University of Windsor
Chemistry and Biochemistry
Chemistry 59-651, Fall Term 2004

Assignment 3

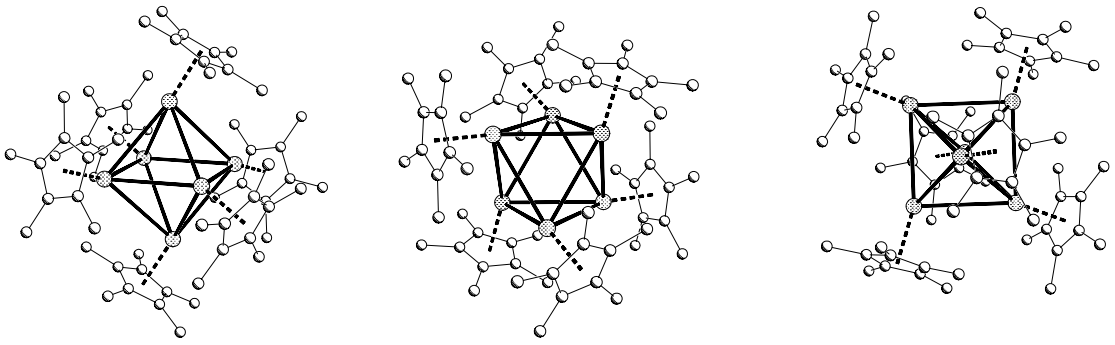
Due: Before Monday, December 20 (if you get it done early and just want to get things out of the way, you can hand it in as early as you want)

Use appropriate concepts that we have discussed in class (e.g. VBT, MO theory, steric interactions, isodesmic comparisons, CGMT theory, etc. – note: it is not necessary to apply each concept to every question, just use those that are appropriate) to explain the following observations:

1) $(B^tBu)_4$ is a cluster with a perfectly tetrahedral structure (Paetzold, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 173), while $(BNMe_2)_6$ adopts a structure with a cyclohexane-like B_6 ring (Noth, *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 482). Use MO diagrams and drawings **of the monomeric BR fragments** to suggest why the borylene fragments make different types of oligomers.

2) $(\eta^5\text{-Cp*})Al$ is a stable Al (I) compound that adopts tetrahedral shaped $((\eta^5\text{-Cp*})Al)_4$ cluster structure in the solid state (Schnoeckel, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564). In contrast, the analogous $((\eta^5\text{-Cp*})B)_4$ cluster has not been made and is unlikely to ever be synthesized (despite the existence of the useful starting material $(BCl)_4$). Provide reasons why the $((\eta^5\text{-Cp*})B)_4$ cluster would be likely not be stable.

3) While $(B^tBu)_4$ is a cluster with a perfectly tetrahedral (T_d) structure that remains as a cluster in solution, $(\eta^5\text{-Cp*})Ga$ (Schnoeckel, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860) and $(\eta^5\text{-Cp*})In$ (Beachley, *J. Am. Chem. Soc.*, **1986**, *108*, 4666) are monomeric in solution and form hexameric structures in the solid state that display S_6 symmetry (not O_h) as shown below. Use MO diagrams and related arguments to explain the differences.



4) Explain why Power's terphenyl Ga (I) compound Ar'-Ga (Power, *J. Am. Chem. Soc.*, **2003**, *125*, 2667) adopts a dimeric structure in the solid state instead of a tetrameric or hexameric structure.