*Using PC Model, answer the three questions below.*

1. Consider the trioxane equilibria illustrated below (trioxane itself is a hypnotic agent used therapeutically). Use PC Model to compute the 298 K heats of formation of the monomers and the trioxanes in kJ mol^{-1}. Find the experimental gas-phase heats of formation (webbook.nist.gov might be a nice resource). How does PC Model do? Assuming the enthalpies are equivalent to free energies (they aren't, but let's make the assumption for the moment), what are the equilibrium constants for the two equilibria in the gas phase?
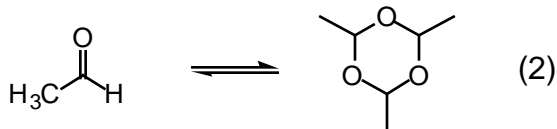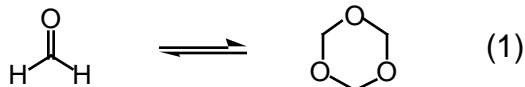

2. Shown below is a rather unusual sugar. Using PCModel, find the lowest energy stereoconformation for this molecule you can (i.e., you get to pick the stereochemistry of all stereogenic centers and the ring geometries, hydroxyl group rotations, etc.—I got down to $H^o{}_{f,298} = -247.5$ kcal mol^{-1} without too much effort). Find two other stereoconformers as well. Using the term-by-term breakdown of the individual force field energies, explain in a chemical fashion the differences in energies for different conformers. To facilitate this analysis, it might be helpful to do some quick calculations on relevant monomers. Include with your answer printouts of the structures/energies for your conformers (note that a ball-and-stick structure is occasionally a bit easier to view than a wire structure for stereochemical purposes).
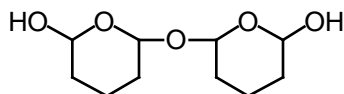
3. Zirconocenes are useful catalysts in the preparation of polypropylene. Shown on the next page is a structure for an intermediate thought to be important in the

polymerization scheme. One of the interesting features about zirconocenes is that they can catalyze polypropylene production in a syndiotactic fashion, and it appears that one control element is the space available to incoming propylene based on the size and nature of the cyclopentadienyl (Cp) substituents. Some work has taken place with "bridged" Cp rings, which are designed to have different "bite angles". Use PCModel to compute the structure of the indicated intermediate for simple Cp rings, and for the case where the two Cp rings are joined together by a methylene unit (CH_2). Report the following distances in each case (Å): Zr–CH3, Zr–CH(CH3), Zr–CH2, and CH3- - - CH(CH3). Based on your results, how might you expect the reactivity of the two complexes to differ with respect to C–C bond formation? Justify your answer.

Zr–CH3

propylene

H
H
CH3
H
Zr
CH3

vs.

H
H
CH3
H
Zr
CH3

CH3
CH3
Zr

repeat for chain growth
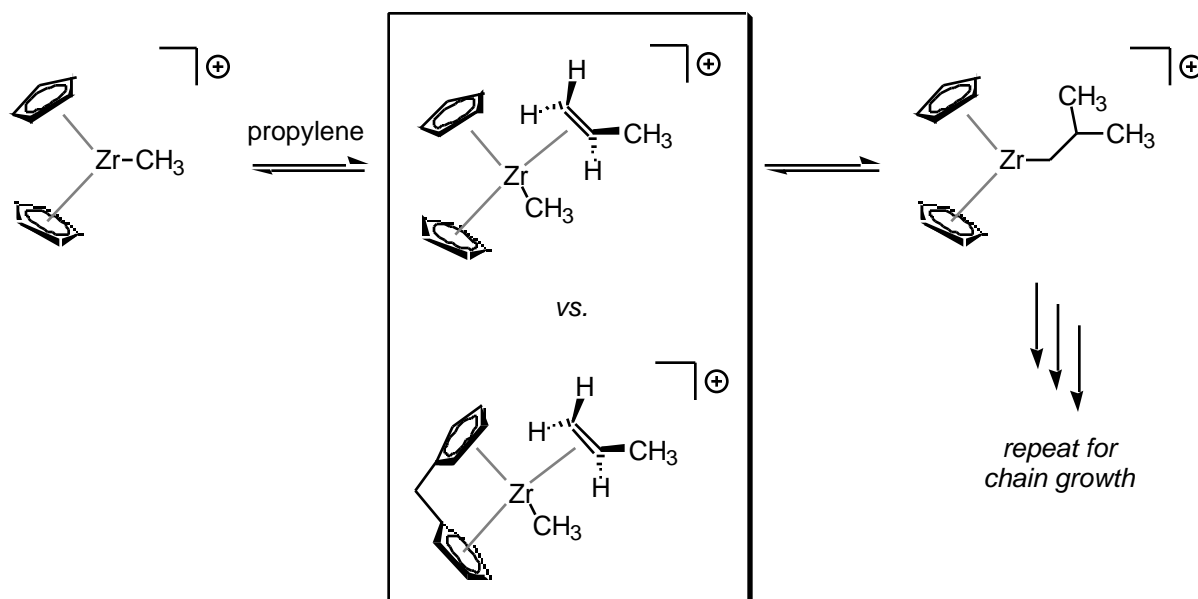
Technical notes: Metallocomplexes are slightly tricky in PCModel. The manual has a section on building ferrocene that you may find useful. Note that all Cp ring carbons should be defined as aromatic carbons (CA), the Zr–CH3 bond is a "real" bond (just draw a connection) but all other Zr–C interactions must be set using the Mark (menu) Metal Coordination option, where the charge on Zr should be set to 1. As a check that you have not done something wrong, I note that optimized MMX energies in both cases should be around -115 kcal mol^{-1}.