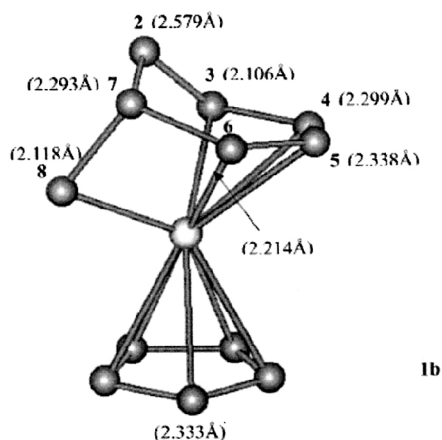


Written Qualifying Examination – Inorganic Chemistry I

January 22, 2007

Questions related to R. F. W. Bader and C. F. Matta, *Inorg. Chem.* **2001**, *40*, 5603-5611

The referenced paper concerns the proposal of possible agostic bonding in a crystalline compound, first synthesized by Ernst, containing titanium bonded to a six-member ring (6-MR) substituted dienyl moiety and a five-member ring (5-MR) cyclopentadienyl moiety. The Ti–C distances and geometry are indicated in the following figure (structure 1b), taken from Ernst and used by Bader and Matta in this paper.

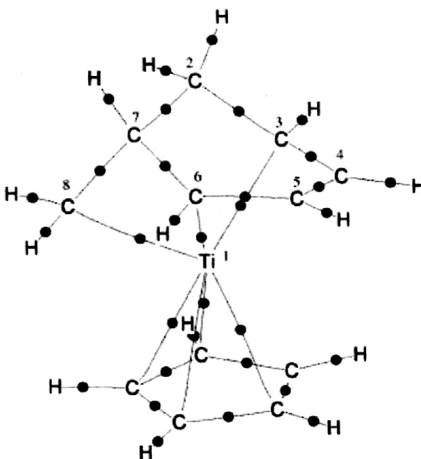


1b

Where necessary use the numbering shown in this diagram to refer to the individual carbon atoms of the 6-MR. Recall that when referring to the 5-MR the authors number the forward-most carbon atom as C1' (the carbon just above the label 2.333 Å in the figure), with successive carbon atoms numbered counter-clockwise around the ring (i.e., C5' is to the immediate left of C1' in the figure above).

Answer **five (5)** of the following six questions. Be sure to indicate clearly the question you are answering in each case. If you answer all six questions, only the first five will be graded. Each of your answers should consist of one or two paragraphs (more if needed) composed of complete sentences in standard English.

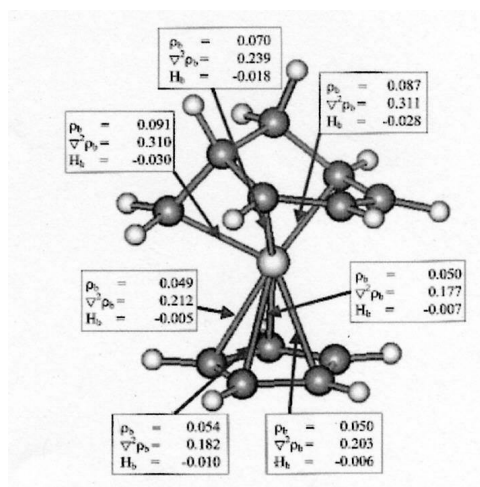
1. Ernst proposed that certain agostic interactions exist in the complex. What is the meaning of the term "agostic" as it has previously been applied and as it is being applied to this complex? Which specific interactions have been proposed as agostic in this complex? On what basis are these interactions presumed to be agostic? What criteria do Bader and Matta propose to determine whether or not these are truly agostic interactions?
2. Bader and Matta present results of a variety of calculations that are a part of QTAIM (now more commonly referred to as AIM theory). What is the starting data (the observable) for all AIM analyses and how are these data obtained? Among the AIM variables that are calculated in this paper are ρ_b , $\nabla^2\rho_b$, H_b , and $\delta(\text{Ti}-\text{C})$. Give the name for each of these variables and briefly describe the significance of each for analyzing the problem addressed in this paper.
3. Bader and Matta present the following molecular graph (Figure 1a).



In general, what does a molecular map show? What are the dots along each line? Relative to the specific problem addressed in this paper, what do these results suggest about the bonding between Ti and the 6-MR?

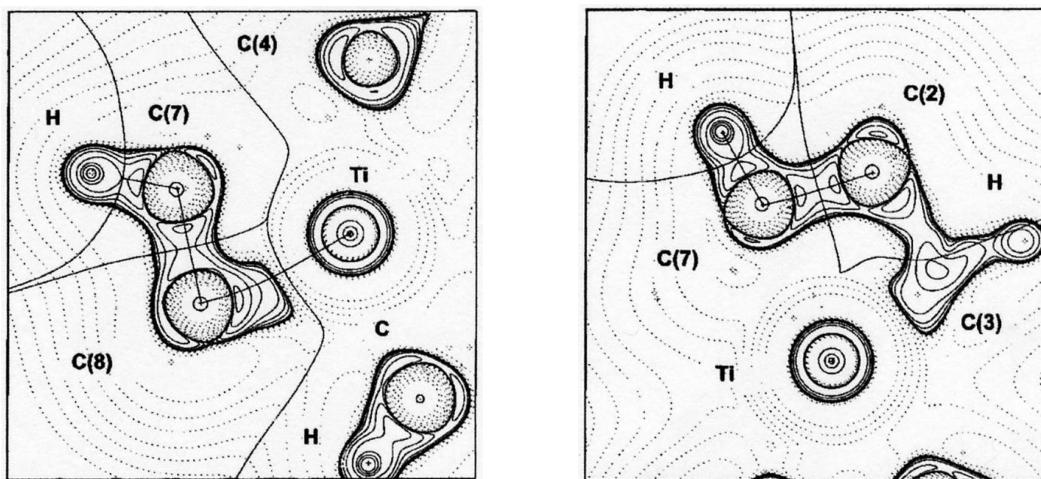
4. The molecular map shows four connections between Ti and C1', C2', C4', and C5'. In addition to ρ_b calculations for each of these, the authors also calculate ρ_r for the three 3-MRs and one 4-MR defined by these connections. They also calculate a ρ_r for the face of the 5-MR cyclopentadienyl ligand. What do their results suggest about the nature of the bonding between Ti and the 5-MR? How does this accord with previous views of the nature of cyclopentadienyl ligand binding to transition metals?

5. Consider the following figure from the paper (Figure 3a).



How do the values given compare to typical values found for closed-shell main group atom interactions (e.g., "ionic" interactions) and main group shared interactions (e.g., "covalent" interactions)? What do the authors conclude about the bond CP characteristics for bonding to a transition metal? Are the results shown for this titanium complex consistent with the charge calculations that the authors carried out? Explain.

6. The figures below (Figures 6a and 6b) show the Laplacian of electron density in planes containing the Ti atom and the C atoms indicated.



Based on these maps, comment on the nature of the bonding or non-bonding between the following pairs of atoms: C(7)–C(8), C(8)–Ti, C(7)–Ti, C(2)–Ti, C(3)–Ti. How do these results relate to the question of the existence or absence of agostic interactions in this compound?

Green Chemistry Question:

Transition metals are often used in catalytic reactions for their ability to form bonding interactions with organic molecules, possibly altering the reactive species' structure in ways that may potentiate some desired reaction. In light of this, how might the application of AIM theory be used in formulating green strategies for organic synthesis?