

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

### IR Spectroscopy

1. [**a** > **b**] because the difference in mass across the C=C double bond is greater in a than in b.
2. [**b** > **c** > **a**] because a CO triple bond is stronger than a CO double bond, which is stronger than a CO single bond, and the difference in mass ratios is negligible. In other words, the spring constant is bigger – the spring is tighter!
3. [**a** > **b**] because Fe is much heavier than C. Put something really heavy on one end of a spring – it then bounces back and forth much more slowly!
4. [**a** > **b** > **c**] because a C(sp<sup>3</sup>)-H bond is stronger than a C(sp<sup>2</sup>)-H bond, which is stronger than a C(sp)-H bond. Greater p-character puts electrons further away from the carbon nuclei, giving the C-H bonds more covalent character (and thus strength).

### <sup>13</sup>C NMR

1. [**a** < **b** < **c**] because chemical shift goes down with increasing electron density (shielding). Li is best at stabilizing a positive charge, so the Li-C bond is the most polarized of the three. In other words, of the three molecules, MeLi puts the biggest partial negative charge on carbon, and thus its carbon atom is the most shielded. Mg is a little worse at stabilizing positive charge, so the carbon atom in MeMgBr has a slightly smaller partial negative charge than in MeLi and is slightly less shielded, and so on.
2. The most electron-rich carbonyl carbon will correspond to the most “anion-like” formate group, and thus the most cationic metal. (For simplicity I’m calling H a metal, too.) Increasing electron density corresponds to decreasing chemical shift (ppm), so the trend in stabilizing cations follows: **Cu(II)** > **Zn(I)** > **H**.

### <sup>1</sup>H NMR

The *N*-arylpyrrole (the third isomer) is easily distinguishable from the first two isomers because it would lack the characteristic broadened singlet resulting from an N-H proton. The first two are easy to tell apart because they have drastically different symmetry with respect to the pyrrole ring. The pyrrole resonances for 2-aryl-4-methylpyrrole (the first isomer) would be two sharp singlets, while the pyrrole resonances for 2-aryl-3-methylpyrrole (the second isomer) would be a doublet and a triplet.

### Misc. NMR

1. We’re used to thinking about things like C-C bonds, which are not very polar and have electron density well spread-out over both atoms. Metals, such as the Cu atom in this case, are electropositive and thus repel electron density. This effectively puts a partial negative charge on the methyl carbon atom. In fact, the carbon atom, and therefore its protons, are so incredibly electron-rich that their NMR resonances come in below 0 ppm.
2. There is so much steric bulk bumping into each other here, that there are many restricted rotations to think about. First of all, each of the N-C(aryl) bonds is restricted, so the diisopropylphenyl groups are stuck in the plane perpendicular to the page. Furthermore, each of the C(phenyl)-C(isopropyl) bonds are restricted as well – there’s that much steric bulk here! That means that, for a given isopropyl group, one of the methyl groups is

stuck pointing towards the copper atom, while the other is forever destined to be pointing away. That makes them chemically distinct, and thus we see separate  $^1\text{H}$  NMR signals.

3. The covalent  $\text{LCuCH}_3$  complex would show only one  $^{63}\text{Cu}$  resonance (only one “type” of copper atom), while the ion-paired  $[\text{L}_2\text{Cu}]^+[\text{Cu}(\text{CH}_3)_3]^-$  complex would show two  $^{63}\text{Cu}$  resonances (two “types” of copper atoms).