Exercises 5

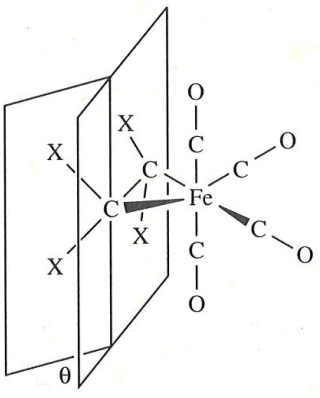
1. A complex of nickel(II), $NiCl_2(PPh_3)_2$, is paramagnetic. The analogous complex of palladium(II) is diamagnetic. Predict the number of isomers that will exist for each of these formulations. Discuss the identification of cis-trans isomers in MA_2B_2 compounds by dipole measurements as a function of complex geometry.

2. Which of the following is the most likely structure of pentacyanocobalt(III)-m-cyanopentaamminecobalt(III)? Explain.

   $[(NH_3)_5Co - CN - Co(CN)_5]$ or $[(NH_3)_5Co - NC - Co(CN)_5]$

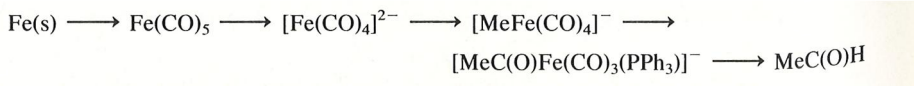
3. Metal complexes with coordination number of 4 can have a tetrahedral (T_d) or square planar (D_{4h}) geometry. Often, complexes with these two geometry are in chemical equilibrium. From the reaction of $NiBr_2$ with Ph_2EtP, it is possible to isolate green crystals of $[Ni(Ph_2EtP)_2Br_2]$, which have a magnetic moment of 3.0 Bohr magnetrons, or red crystals of $[Ni(Ph_2EtP)_2Br_2]$, which have a magnetic moment of zero. When either of these is dissolved in dichloromethane (apolar solvent) at 40°C, the resulting solution has a magnetic moment of 2.69 Bohr magnetrons. Suggest structures for the green and red crystals and offer an explanation for the solution magnetic moment.

4. Bond lengths and angles have been determined for two similar complexes, $Fe(CO)_4(C_2H_4)$ and $Fe(CO)_4(C_2F_4)$. Identify which set of data (I or II) belongs to each complex and justify your answer.



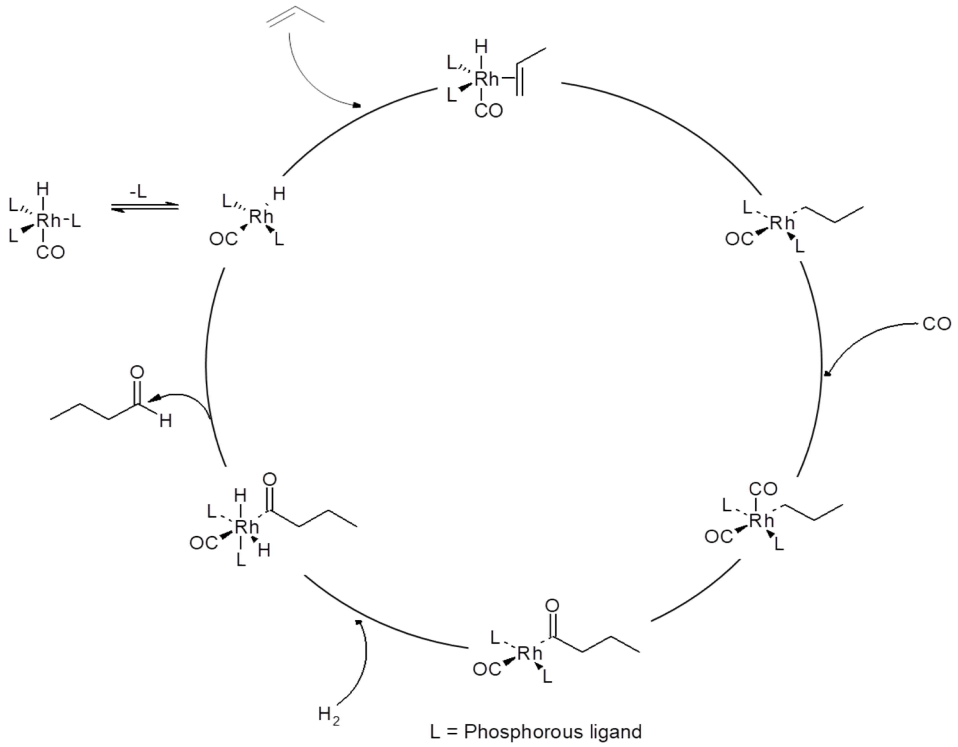
	I	II
C — C (pm)	153.0	146
C — Fe (pm)	198.9	211.7
θ	41.6°	0°

5. Identify a reagent(s) that will effect each of the following transformations (MeC(O)H = acetaldehyde):



   Which Fe complex is formed at the end of the reactions?

6. Considering the following catalytic cycle:



Identify the type of reaction for each step of the catalytic cycle. Explain how:

- the electronic properties of the phosphine ligands affect the reaction rate
- the selectivity to linear products can be tuned by the steric properties of the phosphine ligands.