Chapter 5. $[Mo(CO)_4(N\text{-}N)]$ Laboratory Introduction

Statement of Problem.

As computational chemistry techniques are becoming widely used in the chemical sciences, it is vital that students have exposure to this technology at the undergraduate level. Synthesis and characterization techniques, however, must remain the mainstay of the laboratory curriculum. The focus of the following chapters of this thesis is the development of the synthesis and characterization, which is incorporated with molecular modeling, to form the integrated experiment. A series of $[Mo(CO)_4(N\text{-}N)]$ complexes, where N-N = bidentate nitrogen donor ligand, were chosen for this research because they generally respond well to computational methods, they are amenable to various physical measurements that can be compared to computational findings, and these properties can be modulated by changing the N-N ligand. The complexes were characterized by electronic absorption spectroscopy, cyclic voltammetry, and ^1H NMR spectroscopy; many of them are new.

Review of the Related Literature.

Molybdenum Carbonyl Complexes.

The properties of d^6 metal carbonyl complexes have been thoroughly elucidated within the last thirty years.[71] In particular, the photochemical and thermal reactions of these complexes have been of interest. The d^6 Cr(0), Mo(0), and W(0) complexes are often studied together. Although similar in electronic structure, with the exception of complexes with π-acid ligands, the characteristics of chromium complexes are quite different from those of molybdenum and tungsten.[71] The Cr(0) carbonyl complexes, however, are the most widely investigated.

The area of research most fundamental to this work is the synthesis and characterization of d^6 $[Mo(CO)_4(N\text{-}N)]$ complexes. Unlike other d^6 metal carbonyl complexes, the chemistry of the N-N complexes has been sparsely investigated. Work on

these complexes began with the thermal synthesis of $[Mo(CO)_4(N\text{-}N)]$, where N-N = bpy (or similar N-N), and subsequent investigations into their crystal structures.[72-75] These complexes were synthesized by reacting $[Mo(CO)_6]$ with excess N-N ligand in deoxygenated toluene at reflux. Reaction times for the thermal synthesis of $[Mo(CO)_4(N\text{-}N)]$ complexes vary between 1.5 to 2 hours.

$$[Mo(CO)_6] + N\text{-}N \xrightarrow[\text{toluene}]{\Delta} [Mo(CO)_4(N\text{-}N)] + 2\ CO \qquad (1)$$

Additional thermal syntheses of $[Mo(CO)_4(N\text{-}N)]$ systems are noted in refs 73-75.

Recently, most $[Mo(CO)_4(N\text{-}N)]$ complexes are prepared photochemically (equation 2) rather than thermally (equation 1).[76-86] $[Mo(CO)_4(N\text{-}N)]$ systems are prepared by photolysis of $[Mo(CO)_6]$ with excess N-N ligand in deoxygenated solvent (equation 2).[80] Required photolysis times range from between 30 to 60 minutes, and varies depending on the N-N ligand used.

$$[Mo(CO)_6] + N\text{-}N \xrightarrow{h\nu} [Mo(CO)_4(N\text{-}N)] + 2\ CO \qquad (2)$$

Photochemical substitution is effective for the formation of $[M(CO)_4(diimine)]$ complexes, where M = Cr, Mo, or W, including those shown in Table 5.1. In most cases, these complexes have been characterized by electronic absorption spectroscopy and X-ray crystallography; characterization by infrared and NMR spectroscopy is also present in the literature.

Table 5.1. Select $[Mo(CO)_4(N\text{-}N)]$ Complexes Previously Synthesized and Investigated via Thermal and/or Photolytic Synthesis.

N-N Ligand	
1,10-phenanthroline[a,b]	
4-methyl-1,10-phenanthroline[a]	
5-methyl-1,10-phenanthroline[a]	
5-phenyl-1,10-phenanthroline[a]	
5-chloro-1,10-phenanthroline[a]	
5-nitro-1,10-phenanthroline[a]	
2,2'-bipyridine[a]	
4,4'-diphenyl- 2,2'-bipyridine[a]	
1,4-di-tert-butyl-1,4-diazabutadiene[a,c]	(1,4-dab)
4,5-diazafluorene[b]	(daf)
1,8-diazabiphenylene[b]	
2,2'-dipyridylamine[d]	
ethylenediamine[e]	

a. reference 144
b. reference 82
c. reference 145
d. reference 95
e. reference 74

The mechanism of photochemical substitution of $[Mo(CO)_6]$ is stepwise.[75,82] Electronic absorption spectral evidence showed that upon photolysis, a $[Mo(CO)_5(N\text{-}N)]$ intermediate is formed (equation 3). This is followed by a thermal step, the loss of the second CO ligand, and subsequent N-N ring closure with the molybdenum center (equation 4).

$$[Mo(CO)_6] + N\text{-}N \xrightarrow{h\nu} [Mo(CO)_5(N\text{-}N)] + CO \qquad (3)$$

$$[Mo(CO)_5(N\text{-}N)] \xrightarrow{\Delta} [Mo(CO)_4(N\text{-}N)] + CO \qquad (4)$$

The predominant form of characterization for $[Mo(CO)_4(N\text{-}N)]$ complexes is electronic absorption spectroscopy. Absorption and emission spectra for a series of $[Mo(CO)_4(N\text{-}N)]$ complexes as well as the corresponding tungsten systems revealed that the lowest-lying excited state for all of the complexes in the series resulted from metal to ligand charge transfer (MLCT).[87] This MLCT energy is ordered Mo > W > Cr.[87] For N-N in $[Mo(CO)_4(N\text{-}N)]$, the ligand energy level is ordered 1,10-phen > bpy > 5-Me-1,10-phen > 5-Cl-1,10-phen ≈ 5-Br-1,10-phen > 5-nitro-1,10-phen.[87] The lowest energy transition for the $[Mo(CO)_4(N\text{-}N)]$ complexes is assigned as an MLCT transition, and exhibits a large degree of solvent dependence.[77,80,87-89,90] The other charge transfer transitions are assigned to metal-to-carbonyl CT. These exhibit almost no solvent dependence.[80,87]

Table 5.2. Electronic Absorption Spectral Data for $[Mo(CO)_4(N\text{-}N)]$ Complexes, where N-N is a Bidentate Nitrogen Donor Ligand, daf = 4,5-diazafluorene, and dab = 1,4-di-tert-butyl-1,4-diazabutadiene.

Complex	Solvent	Absorption Maxima (nm)
$[Mo(CO)_4(1,10\text{-phen})]$[a]	methanol	336, 395, 460
$[Mo(CO)_4(4,7\text{-}Ph_2\text{-}1,10\text{-phen})]$[b]	benzene	339, 395, 502
$[Mo(CO)_4(5\text{-chloro-}1,10\text{-phen})]$[b]	benzene	344, 395, 502
$[Mo(CO)_4(5\text{-nitro-}1,10\text{-phen})]$[b]	benzene	340, 390, 512
$[Mo(CO)_4(bpy)]$[a]	methanol	350, 392, 460
$[Mo(CO)_4(4,4'\text{-}Ph_2\text{-bpy})]$[b]	benzene	350, 388, 484
$[Mo(CO)_4(4,4'\text{-}Me_2\text{-bpy})]$[b]	benzene	354, 388, 482
$[Mo(CO)_4(1,4\text{-dab})]$[c]	benzene	375, 532
$[Mo(CO)_4(daf)]$[c]	benzene	388, 478

a. reference 80
b. reference 82
c. references 144, 145

Many of the physical properties of $[Mo(CO)_4(N\text{-}N)]$ and related Cr and Ru complexes exhibit interesting correlations.[91-95] The spectroscopic energy gap can be correlated with the electrochemical energy gap for the $[Mo(CO)_4(bpz)]$ system using a free-energy diagram and physical data.[91,93] E_{op} was determined utilizing electronic absorption spectroscopy data and was plotted versus the electrochemically obtained ΔE ($\Delta E = E_{1/2}^{oxd} - E_{1/2}^{red}$).[91] A plot of this data resulted in a linear correlation with a negative slope. The resulting free-energy relationship of the spectroscopic and electrochemical values is shown in equation 5.

$$E_{op} = [\chi_I + nF\Delta E + \Delta\Delta G_s + Q] + \chi_o + \Delta(sol) \qquad (5)$$

In equation 5, $\chi_o + \Delta(sol)$ = total change in solvation free energy, χ_I = inner sphere (vibrational) component, and χ_o = outer sphere (solvent) component.[91] Although the negative slope obtained in the correlation plot was unexpected, the resulting correlation coefficient (0.98) was reasonable.[91] The authors also concluded that the techniques utilized seemed justified, but higher-quality and more extensive data sets were necessary.[91]