**Water Oxidation Catalyzed by NHC Complexes of Iridium**

"Water Oxidation Catalyzed by Strong Carbene-Type Donor-Ligand Complexes of Iridium" Ralte Lalrempuia, Neal D. McDaniel, Helge Muller-Bunz, Stefan Bernhard, and

Martin Albrecht, *Angew. Chem. Int. Ed.* **2013** 49, 9765-9768.

We will be discussing the paper listed above in class next week. Please prepare yourself to discuss it by writing out the answers to the following questions. Feel free to divide up the work, but each person should get a good overall view of the paper and feel comfortable answering the questions. You will be graded on class participation.

* What significant result(s) presented in this article merited its publication in Angewandte Chemie, the top European chemistry journal?
* Why is water oxidation important?
* What enzyme (and specific subunit) is responsible for water oxidation in nature? What metals are found in the water oxidation site?
* What are some of the challenges for performing water oxidation artificially?
* Find the accepted mechanism for homogeneous water oxidation for iridium and draw it. There is a recent article (Wasylenko, D.J.; Palmer, R.D.; Beringuette, C.P.; *Chem. Comm.*,**2013**, *49*, 218-227.) about water oxidation catalysts which is a good source.
  + What oxidation states for iridium are predicted?
  + What Ir species reacts with water to form an O-O bond?
  + What is the rate determining step proposed in most cases?
* What are the oxidation states and electron counts for complexes **2** and **3**?
* The NHC ligand in **2** and **3** are both formally neutral. Draw resonance structures for the ligands (without circles) indicating how this is possible.
* What is a zwitterion? What is an ylide? How are they different?
* What is "click chemistry"? List at least five properties that an ideal click reaction should have. The review article by Sharpless et al. may be helpful. (Kolb, H. C.; Finn, M. G; Sharpless, K. B. (2001); *Angew. Chem. Int. Ed.*, 2001, *40*, 2004-2021.)
* What is the role of Ag2O in the synthesis of **2** and **3**? Use the following paper to help answer this question: Mathew P.; Neels A.; Albrecht M.; *J. Am. Chem. Soc.* **2008**, *130*, 13534-13535.
* Why can't complex **2** be an intermediate formed in route to complex **3**? Which product is more thermodynamically stable?
* Draw a structure for the monodentate iridium intermediate that is the likely precursor to both **2** and **3**.
* What coupling pattern is observed by 1H NMR spectroscopy for the CH2 protons of the iridium bound carbon in **3**? Why aren't these protons equivalent?
* What is the role of CAN in the water oxidation described in the paper?
* Define TON and TOF.
* What is an abnormal (mesoionic) N-heterocyclic carbene? How do they compare in terms of σ-donation to normal NHC's? Why might they be well suited as ligands for water oxidation?
* Which resonance structure for **2** can best stabilize a higher oxidation state?
* How does the CV data support the idea that the ligand is involved in the oxidation?
* What major hurdles remain for artificial water splitting?