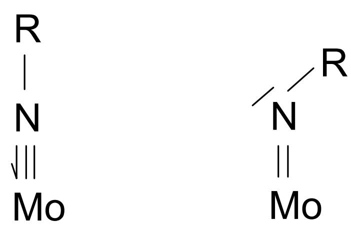
MINELLI, MARTIN (b. 1952) Professor; M.S., 1977, University of Konstanz; Ph.D., 1980, University of Konstanz; Postdoctoral Fellow and Visiting Assistant Professor, 1980-84, University of Arizona; Visiting Associate Professor at the University of Chicago 1991/92; Visiting Professor, Nanjing University, June 2004; Visiting Professor, University of Konstanz, July 2004; sabbatical at the Max-Planck Institute for Bioinorganic Chemistry, Mülheim, Germany, fall 2005; visiting professor at the University of Granada, Spain, fall 2008. **INORGANIC CHEMISTRY**. Coordination chemistry of molybdenum in inorganic and biological systems; multinuclear NMR. (641) 269-3007, Minelli@grinnell.edu.

Molybdenum imido complexes have been studied widely over the past years (1). They are of special interest due to their involvement in the catalysis of olefin metathesis (2) and the Ziegler -Natta olefin polymerization (3). High-yield synthetic routes for di-imido starting materials of the type $Mo(NAr)_2Cl_2(dme)$ (dme= dimethoxyethane) (5) have made it possible to synthesize di-imido complexes with a variety of ligands (6-13). Slight modifications on one of the ligands in an imido complex can have a significant influence on the properties of the compounds. We have shown previously that changing the position of alkyl substituents on the aryl ring of the imido ligand can influence the angle of the imido linkage and the ^{95}Mo NMR chemical shift (4).

Two possible Lewis structures for molybdenum-imido bonds are shown in Figure 1. Many molybdenum(VI) di-imido complexes have a linear and a bent imido linkage in their solid structures, but in solution they interconvert rapidly so that in the NMR spectra, for example, only one signal is seen for both imido linkages (14).



a **b**

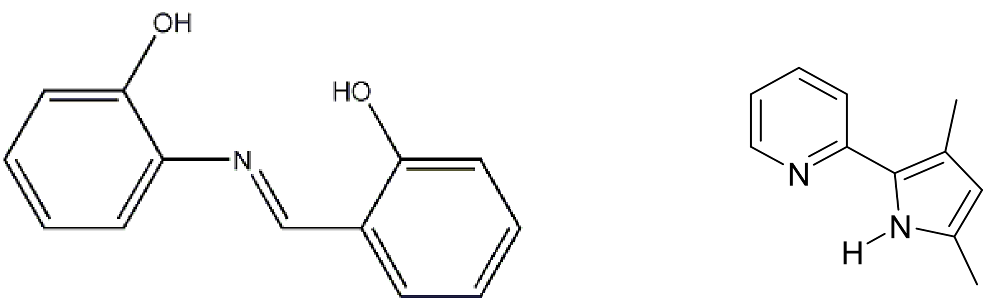
Figure 1: Lewis structures for Mo-imido linkages.

The Projects:

I plan to work with two or three students during the summer 2009. There are no special prerequisites, you will receive the necessary training for the research. During the summer you will learn to use Schlenk technique to perform syntheses under inert atmosphere, to use the dry box, to measure ^{1}H, ^{13}C, ^{14}N, and ^{95}Mo NMR spectra, to take FT-IR and UV-Vis spectra, to measure cyclic voltammograms, and perform spectroelectrochemistry.

Project 1: Synthesis and characterization of molybdenum imido complexes with *N*-salicylidene-2-aminophenol.

The reaction of $Mo(NAr)_2Cl_2(dme)$ with *N*-salicylidene-2-aminophenol (sap, Figure 1a) yields the complex $Mo(NAr)(OC_6H_4(2\text{-})NH)(sap)$. An intermediate in this reaction, $Mo(NAr)(sap)(CH_3O)_2$, has been isolated and used to synthesize a number of complexes with bi-dentate aromatic ligands (Figure 2). The complexes have been characterized by X-ray crystallography, ^{1}H NMR spectroscopy, and cyclic voltammetry (15). The Mo(VI) in the compounds can be reversibly reduced to an EPR-active Mo(V). The reduction potentials depend on the bi-dentate ligand. Complexes with more positive reduction potentials tend to have imido linkages with angles closer to 180^{o}.



a b

Figure 1: a) *N*-salicylidene-2-aminophenol (sap); b) 3,5-dimethyl-2-(2-pyridyl)pyrrole (dpp).

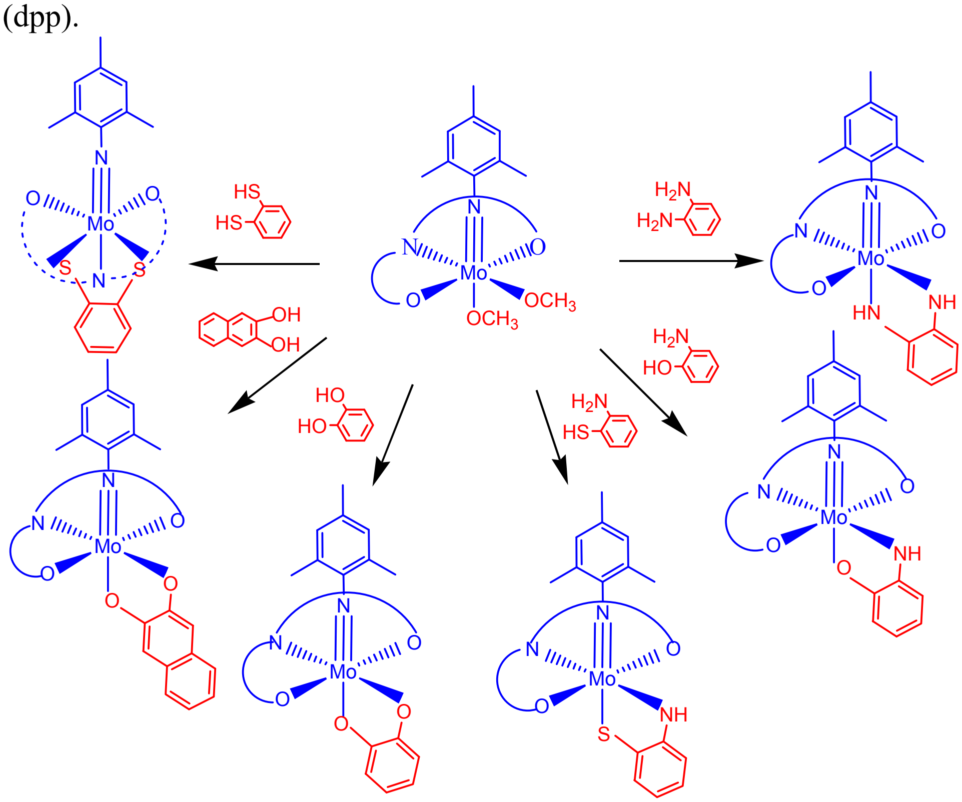


Figure 2: Reactions of $Mo(NAr)(sap)(CH_3O)_2$ (NAr= 2,4,6-trimethylphenylimido) with bi-dentate aromatic ligands.

Last summer, two new imido complexes, $Mo(NC_6H_5)Cl_2(sap)$, **1**, and $Mo(NAr)Cl_2(sap)$, **2**, (sap= *N*-salicylidene-2-aminophenol; NAr=2,4,6-trimethylphenylimido) have been isolated. **1** was obtained by reacting $MoOCl_2(sap)$ with phenylisocyanate, **2** by reacting the same starting material with 2,4,6-trimethylphenylisocyanate. (16, Figure 3). **1** can be reacted with the lithium salt of 2,4,6-trimethylaniline to form the di-imido complex $Mo(NC_6H_5)(NAr)(sap)$ (Figure 3). **3. 1** and **2** show a reversible, one-electron reduction with potentials that are more positive than all previously isolated complexes of the type Mo(NAr)(L)(sap) (L=bidentate aromatic ligand). **Project 1** will involve synthesizing these complexes again in order to grow crystals for an X-ray structure determination. We will also attempt to synthesize the alkylidene derivatives such as $Mo(NAr)(sap)(=C(HC(Me)_3)$.

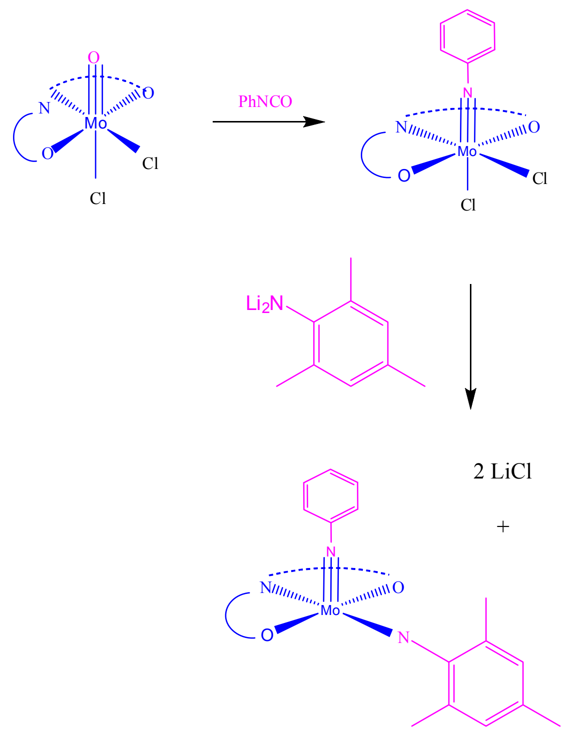


Figure 3: Synthesis of **1, 2** and **3**.

<u>Project 2: Synthesis and characterization of molybdenum imido complexes with *N*-salicylidene-2-aminothiophenol.</u>

Although very similar in the structure to sap, the salicylidene-2-aminothiophenol (sma) ligand does not yield the same products under the same reaction conditions (17). Last summer, we were able to isolate $Mo(NC_6H_5)Cl_2(sma)$, $Mo(NC_6H_5)(NAr)(sma)$, $Mo(NC_6H_5)(sap)$)(OC_6H_4(2-)NH), and)(OC_6H_4(2-)O). The work on this project will continue over the summer with a complete characterization of these new complexes, growing crystals of them and attempting to synthesize the alkylidene derivatives such as $Mo(NAr)(sma)(=C(HC(Me)_3)$.

Project 3: Synthesis of molybdenum di-imido complexes with hydroxylamine and 3,5-dimethyl-2-(2-pyridyl)pyrrole.

When $MoO_2(ONEt_2)_2$ is reacted with two equivalents of phenylisocyanate (PhNCO), a mixture of products is obtained, but the reaction with excess phenylisocyanate yields the imido-ureato complex, $Mo(NC_6H_5)(C_6H_5NC(O)NC_6H_5)(ONEt_2)_2$ (18, Figure 4). We assume that the imido-ureato complex is formed via a di-imido intermediate. **Project 2** will continue work from two summer's ago to isolate the di-imido complex $Mo(NAr)_2)(ONEt_2)_2$ using $Mo(NAr)_2Cl_2(dme)$ as the starting material. We then want to react the di-imido complex with phenylisocyanate and analogs (see Figures 5 and 6). We also want to use $Mo(NAr)_2Cl_2(dme)$ to synthesize complexes with 3,5-dimethyl-2-(2-pyridyl)pyrrole (19, Figure 1b) to study the properties of these compounds.

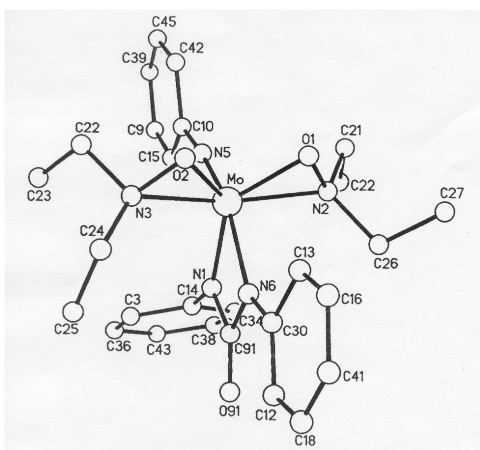


Figure 4: Structure of $Mo(NC_6H_5)(C_6H_5NC(O)NC_6H_5)(ONEt_2)_2$

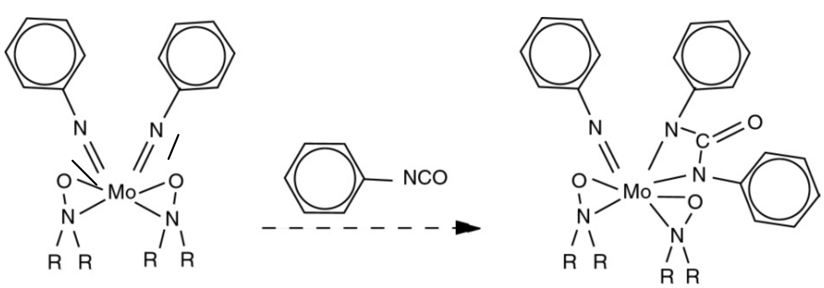


Figure 5: Possible transformation of the di-imido complex to the imido-ureato complex.

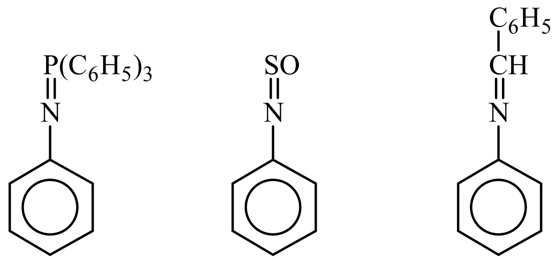


Figure 6: Phenylisocyanate analogs for the reaction with $Mo(NC_6H_5)_2(ONEt_2)_2$

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