

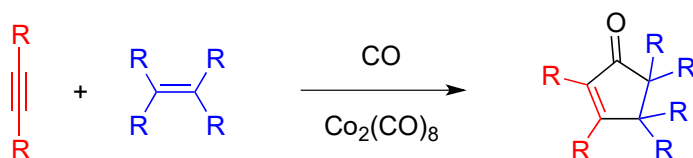
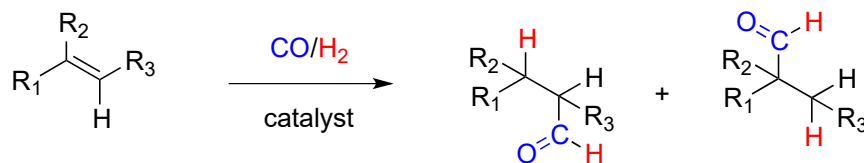
**Recommended reading:** 4.1 – 4.6, 4.8, 17.7-17.9 (3<sup>rd</sup> edition)  
3.1 – 3.6, 3.8, 17.7-17.9 (4<sup>th</sup> edition)

### Ch 102 – Problem Set 1

**Due: Thursday, April 13, 2017– Before Class**

#### Problem 1. (2 points)

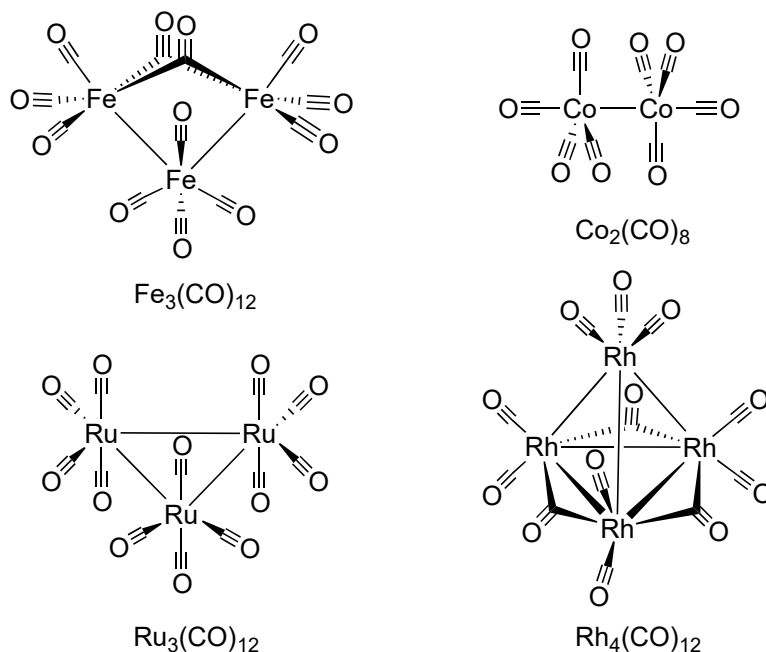
For some transition metals, homoleptic carbonyl compounds (compounds containing only CO as ligands) exist as monomeric species, such as Mo(CO)<sub>6</sub> or Fe(CO)<sub>5</sub>, while for others metal-metal bonds form to generate multinuclear species. Transition metal carbonyl complexes can be utilized as precursors in organometallic synthesis, as well as reagents for organic transformations. For example, Co<sub>2</sub>(CO)<sub>8</sub> is used in the catalytic hydroformylation of alkenes, as well as a stoichiometric reagent in the Pauson-Khand reaction.



Metal carbonyl clusters can also be studied as soluble models of heterogeneous systems, such as the water-gas shift reaction, to gain greater insight into potential mechanisms of the heterogeneous reaction.

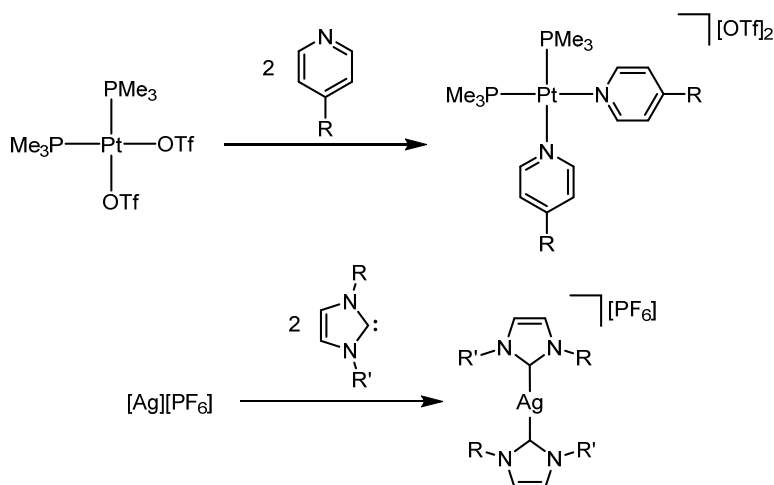
For the metal carbonyls Fe<sub>3</sub>(CO)<sub>12</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, Co<sub>2</sub>(CO)<sub>8</sub>, and Rh<sub>4</sub>(CO)<sub>12</sub> shown below:

- 1) Assign the symmetry point group.
- 2) Using the software, show the perspective along the major C<sub>n</sub> axis and any other symmetry elements that helped you make the assignment.
- 3) Determine the theoretical number of <sup>13</sup>C NMR signals and their relative ratios assuming no interconversion and no dynamic behavior (i.e. as drawn).
- 4) For Co<sub>2</sub>(CO)<sub>8</sub>, determine the symmetry operation that corresponds to C<sub>3</sub>·C<sub>2</sub> (note: the conventional direction of rotation is clockwise)



**Problem 2** (2 points)

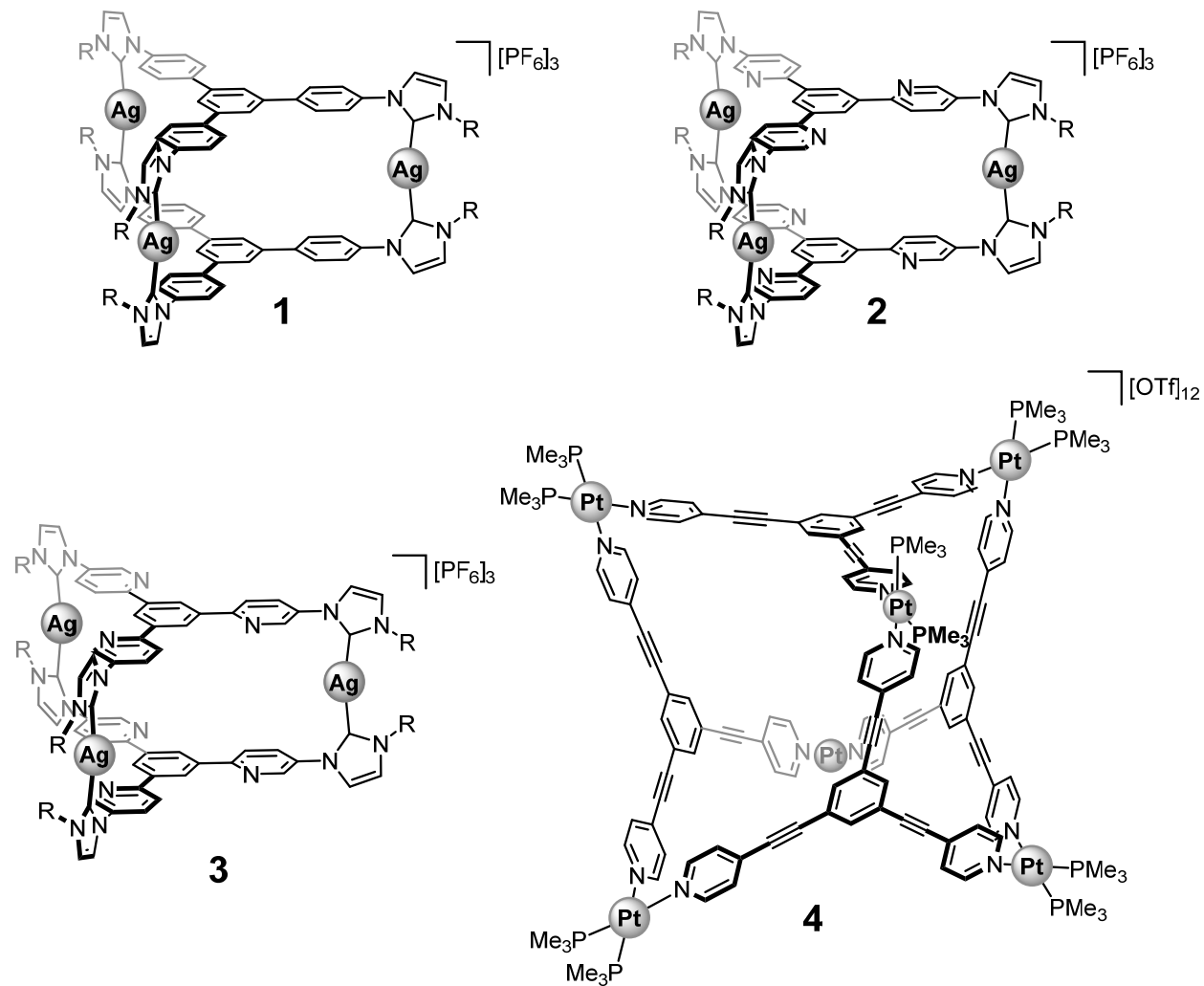
The use of metal coordination complexes to form discrete 3-D structures has been studied in recent decades for their potential to serve as platforms for molecular recognition, guest-host chemistry and catalysis, as well as vehicles for drug delivery. Rational ligand design and choice of metal ions allow for construction of a large number of molecular cages of varying sizes and geometries via self-assembly. Two examples of such synthetic strategies are shown below.



The pyridine nitrogens or carbene carbons of external ligands are capable of substituting the comparatively weaker coordinating triflate ( $\text{OTf}^-$ ) or hexafluorophosphate ( $\text{PF}_6^-$ ) ligands in the fashion depicted. During this process the geometry and angles around the Pt or Ag center remain largely unchanged. Self-assembled molecular cages, such as those shown below, can be

constructed using tris-pyridine or carbene linkers and the  $\text{Pt}(\text{PMe}_3)_2(\text{OTf})_2$  or  $\text{Ag}(\text{OTf})$  complexes.

Identify the point group of each of the below molecular cages. Identify the location of the symmetry elements and determine if the molecular cage is chiral (you only need to identify one element of each kind – i.e. only one vertical and one horizontal mirror plane). If the molecule is achiral, clearly indicate the symmetry element that prevents it from being chiral. Treat all  $\text{PMe}_3$  ligands and R substituents as spheres.

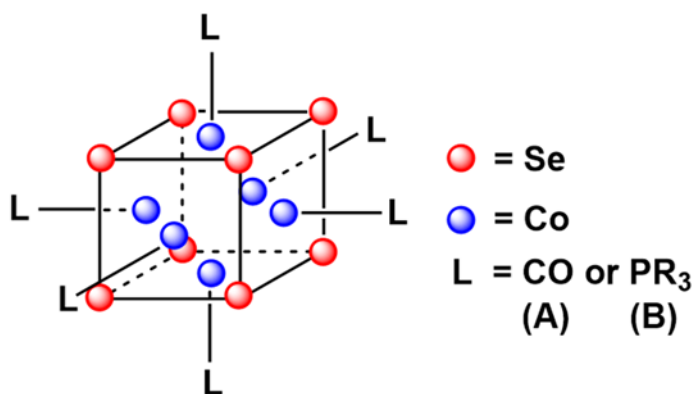


### Problem 3. (4 points)

#### Part A

Apart from their fascinating structures, metal atom clusters possess highly interesting properties for practical applications: 1) homogeneous catalysis 2) photochemical, electronic, and magnetic properties, and 3) mimicking important redox enzyme active sites.

Recently, cobalt selenide clusters of the general formula  $\text{Co}_6\text{Se}_8(\text{CO})_x(\text{PR}_3)_{6-x}$  ( $x = 0-6$ ) have been described in the literature. The synthesis was achieved by combining  $\text{Co}_2(\text{CO})_8$ ,  $\text{PR}_3$ , and Se in certain ratios. The general structure of  $\text{Co}_6\text{Se}_8\text{L}_6$  where L can be CO or  $\text{PR}_3$  can be described as follows: 1) the eight Se atoms are positioned in the vertices of a cube, 2) the six Co atoms are positioned in the center of each face of a cube, and 3) a ligand L is bound to each Co atom.

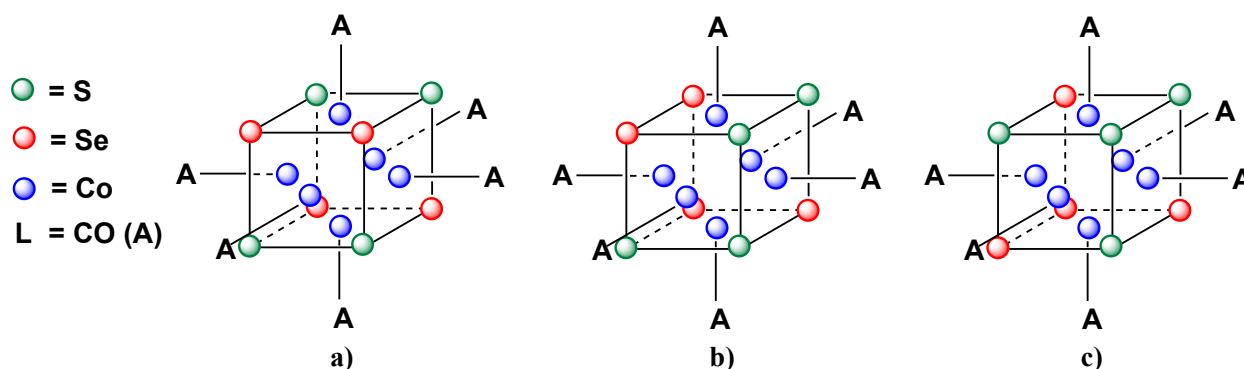


Considering all ten substitutional- and stereo-isomers of the  $\text{Co}_6\text{Se}_8(\text{CO})_x(\text{PR}_3)_{6-x}$  ( $x = 0-6$ ) series, answer the questions below. Assume  $\text{PR}_3$  groups as spherical. Although these compounds are paramagnetic, assume that their NMR spectra still display the number of expected by symmetry.

- 1) What is the point group of each molecule?
- 2) How many  $^{13}\text{C}$ ,  $^{31}\text{P}$ , and  $^{77}\text{Se}$  peaks would you expect in the NMR spectrum of each molecule?
- 3) Is it possible to distinguish among all the possible isomers using only the information obtained from the NMR spectra? Explain why.
- 4) List all symmetry operations present in compound  $\text{Co}_6\text{Se}_8(\text{CO})_6$  that are lost upon ligand substitution of one CO with  $\text{PR}_3$  to give compound  $\text{Co}_6\text{Se}_8(\text{CO})_5(\text{PR}_3)_1$ .

## Part B

Consider variants of the clusters above that contain both Se and S bridges. Three examples are shown below.



- 1) For molecules a), b), and c) Assign the point group and label all symmetry elements. Are these molecules chiral? How many peaks do you expect in their  $^{13}\text{C}$  NMR spectra.
- 2) For molecule a) select a  $C_2$  axis and a mirror plane perpendicular to it. Perform a  $C_2$  operation followed by a reflection using these elements, and indicate what single operation this corresponds to. Label all A, Se, and S moieties to show how they transform.
- 3) Draw all remaining isomers of the formula  $\text{Co}_6\text{Se}_4\text{S}_4(\text{CO})_6$  and indicate their points groups and if they are chiral. If they are not chiral indicate the symmetry operation that prevents chirality.

### Problem 4. (2 points)

Pick a topic of interest from the recommended reading in bold. Prepare two power point slides including relevant descriptive chemistry (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (point group assignment, symmetry elements, etc) and some application of the provided software (for example, highlight symmetry elements / operations). Turn in a printout of the slides with your problem set, and email the TAs the slides in pdf format by 12:00 noon on the due date.