

Chapter 8. [Mo(CO)₄(N-N)] Laboratory Conclusions and Future Work

A series of [Mo(CO)₄(N-N)] complexes have been synthesized and characterized, where N-N = bidentate nitrogen donor ligand. This area of chemistry has not been widely investigated. Therefore, many of these complexes are new, including [Mo(CO)₄(4,4'-Me₂-bpy)], [Mo(CO)₄(4,7-Me₂-1,10-phen)], [Mo(CO)₄(4,7-Ph₂-1,10-phen)], [Mo(CO)₄(2,9-Me₂-4,7-Ph₂-1,10-phen)], and [Mo(CO)₄(TMEDA)]. For the [Mo(CO)₄(N-N)] complexes listed above, [Mo(CO)₄(5-nitro-1,10-phen)], and [Mo(CO)₄(5-Cl-1,10-phen)], this work represents the first report of electrochemical characterization.

Successful syntheses were achieved via both thermal and photolytic synthetic routes. Good product yields have been obtained with both synthetic methods, in short reaction times (one hour). Two exceptions are [Mo(CO)₄(5-chloro-1,10-phen)] and [Mo(CO)₄(5-nitro-1,10-phen)], which are difficult to synthesize via the thermal method.

Cyclic voltammograms for the [Mo(CO)₄(N-N)] systems were assigned to irreversible metal based oxidations and reversible ligand based reductions. As the electron withdrawing character of the N-N ligand increased, the Mo^{0/+} oxidation shifted to more positive potential (harder to oxidize), and the N-N^{0/-} reduction also shifted to more positive potential (easier to reduce). As the electron withdrawing character of the N-N ligand decreased, the affect on the Mo^{0/+} oxidation of ligand substitution was much less pronounced, while the N-N^{0/-} reduction shifted more dramatically to negative potential.

The [Mo(CO)₄(N-N)] complexes were characterized by electronic absorption spectroscopy. Electronic absorption data for the series of [Mo(CO)₄(N-N)] systems with bpy and phen ligands have been assigned to $\pi \rightarrow \pi^*$ ligand localized transitions in the ultraviolet region. The lowest energy transition in the visible region is the Mo (d π) \rightarrow N-

N (π^*) metal-to-ligand charge transfer. As anticipated, this MLCT shifted to lower energy as the π^* energy on the N-N ligand was lowered.

This work may be expanded, by building upon the series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems investigated. Adding additional $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems would provide further information for comparison within the series. $[\text{Mo}(\text{CO})_4(\text{N-N})]$ complexes have been shown to have solvent dependence for the lowest lying transition of the electronic absorption spectra. As several new N-N systems have been synthesized, it may prove valuable to perform electronic absorption spectral solvent dependence studies for the entire series of $[\text{Mo}(\text{CO})_4(\text{N-N})]$ systems to more fully understand the nature of this solvent dependence.