrightarrow{\text{EtI}} \text{[Cp}_2\text{Mo}(	ext{CO})_3]\text{Na} \xrightarrow{\text{MeI}} \text{CpMo(CO)}_3\text{Me} \]

\[ \text{W}(	ext{CO})_6 \xrightarrow{\text{MeLi}} (\text{OC})_5\text{W} \xrightarrow{\text{Li}^+} (\text{OC})_5\text{W} \text{Et}^+\text{BF}_4^- \]

\[ \text{Co}_2(\text{CO})_8 \xrightarrow{\Delta} \text{Co}_2(\text{CO})_8 \xrightarrow{\text{I}_2} \text{OC} \text{Co} \text{-} \text{I} \]

\[ \text{Fe}(	ext{CO})_5 \xrightarrow{\text{Na}_2/\text{IHF}} \text{Na}_2[\text{Fe}(	ext{CO})_4] \xrightarrow{\text{EtI}} \text{Na}[\text{EtFe}(	ext{CO})_4] \xrightarrow{\text{Ph}_3} \text{Ph}_3\text{P-Fe}^+\text{CO} \]

\[ \text{ZrCl}_4 \xrightarrow{2, \text{Na}^+} \text{Cp}_2\text{Zr}^+\text{Cl} \xrightarrow{\text{Et-Mg}^+} \text{Zr}^+\text{Cl} \]
3. (15 pts.) Cr(CO)$_6$ and Ni(CO)$_4$ are so-called 'homoleptic carbonyls' of first row transition metals. The former exhibits one strong band in its IR spectrum at 2000 cm$^{-1}$, whereas the latter has one band at 2057 cm$^{-1}$.

a) Draw qualitative MO diagrams for these two compounds, identifying the orbitals of the metal and the CO ligands that interact, and populate the diagrams with the appropriate number of electrons.

b) What physical process gives rise to the absorption bands in the IR spectra of these two compounds? Compare to CO gas. Explain the relative band positions for the Cr and Ni complexes.

c) The Cr-C distance in Cr(CO)$_6$ is 1.92 Å, whereas the Ni-C distance in Ni(CO)$_4$ is 1.84 Å. Explain!

b) IR is 'vibrational' spectroscopy. The bands correspond to C=O bond stretching vibrations. The occurrence of a single band is due to the high symmetry of Cr(CO)$_6$ - C$_{6v}$, and Ni(CO)$_4$ - Td. Free CO gas has $\nu_{C-O}$ = 2143 cm$^{-1}$; the metal carbonyls have lower frequencies due to $\pi^*$-backbonding. Cr is more electropositive (i.e. reducing) than Ni, hence the lower number (2000 cm$^{-1}$) for Cr(CO)$_6$.

c) The covalent radius of Cr (1.18 Å) is larger than that of Ni (1.15 Å). Also, the lesser coordination number of Ni(CO)$_4$ makes for shorter bonds.
4. (15 pts.) What is meant by the term 'agnostic interaction'? Draw a real example. List as many separate experimental pieces of evidence as you can think of that would support the presence of such an interaction.

An 'agnostic interaction' is a 3-centre-2-electron bond involving a coordinatively unsaturated metal and a C-H bond, i.e.,

\[
\text{\begin{align*}
\text{M} & \equiv \text{H} \\
\text{X} & \equiv \text{H} \\
\text{Y} & \equiv \text{H}
\end{align*}}
\]

e.g.,

- Structural (X-ray, neutron)
  - Short M-H, long C-H distance
  - Distortion of alkyl (short C-C bond, acute U-C angle)

- Spectroscopy
  - \( ^1H \text{-NMR} \): upfield shift of H, low J_C-H
  - IR: Concan V_C-H
  - Isotopic perturbation of resonance & stereochemistry
  - Coalescence phenomena in VT-NMR

5. (15 pts.) In class, you heard about a reaction of Collman’s reagent, \([\text{Fe(CO)}_5]^-\), with a particular alkyl tosylate, which was done to address the mechanism of this oxidative addition. i) Recount the details of this experiment (i.e. show the various steps), ii) state its result (regarding the mechanism of the oxidative addition), and iii) name a critical mechanistic assumption needed (and independently verified) to reach that conclusion.

i) \([\text{Fe(CO)}_5]^2^- + \text{MeI, CO} \rightarrow \text{Fe(CO)}_5 + \text{RCh} \]

\[\downarrow\]

\[\text{Me} - \text{Fe} - \text{co} \rightarrow \text{Co - Fe} \rightarrow \text{MeI} \rightarrow \text{Me-Fe(CO)}_5\]

ii) The first step - i.e. the oxidative addition - goes with inversion of stereochemistry, consistent with an \(S_n^2\) mechanism.

iii) In order for this interpretation to be valid, \(2^\text{nd}\) step (2\textsuperscript{nd} step) has to proceed with retention of configuration at 'C'.
6. (15 pts.) From a recent paper by Puddephatt et al.: “An early mechanistic study of the reaction of [Pt(acac)$_2$] with iodine showed that the reaction proceeded by way of an intermediate [Pt(acac)$_2$(I$_2$)] (A), which rearranged by a free-radical chain mechanism to the product of trans oxidative addition, B”.

Draw the structures of A and B, and write a stepwise mechanism for the transformation of [Pt(acac)$_2$] into B.

\[ \text{Initiation:} \quad Q^+ + I_2 \rightarrow QI + I^· \]

\[ \text{Propagation:} \quad 1) \quad A + I^· \rightarrow \]

\[ \text{2) \quad → B + I^·} \]

\[ \text{Termination:} \quad 2I^· \rightarrow I_2 \]