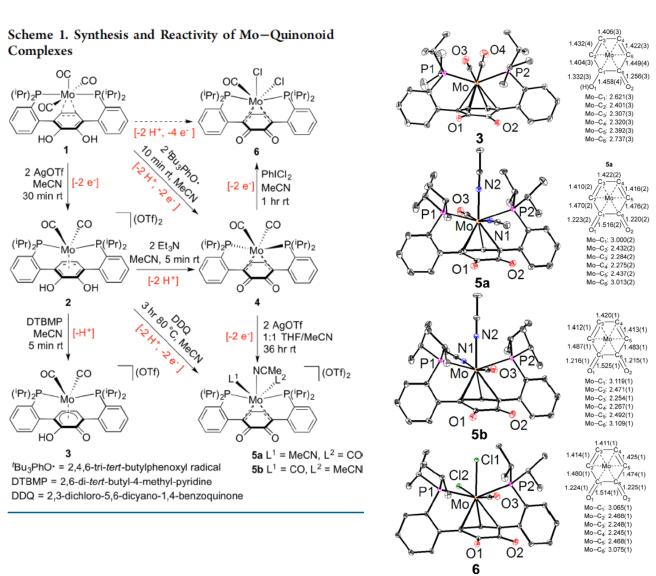Chemistry 462, Fall term, 2017. Project 2. For discussion September 14-19.

The following graphics are lifted from the publication by Agapie and Henthorn, Inorganic Chem. 55, 2016, pp. 5337 – 5342.

Abstract:

Scheme 1. Synthesis and Reactivity of Mo−Quinonoid Complexes

'Bu$_3$PhO· = 2,4,6-tri-*tert*-butylphenoxyl radical
DTBMP = 2,6-di-*tert*-butyl-4-methyl-pyridine
DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

5a L^1 = MeCN, L^2 = CO
5b L^1 = CO, L^2 = MeCN

a) For each of the complexes shown in the Abstract of the paper give the oxidation state of the Mo and overall electron count of the molecule. Clearly show how you arrive at each donor ligand contribution to the oxidation state and to the electron count.

b) For each of the complexes shown in Scheme I, describe the C-C and C-O distances from x-ray diffraction analysis and account for the authors' conclusions regarding the π-interaction of the arene (i.e., the aromaticity, or lack thereof, of the arene).

c) According to C. Tolman's approach and the Ligand Cone Angle, what are the steric parameters for PPh$_3$, P(i-Pr)$_3$, and PPh$_2$(i-Pr)? (For his original presentation of these ideas, see *Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis* Chadwick A. Tolman *Chem. Rev.*, 1977, 77 (3), pp 313–348. However any of the textbooks or Wikipedia will discuss his approach.)

d) Should one consider the P-Aryl-P ligand used by Agapie as a pincer ligand? Why or why not?

e) Is Agapie's P-Aryl-P ligand redox-active or redox innocent? Comment.

f)   What does PCET stand for? How does this study demonstrate PCET?

g) Under what conditions is CO kicked off Molybdenum? How does this result reflect HSAB? (Hint: Discuss the conversion between **4** and **6**. What is the role of the PhICl$_2$ reagent?)