Chapter 6. [$Mo(CO)_4$(N-N)] Laboratory Experimental

Materials.

All chemicals were purchased from Aldrich Chemical Co. and were used as received, unless otherwise noted. Acetonitrile was Burdick and Jackson spectrophotometric grade and was purchased from Baxter Scientific. [$Mo(CO)_6$] was used as received from Acros Organics. Tetrabutylammonium hexafluorophosphate used in electrochemical experiments was made by metathesis of tetrabutylammonium bromide and potassium hexafluorophosphate, both purchased from Aldrich Chemical Co. Bu_4NPF_6 was recrystallized several times from ethanol, filtered, dried in a vacuum oven for 5-6 hours, and stored in a vacuum desiccator.

Table 6.1. [$Mo(CO)_4$(N-N)] Complexes Investigated.

[$Mo(CO)_4$(N-N)] Complex
1,10-phen
5-chloro-1,10-phen
5-nitro-1,10-phen
4,7-Me_2-1,10-phen
4,7-Ph_2-1,10-phen
2,9-Me_2-4,7-Ph_2-1,10-phen
bpy
4,4'-Me_2-bpy
DPA
en
TMEDA

Synthetic Methods.

The [$Mo(CO)_4$(N-N)] compounds can be prepared by either a photolytic or a thermal route (Table 6.1).[73,79,95] Two exceptions are the 5-nitro-1,10-phen and 5-Cl-1,10-phen complexes that are difficult to synthesize by the thermal method.

Photolysis.

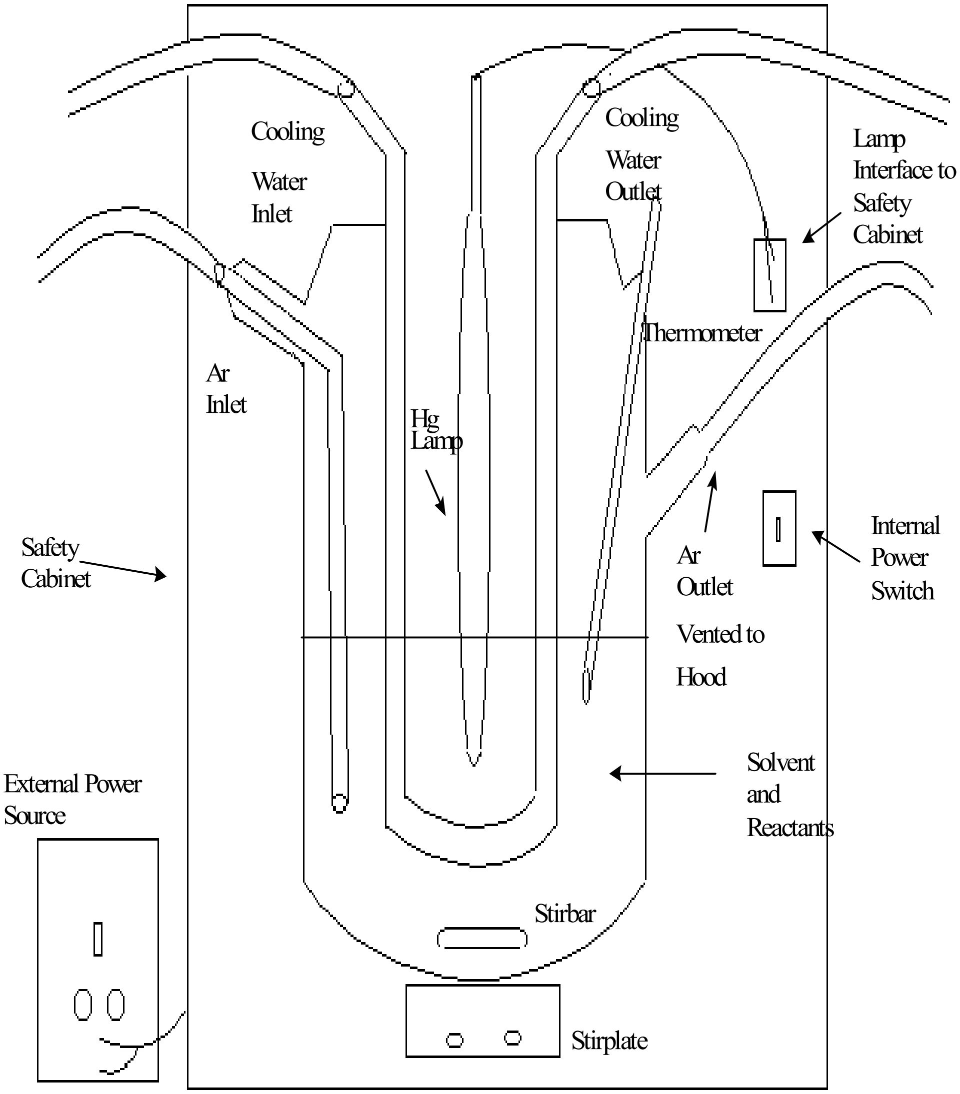
Photolyses were performed in an Ace Glass water-cooled photolysis vessel with a 450 W Hg vapor lamp from Hanovia (Ace Glass Inc.). A schematic for the apparatus is shown in Figure 6.1. The quartz irradiation apparatus was contained in a vented photolysis safety cabinet to shield it from view (Ace Glass). Argon was used for deoxygenation and was vented to a hood prevent ignition of the solvent vapor. Carbon monoxide was liberated during the photolysis and was vented to the hood through the argon gas outlet. Argon flow was maintained after photolysis until the vessel reached room temperature. The lamp was cooled with water to prevent ignition of the residual solvent vapors, both during the photolysis and afterwards, until the system reached room temperature. The Hg vapor lamp must not be handled with bare hands, as hot spots may develop on the bulb from oil or dirt deposits. The bulb was wiped with methanol prior to each use. The reaction solvent was introduced into the container and was deoxygenated by bubbling with argon for 30 minutes. The reagents were then added, and the reaction mixture was stirred with a magnetic stir bar. The cabinet fan was started, the photolysis cabinet was sealed, and the reaction was started by turning the lamp on with the external power supply. In most cases a reaction time of 2 hours was sufficient.

Caution: UV-light should be properly shielded and/or appropriate eye protection should be worn to avoid damage to the eyes. During this experiment, solvent vapors must be properly vented to a fume hood due to the explosion hazards presented and the release of CO.

Synthesis.

[Mo(CO)$_4$(5-nitro-1,10-phenanthroline)]. A photolysis vessel was charged with 5-nitro-1,10-phenanthroline (0.250 g, 1.11 mmol), Mo(CO)$_6$ (0.300 g, 1.13 mmol), and hexanes (30 mL). The slurry was deoxygenated with argon for 30 minutes and photolyzed for 4 hours with stirring and argon bubbling. A burgundy precipitate formed and was collected on a fine glass frit by vacuum filtration. The precipitate was washed with hexanes (4 x 10 mL). Yield: 78%, 0.37 g. ^{1}H NMR (360 MHz) in acetone-d_6 (ppm): 10.13 dd (J = 9.2 Hz, 1.3 Hz), 10.12 dd (J= 8.5 Hz, 1.3 Hz), 9.73 dd (J= 8.8 Hz, 1.3 Hz), 9.67 s, 9.55 dd (J= 8.5 Hz, 1.3 Hz), 8.68 dd (J= 10.3 Hz, 4.9 Hz), 8.65 dd (J= 9.7 Hz, 5.0 Hz). Electronic absorption spectrum in acetonitrile λ_{max} = 520 nm (lowest energy band). Infrared spectrum (KBr pellet, cm^{-1}, CO region): 1827, 1858, 1878, 1911.

Figure 6.1. Apparatus Used in Photochemical Reactions.



[Mo(CO)$_4$(5-chloro-1,10-phenanthroline)]. A photolysis vessel was charged with 5-chloro-1,10-phenanthroline (0.203 g, 0.950 mmol), Mo(CO)$_6$ (0.300 g, 1.13 mmol), and hexanes (30 mL). The slurry was deoxygenated with argon for 30 minutes and photolyzed for 4 hours with stirring and argon bubbling. A dark orange-red precipitate formed, and was collected on a fine glass frit by vacuum filtration, and was washed with hexanes (4 x 10 mL). Yield: 64%, 0.26 g. ^{1}H NMR (360 MHz) in acetone-d$_6$ (ppm): 9.50 dd (J=3.6 Hz), 9.42 d (J= 3.6 Hz), 8.77 d (J= 10.8 Hz), 8.3 d (J= 7.2 Hz), 8.03 s, 7.81 q (J= 10.8, 7.2 Hz), 7.2 q (J= 7.2, 10.8 Hz). Electronic absorption spectrum in acetonitrile λ_{max} = 498 nm (lowest energy band). Infrared spectrum (KBr pellet, cm^{-1}, CO region): 1820, 1859, 1875, 2007.

[Mo(CO)$_4$(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)]. A photolysis vessel was charged with 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (0.358 g, 1.27 mmol), Mo(CO)$_6$ (0.300 g, 1.13 mmol), and hexanes (50 mL). The yellow slurry was deoxygenated with argon for 30 minutes and photolyzed for 18 hours with stirring and argon bubbling. A brown precipitate formed, and was collected on a fine glass frit by vacuum filtration, and was washed with hexanes (4 x 10 mL). Yield: 64%, 0.36 g. ^{1}H NMR (360 MHz) in acetone-d$_6$ (ppm): 7.85 s, 7.52 s, 3.09 s. Electronic absorption spectrum in acetonitrile λ_{max} = 590 nm (lowest energy band). Infrared spectrum (KBr pellet, cm^{-1}, CO region): 1829, 1881, 2000.

[Mo(CO)$_4$(1,10-phenanthroline)]. A photolysis vessel was charged with 1,10-phenanthroline (0.950 g, 5.28 mmol), Mo(CO)$_6$ (1.00 g, 3.79 mmol), and hexanes (100 mL). The yellow slurry was deoxygenated with argon for 30 minutes and photolyzed for 4 hours with stirring and argon bubbling. A bright orange precipitate formed, and was collected on a fine glass frit by vacuum filtration, and was washed with hexanes (4 x 10 mL) and recrystallized from toluene. Yield: 62%, 0.91 g. ^{1}H NMR (200 MHz) in acetone-d$_6$ (ppm): 9.47 d (J= 4.0Hz), 8.43 d (J= 8.0 Hz), 7.97 s, 7.79-7.71 dd (J= 4 Hz).

Electronic absorption spectrum in acetonitrile λ_{max} = 482 nm (lowest energy band). Infrared spectrum (KBr pellet, cm^{-1}, CO region): 2014, 1908, 1890, 1879, 1869, 1868, 1866, 1844, 1830, 1842, 1823, 1807.

[Mo(CO)$_4$(dipyridylamine)]. A photolysis vessel was charged with dipyridylamine (0.780 g, 4.56 mmol), $Mo(CO)_6$ (1.00 g, 3.79 mmol), and hexanes (70 mL). The yellow slurry was deoxygenated with argon for 30 minutes and photolyzed for 4 hours with stirring and argon bubbling. A yellow precipitate formed, and was collected on a fine glass frit by vacuum filtration, and was washed with hexanes (4 x 10 mL). Yield: 33%, 0.47 g. ^1H NMR (360 MHz) in acetone-d_6 (ppm): 9.57 bs, 8.65 d (J= 7.2 Hz), 7.87 dt (J= 7.2, 3.6 Hz), 7.28 d (J= 7.2 Hz), 7.06 t (J= 7.2, 3.6 Hz), 2.85 s. Electronic absorption spectrum in acetonitrile λ_{max} = 582 nm (lowest energy band). Infrared spectrum (KBr pellet, cm^{-1}, CO region): 1782, 1866, 1981, 2012.

[Mo(CO)$_4$(N,N,N',N'-tetramethylethylenediamine)]. A 100 mL two-necked flask was charged with $Mo(CO)_6$ (0.335 g, 1.27 mmol) and toluene (20 mL). A reflux condenser was added to the flask and the suspension was deoxygenated with argon for 30 minutes. N,N,N',N'-Tetramethylethylenediamine (TMEDA) (0.200 mL, 1.30 mmol) was added to the suspension. The mixture was heated at reflux for 90 min with an argon purge during which time the solid [$Mo(CO)_6$] was consumed, resulting in a yellow solution. Upon cooling in an ice bath, a yellow precipitate formed. Hexanes were added (10 mL) to induce precipitation. The product was collected on a fine glass frit, vacuum filtered, and washed twice with 10 mL of hexanes. Yield: 57%, 0.24 g. ^1H NMR (270 MHz) in $CDCl_3$ (ppm): 2.81 s, 2.72 s. Electronic absorption spectrum in acetonitrile λ_{max} = 390 nm (lowest energy band). Infrared spectrum not recorded.

Electronic Absorption Spectroscopy.

All electronic absorption spectra were recorded at room temperature on a Hewlett Packard 8452A spectrophotometer with a 2 nm resolution and 190-820 nm wavelength range. A quartz or glass cell with 1 cm pathlength was used for measurements. All spectral measurements were carried out with either an acetonitrile or ethanol solvent.

Cyclic Voltammetry.

Electrochemical experiments used a BAS 100 W potentiostat. Samples were dissolved in Burdick and Jackson UV-grade acetonitrile with 0.1 M Bu_4NPF_6 supporting electrolyte. Solutions were bubbled with argon for 15 min. prior to each experiment; argon flow was sustained for the duration of the experiments. A standard 3-electrode system was utilized: Ag/AgCl reference electrode (0.29 vs. NHE), 1.9 mm diameter Pt disk or glassy carbon working electrode, and a Pt wire auxiliary electrode. The reference electrode was checked periodically against a 1.0 mM solution of ferrocene in CH_3CN with 1.0 M Bu_4NPF_6. The $FeCp_2^+/FeCp_2$ potential is 0.665 V vs. NHE in 0.1 Bu_4NPF_6, measured in acetonitrile.[69] A scan rate of 200 mV/s was used, unless otherwise noted.

NMR Spectroscopy.

^1H and ^{13}C NMR spectroscopy measurements were obtained in acetone-d_6 or $CDCl_3$ on one of the following spectrometers, as noted by individual experiment: Bruker model WP-270 SY (^1H and ^{13}C only) or a Bruker model AM-360. All spectra were obtained at room temperature.