

## **Chapter 1**

### GENERAL INTRODUCTION

## INTRODUCTION

This dissertation focuses on the study of multifunctional and non-innocent ligands in the context of small molecule activation in a variety of mono- and multinuclear complexes. This general concept was explored in two distinct types of systems: 1) multiple diphosphine ligands containing non-innocent central arene, 1,4-hydroquinone, or pyridine-based moieties poised to interact with supported transition metals, and 2) the incorporation of hydrogen bonding moieties into the secondary coordination sphere of site-differentiated  $[\text{Fe}_4(\mu_4\text{-O})]$ -type clusters as a way to stabilize terminal oxido ligands in multinuclear complexes. In recent decades the use of redox or acid / base non-innocent ligands as well as secondary coordination sphere hydrogen bonding networks to promote novel reactivity, facilitate catalysis, or stabilize otherwise reactive intermediates has grown into an area of substantial research effort. However, the development of ligand scaffolds capable of storing / delivering both protons and electrons to small molecule substrates in transition metal-mediated processes and the study of hydrogen bonding networks in multinuclear complexes are comparatively less so. The work reported herein seeks to address these two concepts with appropriate background and references incorporated into each individual chapter. This chapter aims to discuss the interest in these avenues of research in more general terms and describe the motivations and development of each of the related projects.

For the purposes of this dissertation multiple classes of ligand non-innocence can be defined. The term redox non-innocence will be used to describe systems in which the ligand serves as an electron reservoir. These systems typically have low-lying unpopulated ligand-based orbitals that are more easily reduced than the coordinated metal center. From the discovery of the redox non-innocence 1,2-dithiolene ligands by

Eisenberg and Gray in the 1960s to more recent examples such as bis(imino)pyridine ligands studied extensively by Weighart and Chirik as well as others (Bart, Berben), the use of redox non-innocence has resulted in the ability to mediate a range of challenging chemical transformations, including some more commonly associated with noble metal catalysis, in Earth-abundant first-row transition metals. Work from the Heyduk group has also applied this strategy to achieve a variety of redox transformations at formally  $d^0$  metal centers by taking advantage of redox-active aminophenolate ligand scaffolds.

A second class of non-innocent ligand can be described as acid / base non-innocent whereby the ligand is capable of facilitating the transfer of protons or other electrophiles by serving as a local Lewis basic or acidic site. Inspiration for these systems can be partially attributed to enzymatic systems such as [FeFe]-hydrogenase which takes advantage of an aza dithiolate ligand to facilitate dihydrogen evolution or oxidation by serving as a base during catalysis. A recent example of this type of strategy are the PNN pincers reported by Milstein, which utilize the reversible deprotonation of a benzylic position in the ligand framework to mediate chemical transformation. Work by Mayer and Savéant has demonstrated electrocatalytic systems can take advantage of pendant protic or basic functionalities that alter the product selectivity in dioxygen and carbon dioxide reduction in porphyrin-based systems.

Conceptually, these systems are related to ligand scaffolds which utilize secondary coordination sphere tuning with hydrogen bond donating or accepting moieties to stabilize reactive species. The Borovik group has employed a variety of mono- and multinucleating scaffolds employing hydrogen bonding networks to isolate and study a variety of high-valent metal centers coordinated to terminal oxygenic fragments to spectroscopically characterize and study their reactivity. More recently, others such as

the Fout and Szymczak group have also begun to incorporate hydrogen bonding functionalities into novel ligand scaffolds as well. While most effort has focused on monometallic systems, examples of dinuclear complexes featuring hydrogen bond networks have also been reported to a much lesser extent. These ligands do not facilitate or mediate proton transfer to or from metal-bound species; however, they provide a unique secondary coordination sphere environment whose influence on small molecule reactivity can be studied in its own right.

Finally, there is one last class of non-innocent ligands that can be defined as both redox and acid / base non-innocent, meaning they are capable of storing and delivering both electrons and electrophiles during metal-mediated small molecule activation. Systems capable of this are considerably less common though not unprecedented. Again, Nature can serve as a source of inspiration with NAD<sup>+</sup> whose core pyridinium moiety is capable of serving as an organic hydride acceptor, formally two electrons and a proton. This concept has been recently applied and reviewed by the Colbran group. Another notable example comes from the Heyduk group in the reduction of dioxygen using an amine bis(phenolate) supported Zr complex. Our own group has recently published the use of  $\pi$ -bound Mo-catechol complexes demonstrating the capacity to transfer a variety of electrophiles and electrons to dioxygen. With the reduction of many small molecules including carbon dioxide, dioxygen, and dinitrogen requiring the input of multiple protons and electrons, the exploration of ligand scaffolds capable of facilitating the transfer of multiple electron and electrophile equivalents could serve as a strategy to achieve these challenging reductions and impart selectivity on the types of products produced. Overall, the interest in multifunctional and non-innocent ligands stems from the desire to develop novel strategies to accomplish challenging chemical

transformations. By emphasizing metal-ligand cooperativity, the reactivity observed by these complexes can often be described as greater than the sum of its parts as individually neither component can accomplish the targeted chemical behavior.

Building off the initial reports of non-innocent *para*-terphenyl diphosphine ligands in our group, efforts turned to rationally incorporating multifunctional moieties into both mono- and multinuclear complexes. While a variety of hetero- and homometallic tri- and dinuclear complexes were synthesized (Chapter 2), with evidence for central arene redox non-innocence arising from strong metal-arene interactions that were observed in dinuclear  $\text{Co}_2$  and  $\text{Fe}_2$  complexes (Chapter 2). Efforts to rationally incorporate non-innocent aromatic linkers were then expanded to two new ligand scaffolds: a *para*-terphenyl diphosphine containing a 1,4-hydroquinone fragment as the central arene moiety (Chapter 3), and a 3,5-substituted pyridine diphosphine ligand (Chapter 4). Metal complexes supported by both ligand scaffold showed differing small molecule with the hydroquinone system being capable of rapidly delivering reducing equivalents to substrates, while the pyridine diphosphine system could efficiently add B-H, Si-H, and hydride equivalents into the ligand scaffolds. Most recently, efforts to incorporate hydrogen bonding networks into the secondary coordination sphere of  $[\text{Fe}_4(\mu_4\text{-O})]$ -type complexes have also been attempted (Chapter 5). Overall, this body of work aims to expand the range of ligand scaffolds capable of reversibly storing both protons and electrons during small molecule activation and gain insight into how hydrogen bonding network play into reactivity in multinuclear clusters.