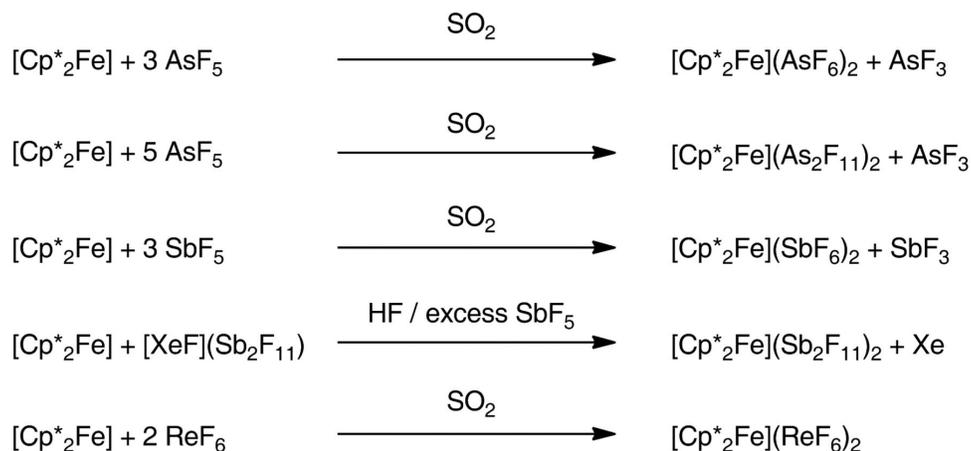


Inorganic Cumulative Exam

Thursday, October 5, 2017

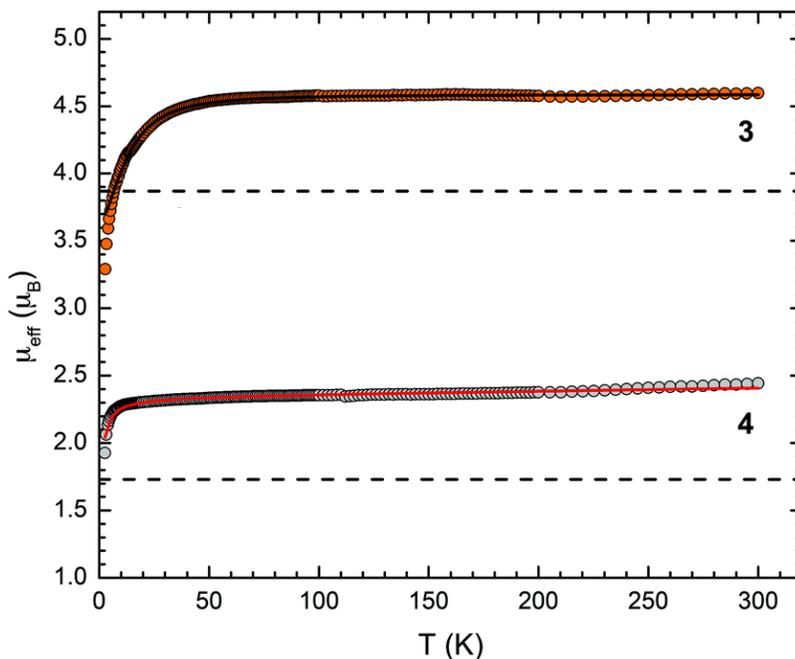
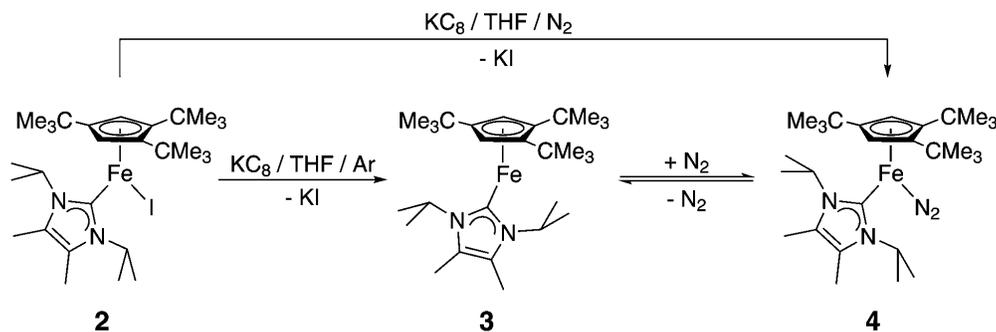
By Neal P. Mankad

1. Ferrocene, FeCp_2 ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$), is one of the most famous of all organometallic molecules. The neutral form FeCp_2 is exceptionally stable and exhibits chemistry reminiscent of organic aromatic compounds. The cationic form, $[\text{FeCp}_2]^+$, is easily isolable and is frequently used as a chemical oxidant. In a recent publication (*Science* **2016**, 353, 678-682), Karsten Meyer and coworkers reported the isolation of dicationic $[\text{FeCp}^*_2]^{2+}$ for the first time ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), from various synthetic routes:

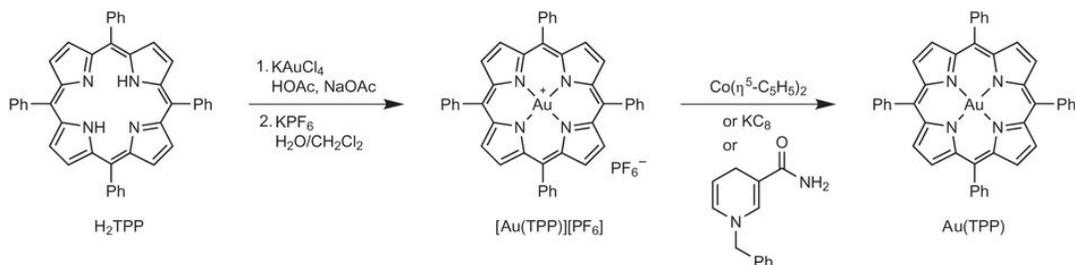


- a. What is the iron oxidation state in $[\text{FeCp}_2]^{2+}$?
- b. What is the iron d-electron count?
- c. Predict the number of unpaired electrons for $[\text{FeCp}_2]^{2+}$.
2. While dinitrogen, N_2 , is one of the most inert compounds on earth, some coordinatively unsaturated metal sites are capable of binding it and activating it for subsequent reaction.
- a. The first coordination complex with an N_2 ligand was discovered by Allen and Senoff (*J. Chem. Soc., Chem. Commun.* **1965**, 24, 621) in 1965. This compound, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, features a terminally bound N_2 ligand with “end-on” binding through a single N atom. What is the total valence electron count of the Ru in this species?
- b. When exposed to vacuum, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ converts to $\{[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-N}_2)\}^{4+}$, which features a bridging N_2 ligand that is bound “end-on” to two Ru centers. For which of these two molecules will the N-N stretching vibration be detectable by IR spectroscopy? Explain your answer.
- c. In biology, N_2 is converted to NH_3 by metalloenzymes called nitrogenases. In industry, the same conversion is accomplished using the Haber-Bosch Process. Which metal(s) are involved in each of these catalytic N_2 reduction systems?
- d. Recently, Walter and coworkers (*Chem. Commun.* **2017**, 53, 7274-7277) reported a 15-electron Fe complex (**3** in the scheme below) capable of reversible N_2 binding to form 17-electron complex **4**. Interestingly, N_2 binding was found to induce a spin state change. Magnetic susceptibility data is given for both complexes below (dotted lines are for

theoretical “spin-only” values). Based on this data, provide either the spin state (i.e. $S = ?$) or the number of unpaired electrons for both **3** and **4**.

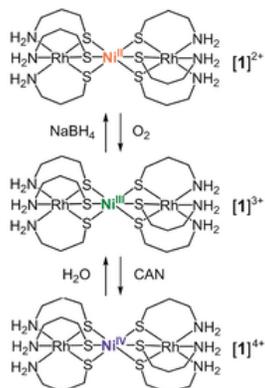


3. Heinze and coworkers (*Nat. Chem.* **2017**, doi: 10.1038/nchem.2836) recently isolated the interesting pair of gold porphyrins shown below. Which of them has an unpaired electron? Do you expect that unpaired electron to be in the $[\text{AuN}_4]$ plane or in a plane orthogonal to the $[\text{AuN}_4]$ core? Explain your answer.



4. Konno and coworkers (*Angew. Chem. Int. Ed.* **2017**, doi: 10.1022/anie.201708169) isolated the triad of trimetallic complexes shown below. Their Ni oxidation state

assignments are given in the scheme. Which of these three Ni centers do you expect to exhibit Jahn-Teller distortion? Explain your answer.



5. Give the catalytic mechanism for alkene hydrogenation (alkene + H₂ → alkane) by Wilkinson's catalyst, RhCl(PPh₃)₃.