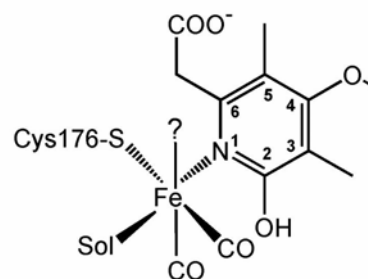


**Inorganic Cumulative Exam**  
**Hydrogen Activation**  
**Donald Wink**

Hydrogenases are important enzymes for certain organisms and, given the potential importance of hydrogen in both chemistry and in energy conversion, very important as possible sources of ideas about effective activation of dihydrogen, H<sub>2</sub>. This exam considers some recent examples of hydrogenase studies.

1. (30 points) To begin, let's consider certain important aspects of hydrogen activation by precious metal small-molecule catalysts, such as the rhodium-based Wilkinson's catalyst or the Schrock-Osborne catalysts.
  - (a) What is the structure of Wilkinson's catalyst?
  - (b) What is the structure of a basic example of the Schrock-Osborne catalyst?
  - (c) For *either* catalyst, write the fundamental catalytic cycle. Note that this may involve conversion of the "original" catalyst to an active catalyst. Explain that if it occurs.
  - (d) Indicate at least three features of one of these catalysts that may make it ideal for the catalytic activation of dihydrogen.
  
2. (10 points) It is improbable that rhodium will ever be found in a biological hydrogenase. Explain why.
  
3. (40 points) Several iron-containing hydrogenases are now known (Armstrong, F. A., Fontecilla-Camps, J. C., *Science* **321** (5888), 498). Remarkably, though they evolved in very different biological contexts, all exhibit convergent evolution of the iron site. The following facts seem reliably established:
  - (i) The iron site consists of a six-coordinate approximately octahedral arrangement with a *fac* arrangement of a CO ligand, a thiolate group, and a third site that is either a CO, a cyanide, or a pyridinol coordinated through the N position.
  - (ii) The Fe exists in the Fe(II) state prior to the addition of dihydrogen.
  - (iii) The mechanism of action may involve H<sub>2</sub> binding followed by either removal of hydride (Fe-H<sub>2</sub> → Fe-H<sup>+</sup> + H<sup>-</sup>) or removal of an electron and loss of a proton (Fe-H<sub>2</sub> → Fe-H<sup>+</sup> + H<sup>+</sup> + 2e<sup>-</sup>)
  - (iv) The Fe returns to its original state by removal of a proton (Fe-H<sup>+</sup> → Fe + H<sup>+</sup>)

- (a) Sketch the catalytic cycle of hydrogen activation, given the most recent example, shown in the Figure at right (Hiromoto, T., Ataka, K., Pilak, O., Vogt, S., Stagni, M. S., Meyer-Klaucke, W., Warkentin, E., Thauer, R. K., Shima, S. and Ermler, U. *FEBS Lett.* 2009, 583, 585– 590). Note that the "?" may be assumed, for the present exam, to be an innocent 2-electron donor and "Sol" is likely a water.



- (b) What factors are necessary to take a first-row transition metal, like Fe(II), and make it useful in hydrogen activation. Specifically, compare and contrast your mechanism in 3(a) with the one you presented in 1(c)

5. (30 points) It is a bit over 25 years since Kubas and coworkers first reported on the isolation and characterization of a stable dihydrogen complexes,  $M(\text{CO})_3(\text{PR}_3)_2(\eta^2\text{-H}_2)$ ,  $M = \text{Mo}, \text{W}$ ;  $R = \text{isopropyl, cyclohexyl}$  (Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451). One interesting aspect of these and other complexes is that they often bind alkenes well, if there is room, or C-H bonds (agnostic). Explain how  $\text{H}_2$  binds to a metal using a molecular orbital discussion. Also, explain how  $\text{H}_2$  and ethylene ligands may be similar or different from each other.