(Spectro)electrochemistry of Organometallic Complexes, Uncovering The Non-Innocence of Ferrocene-Based Ligands

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Several metalloenzymes contain hetero- and homo-bi(poly)metallic clusters in their active sites, which in turn inspires bi(poly)metallic catalysts. The burden of creating homo- and heterobimetallic complexes is facilitated by using ferrocenyl based ligands with the form Fe(C₅H₄-E)₂ where E = donor atom, such as R₂P- or S-. Ferrocenyl based ligands are unique among the vast number of ligands because they can enhance catalysis through cooperative affects and/or flexible binding modes.[1] This property can be beneficial in advancing complexes in “unusual” oxidation states containing unpaired electrons. We have reported several cases of ferrocene based phosphine ligand that behave non-innocently,[2] where an electron-hole on a metal center was stabilized by distributing charge over metal and ligand metal site. Using several spectroscopic and physical techniques including cyclic voltammetry (CV), EPR, UV-Vis, and IR, as well hybrid spectroelectrochemical (SEC) techniques, we were able to demonstrate this unique property of ferrocenyl based ligands.

We have extended the use of SEC towards understanding several metal carbonyl complexes, including Fe,[3] Mn,[4] and Nj[5] carbonyl moieties,[5] and a diiron system.[6] Important to many of our studies is the use of low-temperature SEC. Through these techniques we can determine electrochemical mechanism especially ligand rearrangement and changes in coordination geometry.

Figure 1. Oxidation induced metal-metal interaction