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**Redox-Active Ligands: What Are They? How Do They Work? and How Might They Be Improved**

**The Development of a Highly Active Manganese Hydrosilylation Catalyst**

**Hydrosilylation and Beyond: Expanding the Scope of Redox-Active Ligand Assisted Catalysts**

Although redox-active ligands have played an important role in first-row transition metal catalyst development, their utility has overwhelmingly depended on steric bulk incorporation. In contrast, efforts in our laboratory have focused on the preparation and application of non-innocent ligands that are capable of binding to a metal center beyond their historically investigated redox-active core. While steric bulk and coordinating substituents both serve to prevent catalyst deactivation, the latter approach can enable bifunctional catalytic pathways, prevent ligand dissociation by way of the chelate-effect, and provide a handle for tuning the electronic properties of the metal. These advantages have allowed for the development of a low-valent Mn complex that is capable of mediating the efficient hydrosilylation of ketones and esters with turnover frequencies of up to 15,000 h-1. Furthermore, this approach has enabled the isolation of Fe, Co, and Ni complexes that are active catalysts for the reduction of ketones and alkynes. The electronic structure investigation of each precatalyst will be discussed, in addition to how this synthetic methodology might allow for future catalyst development.