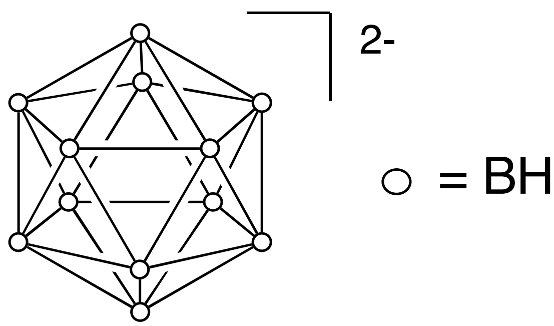
Recommended Reading: 4.1 – 4.6, 4.8, 17.7-17.9

Ch 102 – Problem Set 1
Due: Tuesday, April 5 – *Before Class*

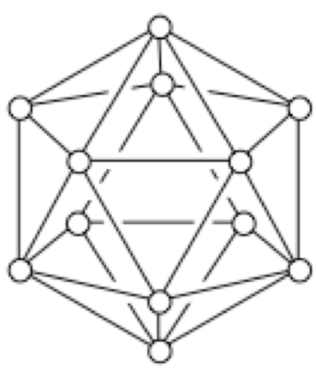
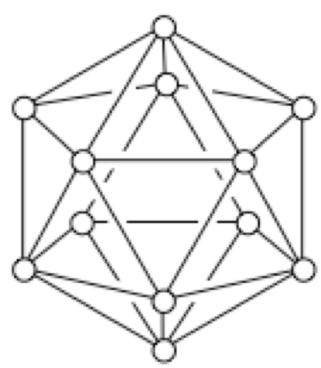
Note that the use of the Symmetrize option in the software is not allowed for the purpose of this problem set.

Problem 1 (35 pts)

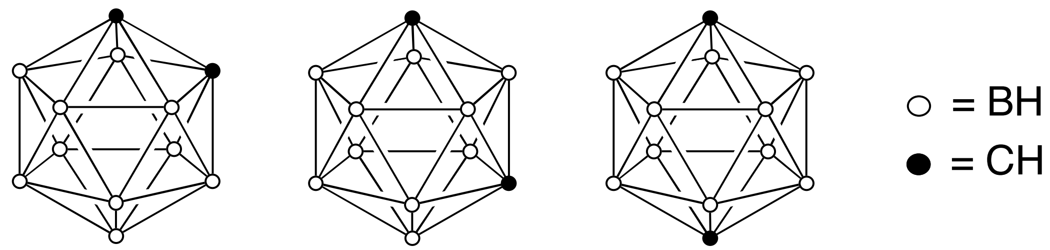
a) Boranes, compounds of boron and hydrogen, can exhibit a variety of structures. One interesting borane form is the dodecaborane dianion, $[B_{12}H_{12}]^{2-}$, which adopts the structure shown below.



Identify the point group of dodecaborane, and using the blank structures below identify the location of the symmetry operations of dodecaborane (you only need to identify one operation of each kind – i.e. only one vertical and one horizontal mirror plane).

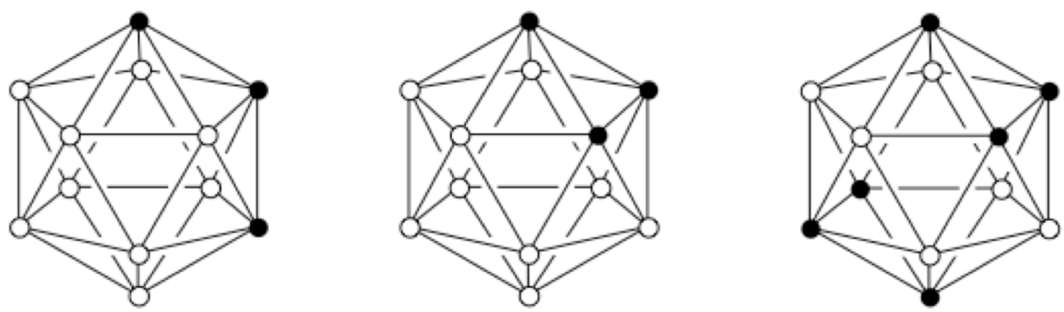



b) Replacement of two B-H units in the dodecaborane dianion with C-H moieties gives rise to neutral compounds called carboranes, $[B_{10}C_2H_{12}]$. These complexes are extremely stable, undergoing isomerization at high temperatures (>500°C) with no decomposition. This stability is due to the fact that they can be considered three-dimensional aromatic molecules (following Huckel's rule). There are three possible carborane isomers, *ortho-*, *meta-*, and *para-*carborane (shown below). Identify the point group of each carborane isomer.

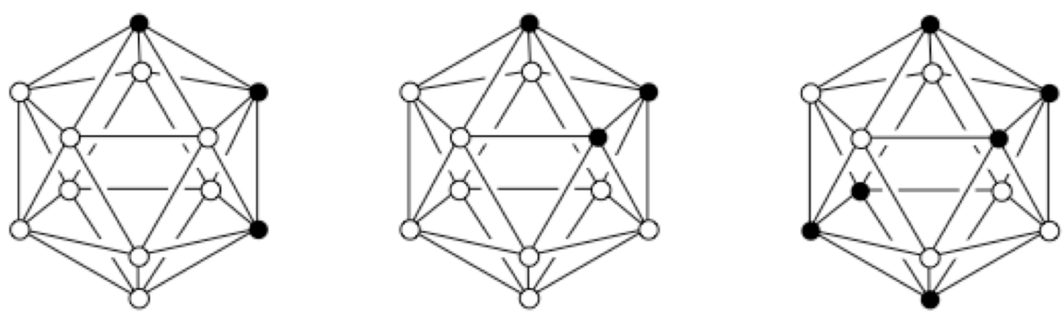


ortho *meta* *para*

c) As demonstrated above, addition of different X-H moieties can give carboranes with different symmetries. Using C-H and/or N-H ‘building blocks’, one could design carboranes as the ones shown below:



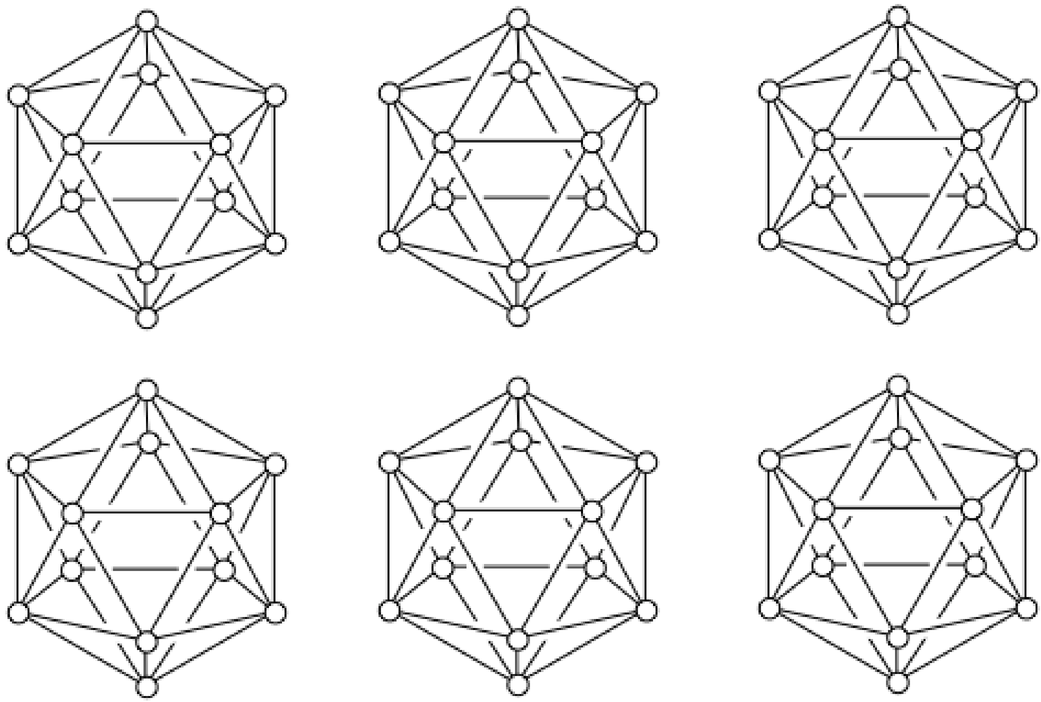
Assign point groups to the given carboranes. Then, using the structures below, locate all the symmetry elements in each molecule (again, only show one symmetry element of each kind).



Now it’s your turn to design new carboranes! Again using C-H and/or N-H moieties, use the blank structures below to design carboranes belonging to the following point groups (fill in the circles for C-H, mark the circles in a clearly different manner for N-H):

C_{2h}, C_{5v}, D_{2h}, C_{2v} (in the last one you must use BOTH N-H and C-H)

For the C_{5v} and D_{2h} cases also indicate the location of the symmetry elements in the molecules (only show one symmetry element of each kind; use the last two blank structures if you need extra space to avoid the structures becoming cluttered), and indicate if any of the seven carboranes in this part of the problem are chiral.

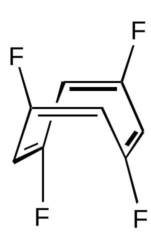


d) Boron-11 (80% natural abundance) has a nuclear spin of 3/2, and can be used to obtain NMR spectra of boron-containing compounds. For all compounds in part (c), predict the number of unique shifts you expect to observe in the ^{11}B-NMR.

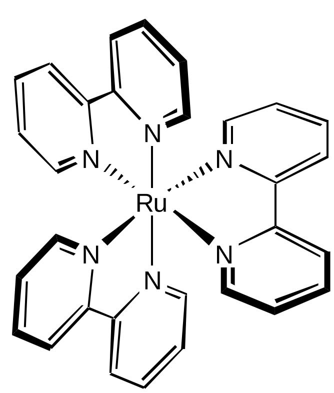
Problem 2 (15 points)

For each of the following molecules, identify the point group and determine if it is chiral. If the molecule is achiral, clearly indicate the symmetry element that prevents it from being chiral.

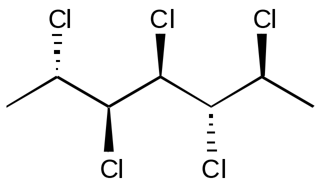
a) 1,3,5,7-tetrafluorooctatetraene



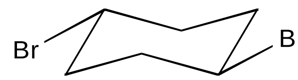
b) $[Ru(bipy)_3]^{2+}$



c) $C_7H_{11}Cl_5$ (as drawn)

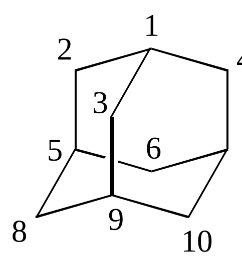


d) *trans*-1,4-dibromocyclohexane



Problem 3 (10 points)

The adamantane molecule was discussed in class and has T_d symmetry. It is drawn below with the carbons numbered.

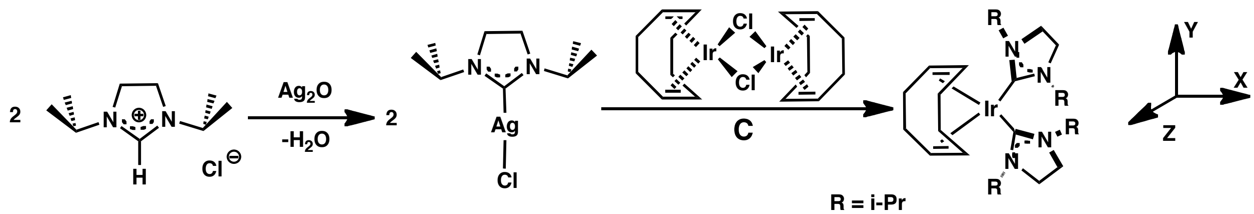


a) T_d point group molecules are characterized by sets of the following symmetry elements: C_2, C_3 and S_4 axes and σ_d planes. How many of each are present?

b) For each type of symmetry element, draw one of them and indicate all the carbon atoms it passes through by number. Also, how many hydrogen atoms remain unmoved by each C_2, C_3, σ_d, or S_4 operation?

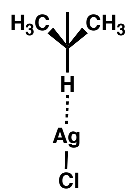
Problem 4 (20 points)

a) A common method to install N-heterocyclic carbene (NHC) ligands onto metal centers is through a process called silver (I) oxide transmetallation. An NHC salt precursor (**A**) is treated with Ag_2O, as shown, forming a (NHC)AgCl complex (**B**). Next, these are treated with $[Ir(COD)Cl]_2$ (**C**, COD = cyclooctadiene), forming $Ir(NHC)_2(COD)$ species (**D**). Provide the point groups of molecules **A**-**D** as they are drawn. For each compound indicate how many peaks are expected in their ^1H NMR spectra; explain.

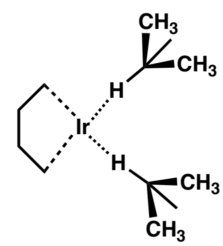


A B D

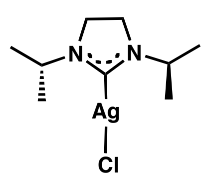
view of **B** along X-axis (the vector perpendicular to the Ag-C bond and contained in the plane of the ring)



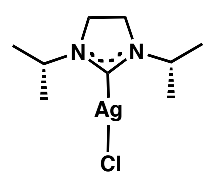
view of **D** along Z-axis (the vector perpendicular to the metal coordination plane)



b) Assign points groups to conformers $\mathbf{B_1}$ and $\mathbf{B_2}$ drawn below (they differ from **B** by rotations around the C_{iPr}-N bonds). Are these conformers chiral?



$\mathbf{B_1}$



$\mathbf{B_2}$

Problem 5 (20 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) and some application of the provided software (for example, different views of the molecules to highlight symmetry elements / operations). Turn in a printout of the slides with your problem set. Bring the slides to class in pdf format on a memory stick and be prepared to present.