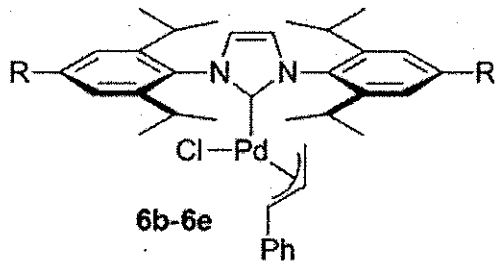
INORGANIC CHEMISTRY CUME
October, 2011
Donald Wink

1. (40 points). On Thursday, September 29 the department received a visit from Pat Holland from the University of Rochester. Prof. Holland presented information on di-iron compounds that he is developing as an enzyme model.
(a-5 points) What is the enzyme that he is seeking to model?
(b-20 points) Describe his strategy for modeling the enzyme. Include the nature of the ligand(s) he is using to create an environment for this model. Also, indicate a reaction that his system can carry out that suggests he is on the way to modeling his target enzyme.
(c-10 points) An important step in his chemistry is the use of KC_8 as a reductant. Explain how you would make this material and why it might be very useful as a source of electrons.
(d-5 points) A key characterization method for Holland's work is Mössbauer spectroscopy. Explain what this method is and how it can give him information on his compounds.

2. (20 points) Holland pointed out that, besides his target enzyme modeling, there are several reasons why iron, cobalt, and nickel should be considered as primary targets for catalysis research. Describe an important reaction of each metal in (a) bioinorganic chemistry and (b) organometallic chemistry. You will need six examples.

3. (20 points). Holland is also active in work in organometallic catalysis. The complexes **6** below (R = H, adamantyl, trityl, etc) were prepared. They are active catalysts for the cross-coupling reaction of chloroarenes with arylboronic acids, with very high turnover numbers (>30,000 turnovers per hour) and extended catalyst stability. It was found that increasing bulk of R leads to faster reactions.



6b-6e

Benjamin R. Dible; Ryan E. Cowley; Patrick L. Holland; *Organometallics* **2011**, 30, 5123-5132.
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Explain how the precatalyst may be an effective cross-coupling catalyst. You do NOT have to explain how the precatalyst is converted into an active catalyst. But you should explain how a catalytic cycle may be enhanced in the rate and the maintenance of catalyst activity with ligands such as **6**.

4. (20 points). Almost 40 years after $[Fe_4S_4](SR)_4^{2-}$ cluster 'cubane] chemistry developed because of the importance of Fe_4S_4 clusters in electron transfer enzymes, Holm and coworkers have shown that if R is a chiral group then the Fe_4S_4 core of the tetrathiolate complexes can be resolved in solution. This is because the twisted cube of the core has a C_2 symmetry. Explain how Fe_4S_4 'cubane' can be chiral, and why a chiral thiolate may be able to resolve the core.