

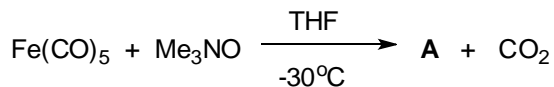
**Organometallic Chemistry**

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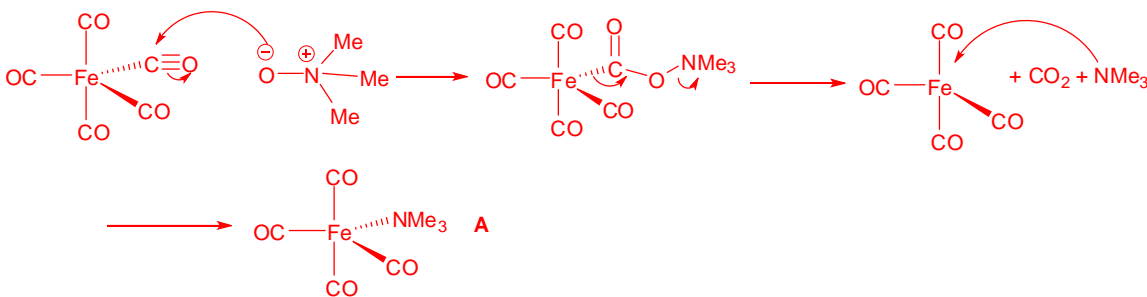
**Problem Set #3**

Due: Oct. 2, 2008

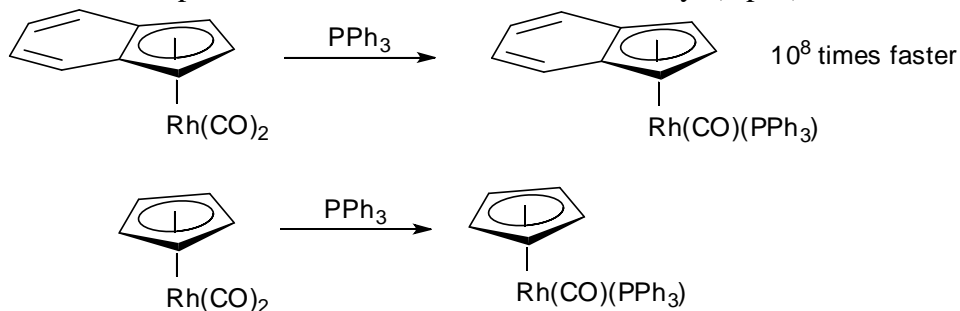
1. Identify **A** and propose a mechanism for its formation. (4 pts.)



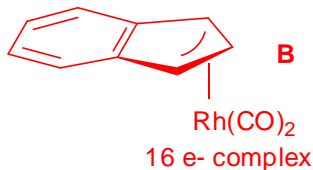
Data for compound **A**:  
 $m/z (M^+) = 227$   
 IR ( $\text{cm}^{-1}$ ): 2050, 1960, 1940-1920  
 $^1\text{H NMR} (\delta)$ : 1.87 (s)  
 $^{13}\text{C NMR} (\delta)$ : 217.5, 61.4



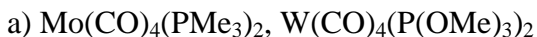
2.  $(\eta^5\text{-Cp})\text{Rh}(\text{CO})_2$  and  $(\eta^5\text{-indenyl})\text{Rh}(\text{CO})_2$  undergo substitution by an associative pathway. The rate for the indenyl complex is  $\sim 10^8$  times greater than for the Cp complex. Provide an explanation for this difference in reactivity. (4 pts.)



The  $\eta^5\text{-indenyl}$  derivative can undergo ring slippage to form the coordinatively unsaturated 16 electron  $\eta^3\text{-indenyl}$  complex **B** (below), thereby facilitating associative substitution of  $\text{PPh}_3$ . In the process, the indenyl ring retains the stable, aromatic benzene portion of the structure in conjugation with the  $\eta^3\text{-allylic}$  ligand. The  $\eta^5\text{-Cp}$  derivative, on the other hand, can undergo ring slippage to  $\eta^3\text{-Cp}$ , but it will result in the loss of stable aromatic character.



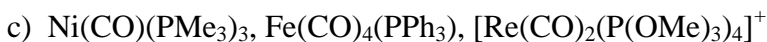
3. Which of the following complexes will have the *highest*  $\nu_{\text{CO}}$  stretching frequency in the IR? Why? (3 pts. each)



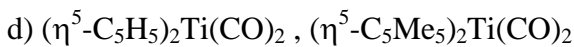
W will be more electron deficient because the  $\text{P}(\text{OMe})_3$  ligands are better  $\pi$  acids than  $\text{PMe}_3$ . With less electron density, the W will have weaker backbonding with the CO ligands, so the CO bonds will be stronger and their stretch will be higher.



Both Cr and Mn will be  $d^6$ , but Mn will be more electronegative since it is in the +1 oxidation state. Since the Mn will be more electronegative, it will be less inclined to donate electron density to the CO's, reducing backbonding, increasing the CO bond strength and the CO stretching frequency.



The Ni will be the most electron rich with three strong sigma donor phosphines like  $\text{PMe}_3$  and only one CO group; consequently it will have a substantial amount of backbonding to the one CO ligand thereby lowering the CO stretching frequency. The Fe complex will also be moderately rich being with  $\text{PPh}_3$  ligands. However, the Re is in a +1 oxidation state and is a  $d^6$  metal with four strong  $\pi$  acid phosphine ligands and two CO's. Therefore it will likely have the highest CO stretching frequency because the Re will have the least amount of electron density to donate to backbonding with the CO's.



The pentamethylcyclopentadiene is more electron rich than just Cp and adds even more electron density to the Ti leading to a greater back-bonding donation to the CO. Greater backbonding causes a reduction in the bond order of the C-O bond which is detected by a lower energy IR stretch.