Literature Discussion of *Organometallics*

Dorsey, C.L. and Gabbai, F.P. *Organometallics* **2008,** *27,* 3065-3069

Learning Goals:

Students will be able to...

* Define an agostic interaction and relate it to other types of bonding.
* Describe how the agostic interaction affects the coordination geometry of a Lewis acidic atom.
* Provide examples of how the presence of an agostic interaction can be determined experimentally and through computational methods.
* Differentiate between computational methods in terms of the information they can provide.
* Find related sources of information to aid in comprehension of the concepts in the article.

BONDING

1. Define an agostic interaction.
2. Compare an agostic interaction with hydrogen bonding.
3. Compare the Si-H interaction (bonding) in this paper with the bonding in diborane.
4. The crystal structure finds that the distance between the hydride and the silicon atoms is 2.32(2) Angstroms “which is well within the the sum of the van der Waals radii of the two elements”. What are the van der Waals radii of silicon and hydrogen and how does the sum compare to the value from the text? Why is this important to defining the interaction between the silicon and hydride as an agostic interaction?
5. The paper states that this agostic interaction is weaker than the classical agostic interactions because of the absence of back-bonding. What is back-bonding and why how does it strengthen a bond. Why is back-bonding not possible in an interaction with silicon?
6. Identify the donor-acceptor interactions in R3C-H→SiFR3?

STRUCTURE

1. How were the crystals obtained that were used for structure determination? Briefly explain the physical processes behind these techniques.
2. How do the bond angles around the methylium carbon (C(11)) in Figure 1 (compound **[II+]** confirm that the interaction with F is a weak interaction and not a formal bond?
3. How do these bond angles change in compound **3 (Figure 4)** to indicate that a hydride is bound to that carbon?
4. For compound **3**, draw the silicon and attached atoms like a coordination compound in its correct geometry. From **Figure 4** label the bond angles for F(1)-Si(1)-C(24), C(24)-Si(1)-C(1), and F(1)-Si(1)-H(1). How do these angles compare to those in an “ideal” trigonal bipyramidal complex? Why are they different?
5. The sum of the carbon-silicon-carbon angles is 333.2° in [**2]+** and 345.27° in **3**. Compare these sums to the “ideal” values expected for tetrahedral or trigonal bipyramidal geometries.
6. Briefly describe the general principles behind X-ray diffraction.
7. Why might it be difficult to locate the hydrogen atoms in a molecule using X-ray diffraction?
8. Neutron diffraction is often used to determine the location of hydrogens in a molecule. Briefly explain why neutron diffraction can reliably detect hydrogens whereas X-ray diffraction cannot.

SYNTHESIS

1. Under General Considerations of the experimental section, the authors describe drying the solvent (THF) and working with air-sensitive compounds. Why was it necessary to exclude water and air from the synthesis of compound **1**?
2. In Scheme 1, 1,8-dilithionaphthalene is reacted with xanthone. Draw the structure of xanthone.
3. According to the experimental section, in the synthesis of **1**, which reactant was the limiting reactant in step (a) of Scheme 1? Explain your answer.
4. Draw curved arrows to show the mechanism of the reaction between 1,8-dilithionaphthalene and xanthone.
5. In the synthesis of compound **2**, what is the source of fluoride that generates the Si-F bond?
6. In the synthesis of compound **3** from compound **2**, describe the role of NaBH4 in forming the new C-H bond. Draw curved arrows to show the mechanism.

CHARACTERIZATION

1. What information can be gained about the structure of a compound using IR and NMR spectroscopy?
2. The 1H NMR spectrum of compound **1** suggests that that the molecule is *Cs* symmetric. Based on the number of peaks reported, rationalize this observation.
3. Identify the heteronuclear NMR experiments used in this article. What are the respective natural abundances and nuclear spin of the NMR-active nuclei studied? Cite your sources.
4. How are the JSi-F values obtained from the NMR spectra?
5. Explain how the IR peak at 2928 cm-1 in **3,** vs. the IR peak at 2937 cm-1 in 9-(naphthalen-1-yl)-9H-xanthene, is used to support the agostic C-H to silicon interaction. Start by drawing the structure of 9-(naphthalen-1-yl)-9H-xanthene and comparing it to the structure of **3**.

THEORY/COMPUTATIONAL

1. What functional was used to optimize the molecular geometry for theoretical calculations?
2. The electron density of the DFT-optimized structures of **[2]+** and **3** were subjected to an atoms-in-molecules (AIM) analysis. What type of information does AIM provide?
3. Table 2 compares three different calculated properties for four different but related molecules. (a) Do you expect the Lewis acidity of the silicon to increase or decrease as one goes down the table? Explain briefly. (b) Explain how the information in each of the columns supports the hypothesis that agostic interactions become stronger as one goes down the table.
4. The natural bond order contour plot in **Figure 5** shows the interaction between the C-H bond and the Si atom. What orbitals are interacting based on the plot?