**Determining transition metal oxidation states: Recognizing bond metal-ligand types**

**Introduction**:

This in-class assignment is designed to help you determine the bonding interaction between the metal and the ligand in transition metal complexes and use them to calculate the formal oxidation state of the metal.

There are two principle bonding interactions that you must recognize: (1) Lewis acid/base interactions (dative bonds) and (2) σ-bonding interactions.

In most of the examples shown in this exercise the metal will be more electropositive than the ligand, thus upon heterolytic cleavage of the ligand-metal bond, the pair of electrons will be on the ligand.

Once the ligand has been removed from the metal, calculate the formal charge (FC) for the ligand that was bonded to the metal

* + **FC=# Valence electrons - 1/2 # bonding electrons – # non-bonding electrons  
     or   
    FC = Valence electrons - # lines - #dots**
  + If the ligand is neutral with the pair of electrons, there is no net oxidation of the metal.
  + If the ligand receives a negative charge, the metal is oxidized by +1.

Example:



**Figure 1.** Schematic showing removal of ligands from metal and resultant effect on the oxidation state based on its charge

π-Interactions are common for organometallic complexes and because multiple atoms are associated with the bonding, the number of interactions (ηn­­; η = eta) need to be specified. These are “side-on” interactions between the metal d-orbitals and the π-orbitals of the ligand

lewis ethylene.tif pi backbonding.tif

**Figure 2.** Orbital description of metal d−π-orbital interactions in “eta” bonding. For example, the side-on interaction of a double bond with a metal is called an η2­-interaction because the two adjacent carbons are both involved in bonding to the metal. If the ligand does not have a charge, it does not contribute to the oxidation state of the metal.



**Figure 3.** η2-bonding interaction of ethylene and transition metal (no net oxidation)

Arenes and other aromatic species can also participate in eta-bonding. The same rules apply for determining their effect on oxidation states.

Lastly, one must consider the formal charge of the metal when ligands are present in the outer coordination sphere. It may be easier for you to consider these complexes as “inorganic salts” wherein the outer sphere ion balances the charge of the metal complex. A negative outer sphere anion balances the positive charge of the metal and vice versa. A negatively charged counter ion will cause a net oxidation of the metal (+1), while a cationic counter ion will cause a net reduction (-1). This becomes important in overall d-electron count which we will see later.

Below is an example of the negatively charged PF6- molecule acting as a cation for cobaltocenium hexafluorophosphate. Because PF6- and thetwo cyclopentadienyl ligands (C5H5-) are negatively charged, the metal must counter all three charges. Summation of the charges provides the oxidation state of +3 for the metal.



**Assignment:**

Calculate the oxidation state for the metals in the following examples. Begin by breaking the metal ligand bond then assigning the net charge of the ligand.

















8)



9)



10)

