5.05 *2005* Exam 1.

INSTRUCTIONS

This exam is not "open-book", so do not take answers directly from the reading. Rather, you should reason out your answers based on your understanding of the material presented thus far. You may use a periodic table and other standard reference works. Work alone. Spend no more than 2 hours working on the exam.

1. Use Gaussian/Xaim to analyze vinyl chloride.
   a. Model building. What will you use as your initial guess as to the C-Cl interatomic distance in vinyl chloride? Where do you get this number in the absence of the helpful MOLDEN program? What is the optimized distance?
   b. Which of the C-H bonds does your analysis predict to be the strongest? By how much? (answer with a percentage). Explain the basis for your answer, and also explain why the analysis does or why it does not agree with your chemical intuition.
   c. Provide a Laplacian plot in-plane for vinyl chloride. Explain how its appearance is consistent with the answer you gave in 1b.
2. Describe how an AIM analysis partitions space, and how the partial charge on an atom in a molecule can be calculated using an AIM analysis.
3. Draw the best Lewis structure for carbon monoxide including formal charges. Explain why you do or do not think the formal charges would agree with charges calculated according to the method of problem 2.
4. What was the first structurally characterized aluminum(I) compound and how was its structure determined?
5. Explain how to calculate the average Al oxidation state in the aluminum cluster having the greatest number of "naked" aluminum atoms described to date.
6. Give an orbital analysis explaining why LAl, where L is the Nacnac ligand type, fails to react with alkynes.
7. The reaction Mes*PCl$_2$ + (DMP)PPMe$_3$ → Mes*PPMe$_3$ + (DMP)PCl$_2$ is catalyzed by PMe$_3$. Draw a cycle to explain the catalysis.
8. In the phospha-Wittig reagent (DMP)PPMe$_3$, the ^{31}P NMR signal for the two-coordinate phosphorus is found *upfield* of that for the four-coordinate phosphorus. Is the two-coordinate phosphorus electron-rich, or is it electron-deficient? Explain.
9. Predict both the products and the mechanism of reaction of (DMP)PPMe$_3$ with benzaldehyde.
10. Draw the hypothetical *singlet* phosphinidene (Me$_2$N)P and assign to it a coordinate system with P at the origin. Assume C_{2v} point symmetry.
    a. Which of the Cartesian axes corresponds to δ_{11}?
    b. To what aspect of the phosphinidene electronic structure is δ_{11} exquisitely sensitive?
    c. What type of experiment could be used to extract the value of δ_{11}?