1. Show all the steps (i.e., draw the catalytic cycle) for the Monsanto acetic acid synthesis. Include a detailed description of the processes taking place and point out the rate determining step. (10 points)

\[
\text{MeOH} + \text{CO} \rightarrow \text{MeCO}_2\text{H}
\]

Two interrelated cycles:

I: MeOH is converted to Mel, rate determining step, critical for whole process;
II: Mel enters the Rh-cycle, oxidative addition to the 16-electron complex \(\text{cis-}[\text{Rh(CO)}_2\text{I}_2]\);
III: methyl migration to form 5 coordinate, 18 electron species (dimer at 253 K, solvated monomer above 273 K);
IV: addition of CO, formation of octahedral 18-e\(^{-}\) complex;
V: elimination of MeC(O)I, enters left handed cycle;
VI: formation of acetic acid.
2. $[\text{Co(NH}_3)_6]^2^+\text{ has absorption bands at } 9,000 \text{ and } 21,100 \text{ cm}^{-1}. \text{ Calculate } \Delta_0 \text{ and } B \text{ for this ion, using the attached Tanabe-Sugano Diagram. Hint: The } ^4T_{1g} \rightarrow ^4A_{2g} \text{ transition in this complex is too weak to be observed. (10 points) }

$[\text{Co(NH}_3)_6]^2^+\text{, }d^7$.  
$\nu_2 / \nu_1 = 2.34 \text{ at } \Delta_0/B = 11$

From the Tanabe-Sugano diagram at $\Delta_0 = 11$

$\nu_1: E/B = 10 \quad E = 10 \quad B = 9000 \text{ cm}^{-1} \quad B = 900 \text{ cm}^{-1}$

$\nu_2: E/B = 22.5 \quad E = 22.5 \quad B = 21,100 \text{ cm}^{-1} \quad B = 938 \text{ cm}^{-1}$

Average $B = 920 \text{ cm}^{-1}$

$\Delta_0 = 10,120 \text{ cm}^{-1}$
3. State the types of isomerism that may be exhibited by the following complexes, and draw structures of the isomers. (4 points each)

a. \([\text{Co(en)}_2(\text{ox})]^+\)
   
   **optical isomers**

\[
\begin{align*}
\text{Optical isomers} \\
\begin{array}{c}
\text{cis} \\
\text{trans}
\end{array}
\end{align*}
\]

b. \([\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^–\)
   
   **trans isomer, cis isomer with two optical isomers**

\[
\begin{align*}
\text{Trans isomer} \\
\text{Cis isomer}
\end{align*}
\]

c. \([\text{Co(en)}(\text{NH}_3)_2\text{Cl}_2]^{2+}\)
   
   may have **trans-Cl, trans-NH}_3, or both sets mutually cis** and for the latter, there are also optical isomers.

\[
\begin{align*}
\text{Trans-Cl} \\
\text{Trans-NH}_3 \\
\text{Cis-Cl} \\
\text{Cis-NH}_3
\end{align*}
\]

d. \([\text{PtCl}_2(\text{PPh}_3)_2]\)
   
   **cis- and trans-isomers**

\[
\text{cis-isomer} \quad \text{trans-isomer}
\]

e. \([\text{Co(en)}_3]^{3+}\)
   
   **optical isomers**

\[
\begin{align*}
\text{Optical isomers} \\
\begin{array}{c}
\text{cis} \\
\text{trans}
\end{array}
\end{align*}
\]
4. Describe the bonding in ($\eta^4$-C$_4$H$_4$)Fe(CO)$_3$ (i.e., develop MO diagrams for both the C$_4$H$_4$ fragment and the Fe(CO)$_3$ fragment). Explain why the complex is diamagnetic. (10 points)

The Fe(CO)$_3$ unit provides 2 electrons and the C$_4$H$_4$ ligand has 4$\pi$-electrons. Match fragment orbitals by looking at their symmetry: the Fe $p_zd_z^2$ hybrid overlaps with $\psi_1$ of the organic ligand, and the Fe $d_{xz}$ and $d_{yz}$ orbitals overlap with $\psi_2$ and $\psi_3$ of the ligand. Orbital $\psi_4$ becomes non-bonding in ($\eta^4$-C$_4$H$_4$)Fe(CO)$_3$. In the complex, there are 3 bonding MOs involving Fe-C$_4$H$_4$ character and the 6 electrons fully occupy there MOs – electrons are paired and the complex is diamagnetic.
5. Give likely products for the following reactions. Do not forget to assign stereochemistry where appropriate. (2 points each)

a. \( \text{Fe(H}_2\text{O)}_6^{3+} + \text{SCN}^- \rightarrow [\text{Fe(H}_2\text{O)}_5(\text{SCN-}N]^2+ + \text{H}_2\text{O} \)

b. \([\text{(C}_2\text{H}_4)\text{PtCl}_3]^- + \text{NH}_3 \rightarrow \text{trans-}[\text{(C}_2\text{H}_4)\text{PtCl}_2(\text{NH}_3)] + \text{Cl}^- \)

c. \(\text{cis-[RhCl}_4(\text{H}_2\text{O})_2]^- + \text{H}_2\text{O} \rightarrow \text{fac-[RhCl}_3(\text{H}_2\text{O})_3] + \text{Cl}^- \)

d. \(\text{NiCl}_2 + 2\text{C}_3\text{H}_5\text{MgBr} \rightarrow (\eta^3-\text{C}_3\text{H}_5)_2\text{Ni} + 2\text{MgBrCl} \)

e. \(\text{(η}^5-\text{Cp})_2(\text{CH}_3)\text{Ta=CH}_2 + \text{Al(CH}_3)_3 \rightarrow (\eta^5-\text{Cp})_2(\text{CH}_3)\text{Ta}^+\text{CH}_2\text{Al}^-\text{(CH}_3)_3 \)

6. Give chemical names for the following compounds or ions: (2 points each)

a. \([\text{ReH}_9]^2-\)
\(\text{nonahydridorhenate(VII)} \)

b. \(\text{Rb[AgF}_4\text{]}\)
\(\text{rubidium tetrafluoroargentate(III)} \)

c. \(\text{Na[AlCl}_4]\)
\(\text{sodium hexachloroaluminate(III)} \)

d. \([\text{Ag(NH}_3)_2][\text{BF}_4]\)
\(\text{diamminesilver(I) tetrafluoroborate(III)} \)

e. \([\text{Mn(CN)}_6]^4-\)
\(\text{hexacyanomanganate(II)} \)
7. Carbonic anhydrase II is present in red blood cells and catalyzes the reversible hydration of CO₂:

\[ \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow [\text{HCO}_3^-] + \text{H}^+ \]

Based on the schematic representation of the active site in human carbonic anhydrase II (CAII) given below, develop a detailed catalytic cycle for the hydration of CO₂ catalyzed by CAII. (10 points):

Mechanism:
8. At low temperature and pressure a gas-phase reaction can occur between iron atoms and toluene. The product A, a rather unstable sandwich compound, reacts with ethylene to give compound B. Compound B decomposes at room temperature to liberate ethylene; at −20 ºC it reacts with P(OCH₃)₃ to give Fe(toluene)[P(OCH₃)₃]₂. C. Suggest structures for compounds A, B, and C. (10 points)

![Structures of A, B, and C]

9. Determine the number of valence electrons in each of the following compounds. **Hint:** Not all of the compounds obey the 18-electron rule! (2 points each)

a. Fe(CO)₅

\[
\begin{array}{ccc}
\text{Fe} & 8\text{e}^- \\
\text{5 Co} & 10\text{e}^- \\
\hline
& 18\text{e}^- \\
\end{array}
\]

b. [Rh(bipy)₂Cl]⁺

\[
\begin{array}{ccc}
\text{Rh} & 9\text{e}^- \\
2 \text{bipy} & 8\text{e}^- \\
\text{Cl} & 1\text{e}^- \\
\text{+} & \text{-1e}^- \\
\hline
& 17\text{e}^- \\
\end{array}
\]

c. [HFe(CO)₄]⁻

\[
\begin{array}{ccc}
\text{Fe} & 8\text{e}^- \\
\text{H} & 1\text{e}^- \\
4 \text{CO} & 8\text{e}^- \\
\text{-} & 1\text{e}^- \\
\hline
& 18\text{e}^- \\
\end{array}
\]

d. RhCl(H)₂(η²-C₂H₄)(PPh₃)₂

\[
\begin{array}{ccc}
\text{Rh} & 9\text{e}^- \\
\text{Cl} & 1\text{e}^- \\
2 \text{H} & 2\text{e}^- \\
\eta²-C₂H₄ & 2\text{e}^- \\
2 \text{PPh₃} & 4\text{e}^- \\
\hline
& 18\text{e}^- \\
\end{array}
\]

e. Fe₂(CO)₉

\[
\begin{array}{ccc}
2 \text{Fe} & 16\text{e}^- \\
9 \text{CO} & 18\text{e}^- \\
\text{Fe-Fe} & 2\text{e}^- \\
\hline
& 36\text{e}^- \rightarrow 18\text{e}^- \text{ per Fe}
\end{array}
\]