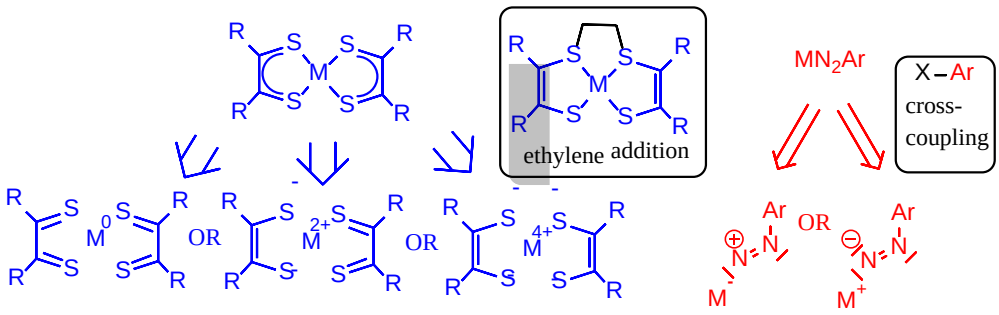
Ligand Non-Innocence in Dithiolenes and Arylazo Ligands:

From Sulfur-Carbon Bond Formation to C-C Coupling

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The oxidation state of the metal in a complex is normally easily determined using just its composition as input, based on the assumption that the charge on each ligand can be straightforwardly assigned. However, the number of exceptions, complexes where the ligand is redox-active (non-innocent), is growing. We have been studying complexes with redox-active ligands for many years. While spectroscopy of such systems is important (and while some spectroscopic results will be discussed), we focus on reactivity. How is redox non-innocence involved in bond-forming reactions? This question is particularly relevant for many sulfur compounds. Sulfur-carbon and sulfur-phosphorus bond-forming reactions at dithiolenes will be discussed. More recently, we began to study potentially non-innocent nitrogen ligands as well, in particular arylazo compounds. The usefulness of arylazo compounds in metal-catalyzed cross-coupling reactions makes the study of their redox-active behavior in the coordination sphere of a metal particularly worthwhile. First results on the aryldiazonium-Pd(II)/aryldiazenido-Pd(IV) system will be discussed.