

## CM 1111 Tutorial 6

### Question 1

Which of the following compounds, B<sup>t</sup>Bu<sub>3</sub> or BMe<sub>3</sub> (<sup>t</sup>Bu = tertiary butyl group C(CH<sub>3</sub>)<sub>3</sub>), will form a more stable complex with NMe<sub>3</sub>?

Trialkylboron compounds are Lewis acids, whereas amines are Lewis bases. NMe<sub>3</sub> would form a more stable complex with the stronger Lewis acid, which is in this case BMe<sub>3</sub>. B<sup>t</sup>Bu<sub>3</sub> is less Lewis acidic due to the increased positive inductive (i.e. electron-donating) effect of the tertiary butyl group compared to the Me group. Moreover, the <sup>t</sup>Bu group is very bulky leading to overcrowding in the complex B<sup>t</sup>Bu<sub>3</sub>·NMe<sub>3</sub>, which in turn destabilizes the complex.

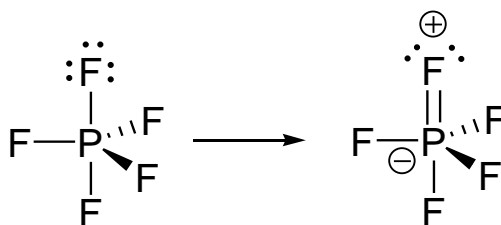
### Question 2

When PF<sub>5</sub> and SbF<sub>5</sub> are mixed, the following reaction occurs. Identify the role of PF<sub>5</sub> and SbF<sub>5</sub> and rank the pnictogene pentafluorides PF<sub>5</sub>, AsF<sub>5</sub>, SbF<sub>5</sub> in order of increasing Lewis acidity. Briefly explain your answer.



In this reaction, PF<sub>5</sub> acts as a fluoride donor and SbF<sub>5</sub> as a Lewis acid, which accepts the fluoride to form the octahedral [SbF<sub>6</sub>]<sup>-</sup> complex anion. Thus, SbF<sub>5</sub> should be a stronger Lewis acid compared to PF<sub>5</sub>. Since As is found in between P and Sb in the Pnictogene group, the following order of increasing Lewis acidity can be estimated: PF<sub>5</sub> < AsF<sub>5</sub> < SbF<sub>5</sub>.

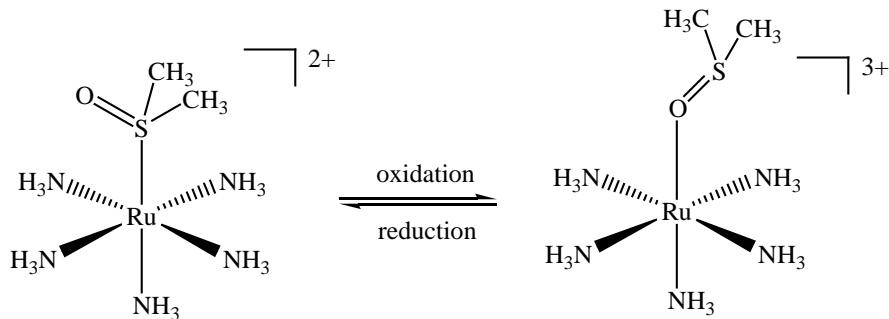
Explanation: A possible explanation may involve π-donation of the fluoride anion to the central atom, which leads to a build-up of partial negative charge at the central atom. This in turn reduces its Lewis acidity. The P and F<sup>-</sup> atom have the smallest difference in size, providing the “best” orbital overlap. As and Sb orbitals may be too large to accept π-donation from the small F<sup>-</sup> anion.



### Question 3

In 1982, Professor Henry Taube at Stanford University reported the following isomerization of a ruthenium complex. The dimethylsulfoxide ligand (O=SMe<sub>2</sub>) can change its donor atom upon one-electron oxidation and one-electron reduction as shown in the figure below. Briefly rationalize this finding.

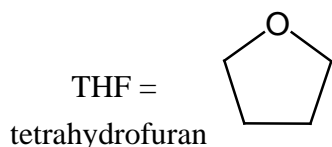
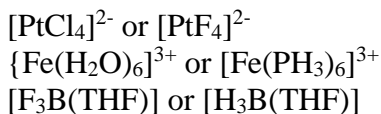
Can you suggest a proper term to describe the behavior of DMSO ligand in analogy to a substance that can act as both an acid and base?



$\text{Ru}^{\text{II}}$  is “softer” than  $\text{Ru}^{\text{III}}$  and prefers to be bound by the “softer” sulfur donor of the DMSO molecule. Upon metal-centered 1-electron oxidation, the metal center changes to  $\text{Ru}^{\text{III}}$ . With a higher oxidation state  $\text{Ru}^{\text{III}}$  is “harder” than  $\text{Ru}^{\text{II}}$  and binding of the “harder” oxygen donor in DMSO becomes preferable. This process is reversible, and reduction of the  $\text{Ru}^{\text{III}}$  to  $\text{Ru}^{\text{II}}$  leads to binding through the softer “sulfur” atom again. The DMSO ligand is ambidentate in this example (although not in use, “amphidentate” in analogy to amphiprotic is already a very good answer).

#### Question 4

Which members of the following pairs would you expect to be more stable?



According to the HSAB concept,  $[\text{PtCl}_4]^{2-}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  are expected to be more stable.  $[\text{H}_3\text{B}(\text{THF})]$  should be more stable due to the inability of H for  $\pi$ -donation (also see Q2).

#### Question 5

In qualitative analysis of inorganic compounds, metal ions are divided into several groups. In Group 2 are  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Sn}^{2+}$  and in Group 3 are  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ . One way to distinguish the two groups of ions is to bubble  $\text{H}_2\text{S}$  gas into solutions containing the ions. The Group 2 ions will form precipitates in acidic condition while the Group 3 will not. On the other hand, the Group 3 ions will form precipitates in basic solutions. Explain the different behaviors of the Groups 2 and 3 ions.

Group 2 cations are softer than those in Group 3. Thus, they will form more stable compounds with the soft  $\text{S}^{2-}$  anion with solubility products of the respective sulfides

much smaller than those of Group 3. In acidic media,  $S^{2-}$  concentration is smaller than in basic media, but sufficient for the sulfides of Group 2 cations to precipitate. Group 3 cations remain in solution probably as aqua species. Upon increasing the pH value, the  $S^{2-}$  concentration increases (from deprotonation of  $H_2S$ ) leading to the precipitation of Group 3 sulfides (or hydroxides) as well.