

### 5.13 Drill Problems for 9/17/03-9/24/03

*Disclaimer: I apologize for the fact that some of my problems contain metals; I just couldn't resist. However, these problems are supposed to enrich your ever-growing knowledge of chemistry, so that's my excuse. --NM*

#### IR Spectroscopy

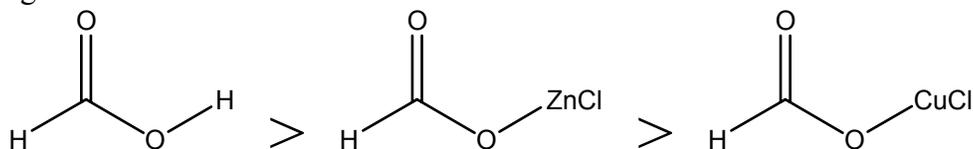
Order the following from highest to lowest frequency ( $\text{cm}^{-1}$ ) with the respect to the indicated vibration.

1. C=C stretch in a) 1-butene, b) 2-butene
2. CO stretch in a) methanol, b) carbon monoxide, c) formaldehyde
3. X-Cl stretch: a) C-Cl, b) Fe-Cl
4. C-H stretch in a)  $\text{C}_2\text{H}_6$ , b)  $\text{C}_2\text{H}_4$ , c)  $\text{C}_2\text{H}_2$

#### $^{13}\text{C}$ NMR

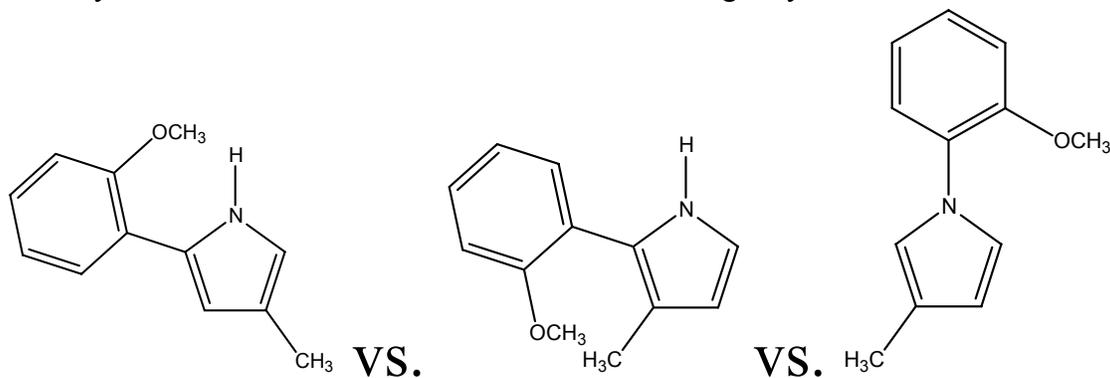
NMR data can give insight into the distribution of electron density in a molecule.

1. Rank the following according to your expectation of increasing  $^{13}\text{C}$  chemical shift (ppm):  
a) MeLi, b) MeMgBr, c)  $\text{Me}_3\text{Al}$
2. Based solely on the following trend in  $^{13}\text{C}$  chemical shift in ppm (which may or may not be true), rank H, Zn(II), and Cu(II) in order of increasing ability to stabilize a positive charge:



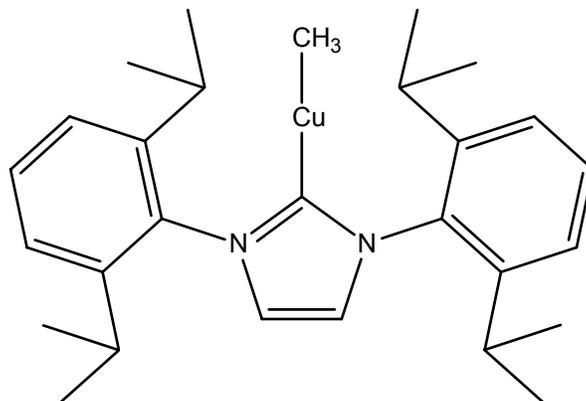
#### $^1\text{H}$ NMR

The following regioisomers are indistinguishable by elemental analysis and mass spectrometry. How would you tell the difference between each of them using only  $^1\text{H}$  NMR?



### Misc. NMR questions

Transition metal complexes of Arduengo carbenes are becoming increasingly important in organometallic catalysis. Consider the following Arduengo carbene copper complex:



1. The  $^1\text{H}$  NMR resonance for the copper-bound methyl group comes in at  $-0.491$  ppm. In general, most alkyl resonances fall between 0 and 3 ppm. Qualitatively, why does this unusual methyl group exhibit a resonance with a chemical shift less than 0 ppm?
2. The  $^1\text{H}$  NMR resonances for the isopropyl groups are as follows: 1.11 ppm (doublet, 12H), 1.45 ppm (doublet, 12H), and 2.69 ppm (septet, 4H). Normally, the methyl groups in an isopropyl group are chemically equivalent, and so one only observes two resonances attributable to the isopropyl group. Why, in this case, are there three distinct isopropyl resonances? (I.e., why are all three carbons in each of the isopropyl groups chemically inequivalent from each other?)
3. Represent the above molecule as  $\text{LCuCH}_3$ , and pretend that NMR is your only tool of characterization. Using  $^1\text{H}$  and  $^{13}\text{C}$  NMR, the above structure would be indistinguishable from the ion-paired structure  $[\text{L}_2\text{Cu}]^+[\text{Cu}(\text{CH}_3)_2]^-$ . If  $^{63}\text{Cu}$  NMR were a viable method, how could you tell the difference between the ion-paired  $[\text{L}_2\text{Cu}]^+[\text{Cu}(\text{CH}_3)_2]^-$  structure and the covalent  $\text{LCuCH}_3$  structure shown above?