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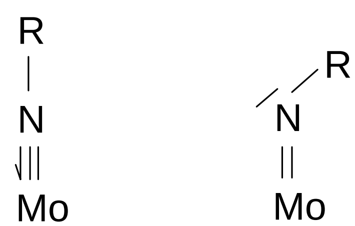
Molybdenum imido complexes have been studied widely over the past years (1). They are of special interest due to their involvement in the catalysis of olefin metathesis (2) and the Ziegler -Natta olefin polymerization (3). High-yield synthetic routes for di-imido starting materials of the type $Mo(NAr)_2Cl_2(dme)$ (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**

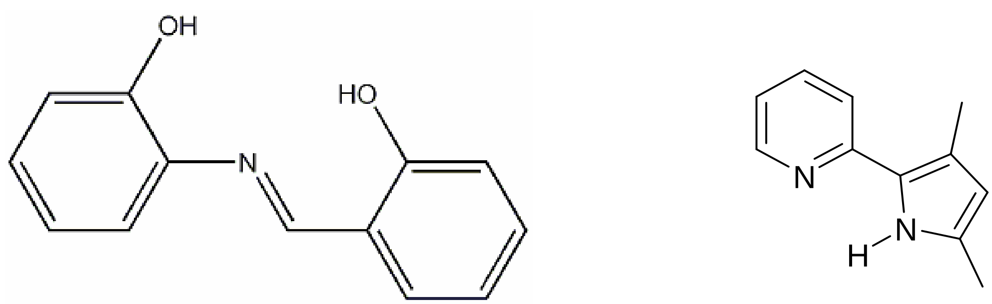
Figure 1: Lewis structures for Mo-imido linkages.

The Projects:

I plan to work with two students during the summer 2008. 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, ^1H 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°.



a **b**

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

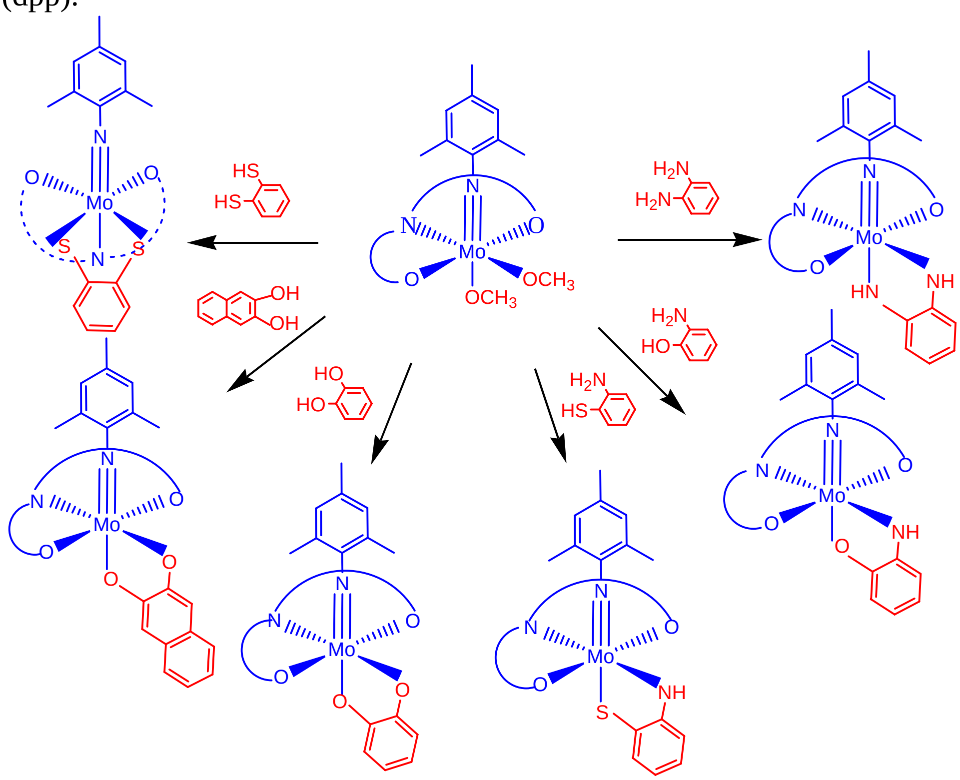


Figure 2: Reactions of $Mo(NAr)(sap)(CH_3O)_2$ (NAr= 2,4,6-trimethylphenylimido) with bi-dentate aromatic ligands.

Last summer, two new mono-imido complexes, $Mo(NC_6H_5)Cl_2$(sap), **1**, and Mo(NAr)(3,4-dimercaptolatotoluene)(sap), **2**, (sap= *N*-salicylidene-2-aminophenol; NAr=2,4,6-trimethylphenylimido) have been isolated and characterized. **1** was obtained by reacting $MoOCl_2$(sap) with phenylisocyanate, **2** by reacting $Mo(NC_6H_5)(OCH_3)_2$(sap) with 3,4-dimercaptotoluene. (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 $Mo(NAr)(sap)(=C(HC(Me)_3)$.

Depending on the time available, we may also continue the study of the reaction of $Mo(NAr)_2Cl_2$(dme) with salicylidene-2-aminothiophenol (sma) which yielded Mo(NAr)O(sma) two summers ago (17).

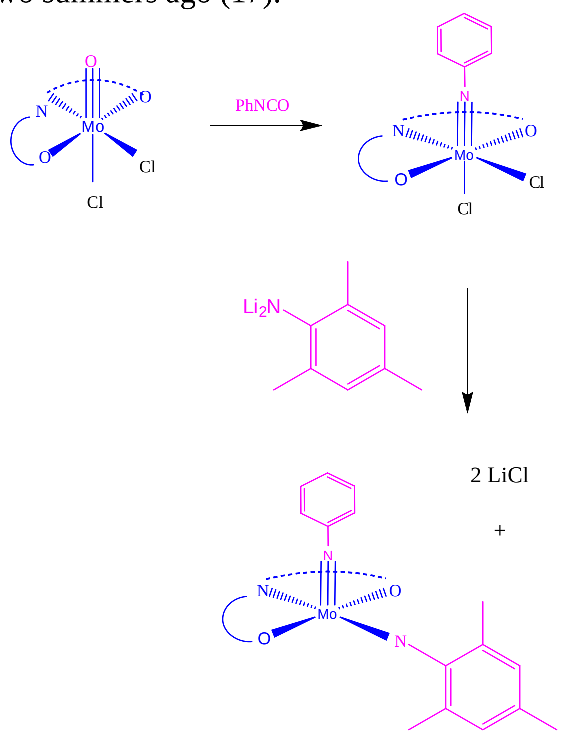


Figure 3: Synthesis of **1** and **3**.

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

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 last summer's work 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.

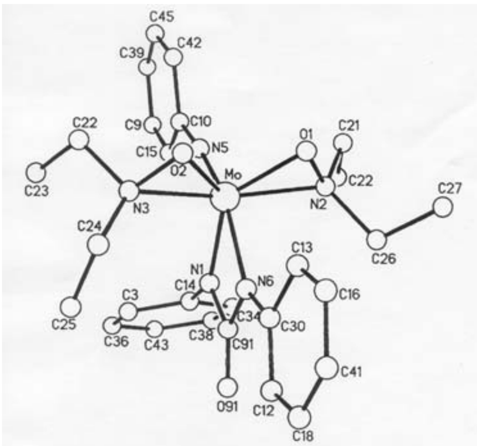


Figure 4: Structure of $Mo(NC_6H_5)(C_6H_5NC(O)NC_6H_5)(ONEt_2)_2$

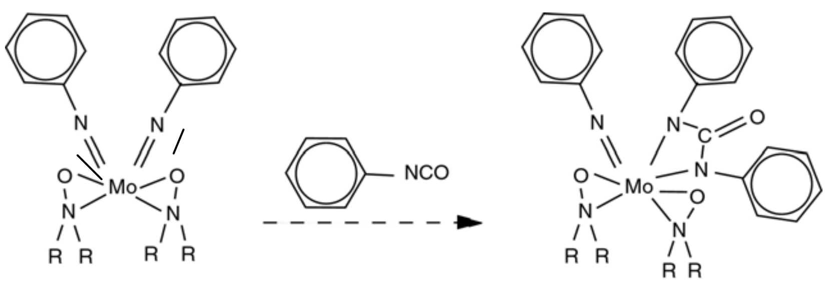


Figure 5: Possible transformation of the di-imido complex to the imido-ureato complex.

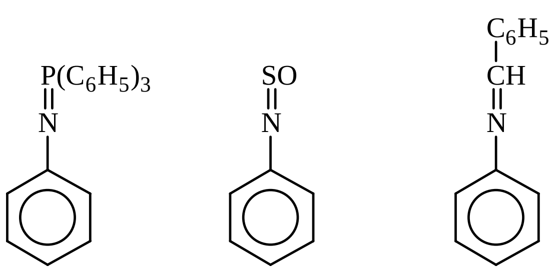


Figure 6: Phenylisocyanate analogs for the reaction with $Mo(NC_6H_5)_2(ONEt_2)_2$

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Previous support and progress:

This project was supported last year with three student (2 from Grinnell, one from Nanjing) salaries and $3000 in supply money. We have been able to synthesize three new compounds and characterize them. All students wrote final papers and presented their results at the end of the summer. Luis Arizpe and Kinnear Theobald have presented their results during the family weekend at Grinnell College. Luis Arizpe presented his results at the Physical Sciences Midstates Consortium Meeting at the University of Chicago in November 2007. He will present them again at the meeting of the American Chemical Society in New Orleans in April 2008. The abstract has been accepted.

The students who do research during the summer 2008 will give a talk at the beginning of the summer and present their results at the end of the summer. Like last year, I also expect them to present at different meetings after the summer research has finished.