

**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)

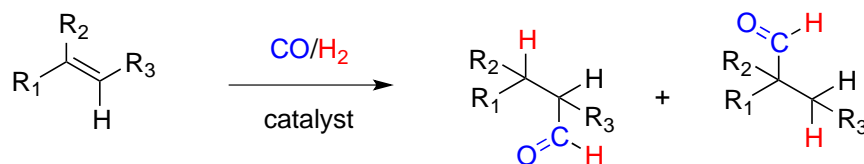
### 2016 Ch 102 – Problem Set 1

**Due: Thursday, April 7 – Before Class**

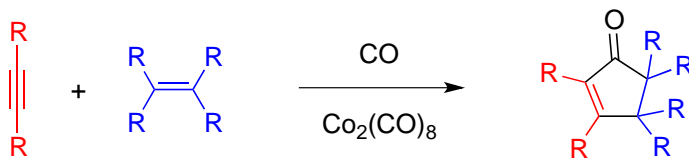
Note that the use of the Symmetrize option in the software is not allowed for the purpose of this problem set.

#### Problem 1. (2 points)

For some transition metals, homoleptic carbonyl compounds (compounds containing only CO as ligands) exist as monomeric species, such as  $\text{Mo}(\text{CO})_6$  or  $\text{Fe}(\text{CO})_5$ , 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,  $\text{Co}_2(\text{CO})_8$  is used in the catalytic hydroformylation of alkenes, as well as a stoichiometric reagent in the Pauson-Khand reaction.



Hydroformylation



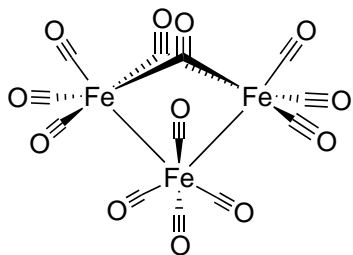
Pauson-Khand

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.

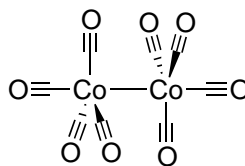
For the metal carbonyls  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Co}_2(\text{CO})_8$ , and  $\text{Rh}_4(\text{CO})_{12}$  shown below:

- Assign the symmetry point group.
- Using the software, show the perspective along the major  $C_n$  axis and any other symmetry elements that helped you make the assignment.
- Determine the theoretical number of  $^{13}\text{C}$  NMR signals and their relative ratios assuming no interconversion and no dynamic behavior (i.e. as drawn).

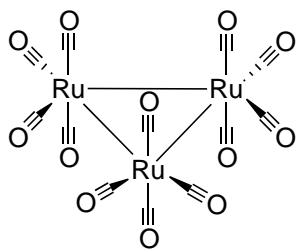
- d) For  $\text{Co}_2(\text{CO})_8$ , determine the symmetry operation that corresponds to  $C_3 \cdot C_2$  (note: the conventional direction of rotation is clockwise)



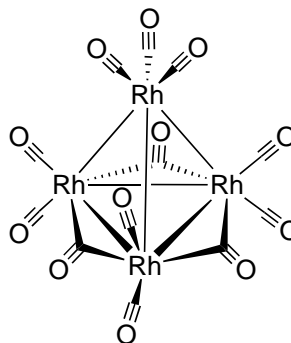
$\text{Fe}_3(\text{CO})_{12}$



$\text{Co}_2(\text{CO})_8$



$\text{Ru}_3(\text{CO})_{12}$



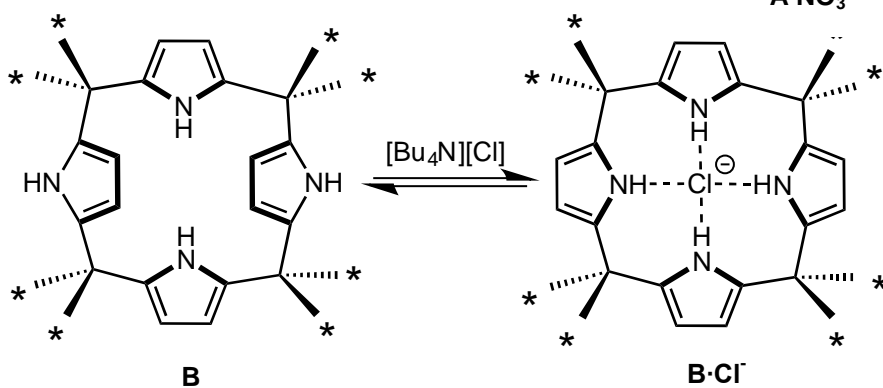
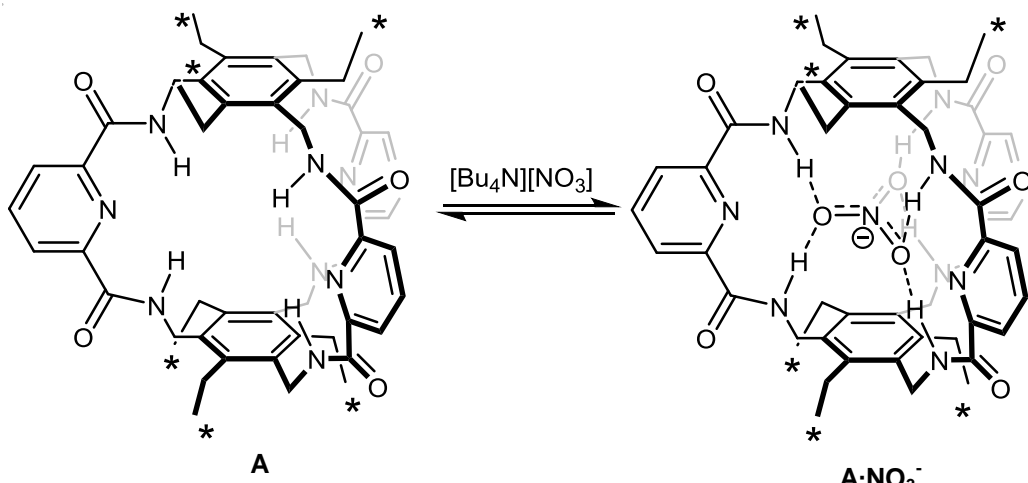
$\text{Rh}_4(\text{CO})_{12}$

**Problem 2.** (2 points)

Compounds that can selectively recognize and bind various anions have applications in selective optical sensing or extraction of anions in solution. Some anion receptors have been designed to take into account the geometry of the target species to increase selectivity.

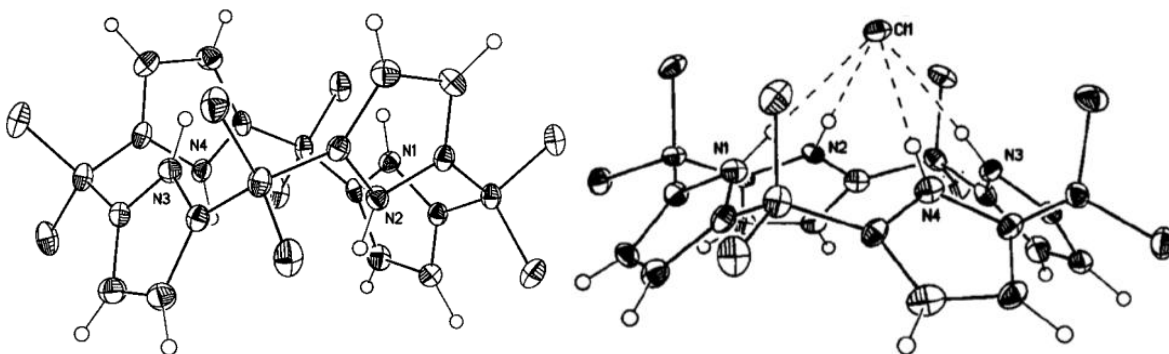
Find below two examples of anion receptors (**A** and **B**) (Beer PD, and Gale PA. (2001) *Angew. Chem. Int. Ed.*, 40, 486). Similar principles have been used for ion pair recognition, which is a coordination complex of a specific cation-anion pair (**C**· $\text{NiSO}_4$ ). The principles of anion binding have also been studied in metal complexes that can be formed by anion templation (**D**). For anion receptors **A-C**, as drawn (consider methyl groups to be spherical due to fast rotation):

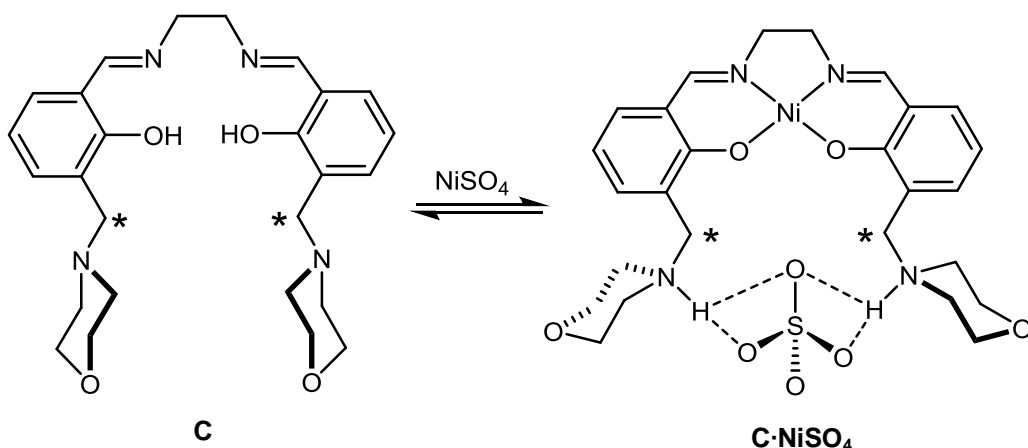
- a) Assign the point group for the free receptor and anion-bound complex, clearly labeling an example of each type of symmetry element present.
- b) Indicate the number of signals corresponding to positions starred in the drawings below in the  $^1\text{H}$  NMR spectra of free receptor and anion-bound complex (assume the molecules are frozen in the conformation). For **A** and **B**, the methyl groups, and for **C**, two methylene groups are labeled.



*B crystal structure*

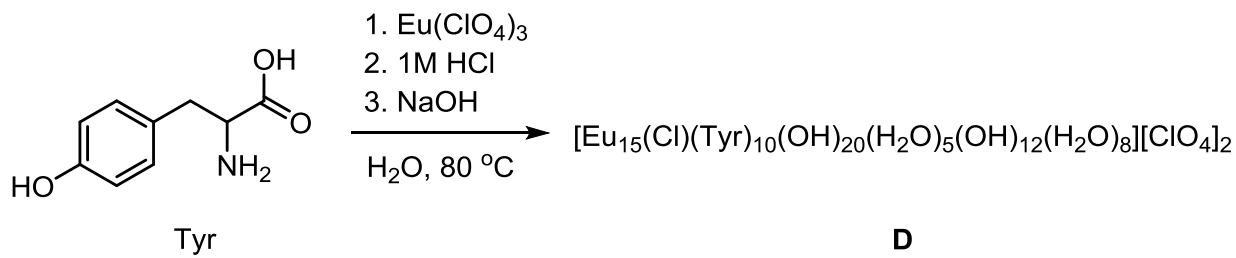
*B·Cl<sup>-</sup> crystal structure*





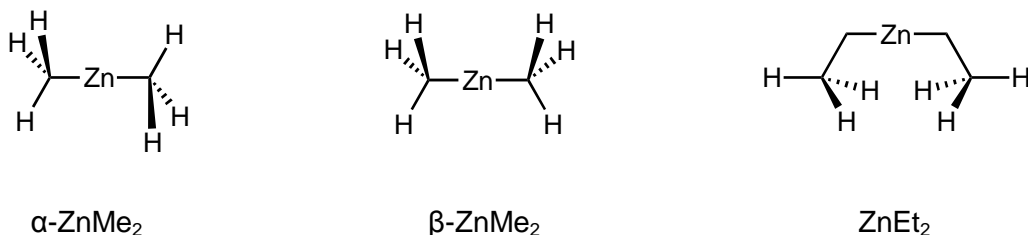
The pentadecanuclear lanthanide cluster, **D**, forms from the reaction between europium (III) perchlorate and the amino acid tyrosine. 1M HCl is added to the reaction before adjusting the pH of the solution to ~6 with NaOH, precipitating the complex. The presence of the bridging chloride in the center suggests this large cluster is formed by anion templation. The crystal structure of **D** also contains an example of anion guest-host interactions relevant to anion coordination chemistry.

- c) Using the provided software, assign the point group of **D** (with and without the perchlorate anion taken into account) and show the perspective along the highest order rotation axis. A .mol file for this molecule is available on the course website.



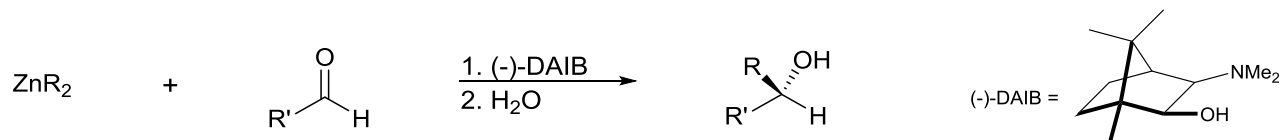
**Problem 3.** (2 points)

The addition of organometallic reagents to carbonyl compounds constitutes an important class of carbon-carbon bond forming reactions in organic synthesis. Classic reagents include strongly nucleophilic Grignard and organolithium reagents. Mildly nucleophilic dialkyl zinc species have also been used to this effect. Although both  $\text{ZnMe}_2$  and  $\text{ZnEt}_2$  are liquids at room temperature, both have been crystallized at low temperatures.  $\text{ZnMe}_2$  forms  $\alpha\text{-ZnMe}_2$  at 200K, and crystallizes in a different form,  $\beta\text{-ZnMe}_2$ , below 180K as shown below.  $\text{ZnEt}_2$  crystallizes at 100K in the geometry shown:



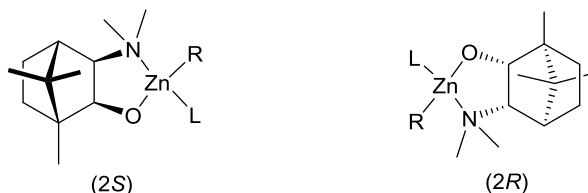
- a) List all the symmetry operations of  $\alpha\text{-ZnMe}_2$ ,  $\beta\text{-ZnMe}_2$ , and  $\text{ZnEt}_2$  respectively and determine the point groups of each molecule *in the geometry that is shown*.

Noyori (Nobel Prize winner 2001) et al. have developed a method for the asymmetric addition of alkyl zinc reagents to aldehydes as shown below (Noyori, R. et al. *J. Am. Chem. Soc.* **1989**, *111*, 4028-4036):

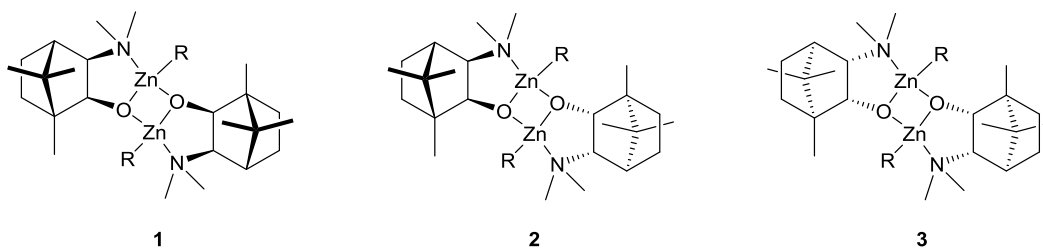


The organic auxiliary (-)-3-*exo*-(dimethylamino)isoborneol ((-)-DAIB) is used to achieve enantioselectivity in the product alcohol. Interestingly, the authors found that only a 15% enantiomeric excess (ee) in the (-)-DAIB was required to achieve up to 95% ee in the product alcohol - normally one would expect a linear relationship, or 15% ee in the product.

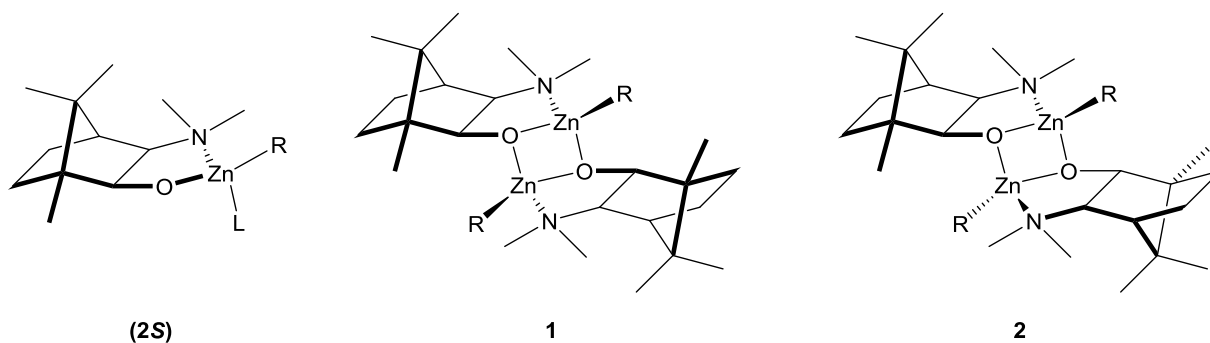
The DAIB auxiliary can bind to Zn, eliminating R-H to form the active alkylating Zn species. If enantiomerically impure DAIB is used (both *S* and *R* isomers are present) then two isomers of the Zn complexes will be generated:



Throughout the reaction, the active monomeric complexes are reversibly forming more stable, but inactive dimers. Given the presence of the *2S* and *2R* isomers of the monomeric species, we can consider the possible isomeric dimers:



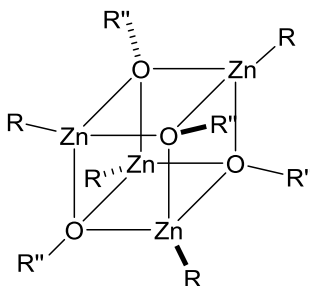
- b) Give the point group of the monomeric (**2S**) species, dimer **1**, and dimer **2**, and determine whether each complex is chiral or achiral. If the molecule is achiral, indicate a symmetry element that precludes chirality. The perspectives shown below, taking account of the pseudo-tetrahedral coordination at Zn, should be used for your analysis.



Ultimately, dimer **2** is the more thermodynamically stable complex, pairing the (**2S**) and (**2R**) monomeric species together. Thus, when using 15% ee (**-**)-DIAB, there is an average 15% excess of the (**2S**) isomer that does not have a (**2R**) partner to dimerize with and goes on to do the majority of the alkylation. This phenomenon results in the authors' observed amplification of enantiopurity in the end product.

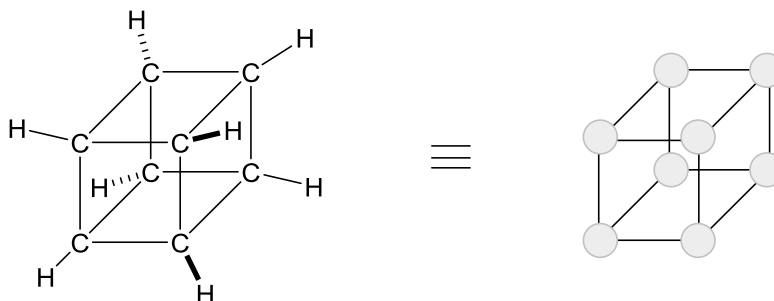
Prior to aqueous work-up, the authors were able to determine the presence of a stable tetramer that forms after alkylation has occurred, shown below where OR'' is the product alkoxide.

- c) Assuming *R* and *R''* to be spherical, determine the point group of the zinc alkoxide tetramer.



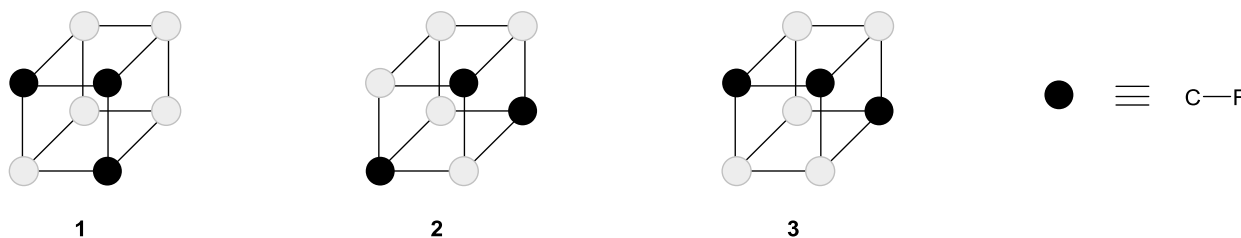
**Problem 4.** (2 points)

Cubane ( $C_8H_8$ ) is a highly strained synthetic hydrocarbon, as shown below:



- a) Determine the point group of cubane and predict the number of  $^1H$  and  $^{13}C$  signals one would expect to find in the NMR spectra of the compound.

Consider the fluorination of cubane and stopped after three C-H bonds have been replaced with three C-F bonds, giving isomers of  $C_8H_5F_3$ , including the ones shown below.



- b) List the symmetry operations and determine the point group of isomers **1**, **2**, and **3**. Additionally, predict the number of  $^1H$ ,  $^{13}C$ , and  $^{19}F$  NMR signals we would expect to find for each isomer. Are these isomers chiral? If the molecule is achiral, indicate a symmetry element that precludes chirality.
- c) Now consider the case where fluorination and chlorination results in  $C_8H_4F_3Cl$ . Determine the number of pairs of enantiomers possible given the formula. Draw each isomer (one per pair of enantiomers). *You may draw the cubane with shaded and unshaded corners to represent C-F and C-H bonds but please clearly label which carbon the chlorine is attached to!* Which of these isomers can be distinguished by  $^1H$ ,  $^{13}C$ , and  $^{19}F$  NMR and why?

**Problem 5** (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.