MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemistry
5.33 Advanced Chemical Experimentation
Fall Semester 2005

Experiment #4:
Nitrogen Scission by a Molybdenum(III) *tris*-Amide Complex.[1]

I. Introduction

The N_2 molecule is so unreactive that it is generally considered inert. It is frequently used to provide an inert atmosphere for air- and water-sensitive chemistry in the food industry and in laboratories in academia and industry.[2] The unusually high stability of nitrogen can be attributed to (*i*) its large heat of dissociation, $\Delta H_0 = 944.7$ kJ mol^{-1} (225.7 kcal mol^{-1}), and (*ii*) the difficulty of oxidizing or reducing nitrogen ($E_{red} = -7.8$ eV). Therefore, it is not surprising that in order to produce nitrogen compounds it is generally necessary to use energy-rich conditions.

Ammonia is a basic component in and starting material for nitrogen-containing fertilizers, of which millions of tons are produced each year worldwide. Presently, the only commercial process to reduce dinitrogen to ammonia is the **Haber-Bosch process**.[3] In this process, ammonia is synthesized catalytically from the reduction of N_2 by H_2. To complete this reaction, very high temperatures and pressures must be utilized.

$$N_2 + 3H_2 \xrightarrow[\text{450-650 }^{o}\text{C}\\ \text{200-600 atm}]{\text{Fe catalyst}} 2NH_3$$

In contrast to the Haber-Bosch process, the reduction of dinitrogen by biological systems (nitrogen fixation) is conducted in a very economical manner! Blue-green algae and some bacteria (such as *Rhizobium*, found in the root nodules of certain legumes) fix nitrogen **at ambient temperature and pressure!** In nature the enzyme **nitrogenase** (isolated in 1960) plays a key role in the fixation of nitrogen, acting via a molybdenum- and iron-containing protein. Biological nitrogen fixation and photosynthesis are the most important natural processes for food production.

In the early 1990s some small molecule (non-biological) systems were identified for fixing dinitrogen. The experiment described here has been adapted from work done in Professor

[1] This experiment has been designed and adapted from the work of Prof. C. C. Cummins: Laplaza, C. E.; Johnson, M. J. A.; Peters, J. C.; Odom, A. L.; Kim, E.; Cummins, C. C.; George, G. N.; Pickering, I. J. *J. Am. Chem. Soc.* **1996**, *118*, 8623-8638.; Laplaza, C. E.; Cummins, C. C. *Science*, **1995**, *268*, 861. See also the review paper: Cummins, C.C. *Chem. Commun.*, **1998**, 1777.

[2] Rawls, R. L. Chem. & Eng. News, **1998**, 76, 29-34.

[3] Ertl, G. in "Catalytic Ammonia Synthesis," Jennings, J. R. Eds: Plenum, New York, 1991.

C.C. Cummins' laboratory during 1995-1996. Prof. Cummins discovered a molybdenum complex that fixes dinitrogen at -35 °C (*Wall Street Journal*, May 12, 1995; pp. 5-13).

Yield, Atom Economy, and E-Factor

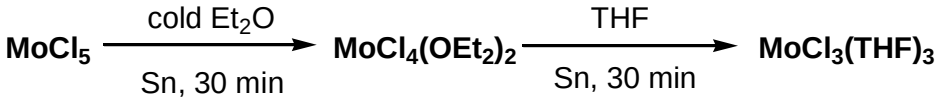
Since this experiment involves a large number of synthetic steps, it provides an excellent opportunity to introduce the concepts of *atom economy* and *E-factor* in addition to the reaction yield that you are already familiar with. The % yield, as you know, is given by

% yield = (actual yield of product)/(theoretical yield of product) x 100

Atom economy simply measures how many reactant atoms are incorporated into the desired product and how many end up in waste products[4]. It is calculated as

$$\%\ \text{atom economy} = \frac{\text{molecular weight of desired product}}{\text{molecular weight of (desired product + waste byproducts)}} \times 100$$

For example, in the first reaction you will carry out



black-brown solid brown solution	orange suspension in diethyl ether	bright orange powder

even if your yield of $MoCl_3(THF)_3$ were 100%, the atom economy would be less than 100% because 2 equivalents of diethyl ether, chlorine, and tin end up in the waste byproducts.

The *E-factor* is just the ratio of the total amount of waste generated in the reaction (in grams) per gram of desired product actually obtained[5]. This includes all byproducts, solvents, separation media, spent catalysts – everything that goes into the waste accumulation bottles. In order to determine the E-factors for each of your reactions, you will have to record an (approximate!) weight for the waste products generated and disposed of in each step of the synthesis. A waste inventory sheet is included in this section of the manual to help you with this process.

Include yield, atom economy, and E-factor calculations in your report for each reaction step you carry out.

Essential Reference!!

[4] M.C. Cann and M.E. Connelly, *Real World Cases in Green Chemistry* (American Chemical Society, Washington, D.C., 2000)

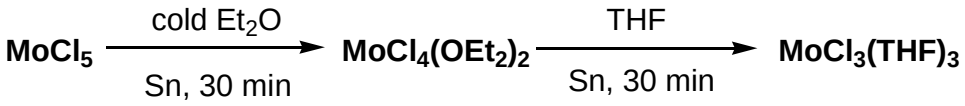
[5] R.A. Sheldon, "Atom Utilization, *E* Factors and the Catalytic Solution", *C. R. Acad. Sci.* **2000**, *3*, 541-551. Available from MIT Libraries, Vera E-journals as **Comptes Rendus de l'Académie des Sciences, Series IIC: Chemistry**

C.C. Cummins. "Reductive cleavage and related reactions leading to molybdenum-element multiple bonds: new pathways offered by three-coordinate molybdenum (III)," *Chem. Commun.* **1998**, *1777;* available on-line at http://www.rsc.org/is/journals/current/chemcomm/cc998017.htm

This experiment consists of four principal steps:

1. Synthesis of the molybdenum precursor $MoCl_3(THF)_3$ from $MoCl_5$.

Molybdenum(V) pentachloride can be reduced using tin as a reducing agent. This series of reactions will be completed in one laboratory period.



black-brown solid
brown solution

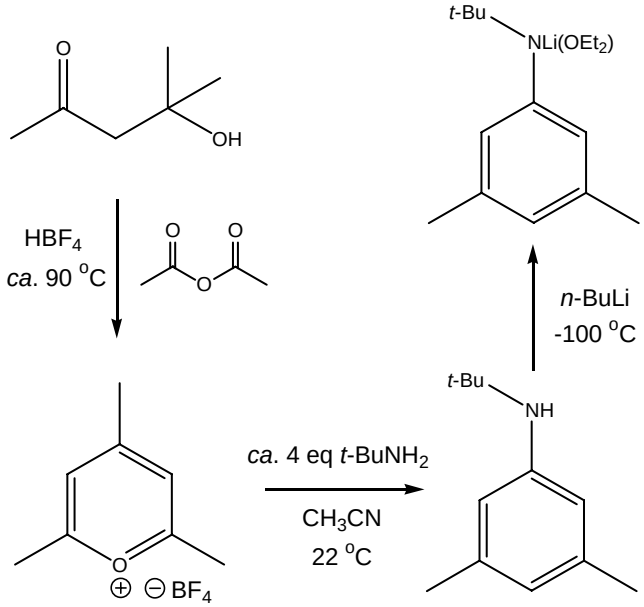
orange suspension
in diethyl ether

bright orange powder

2. Synthesis of the lithium salt of HN[*t*-Bu]Ar.

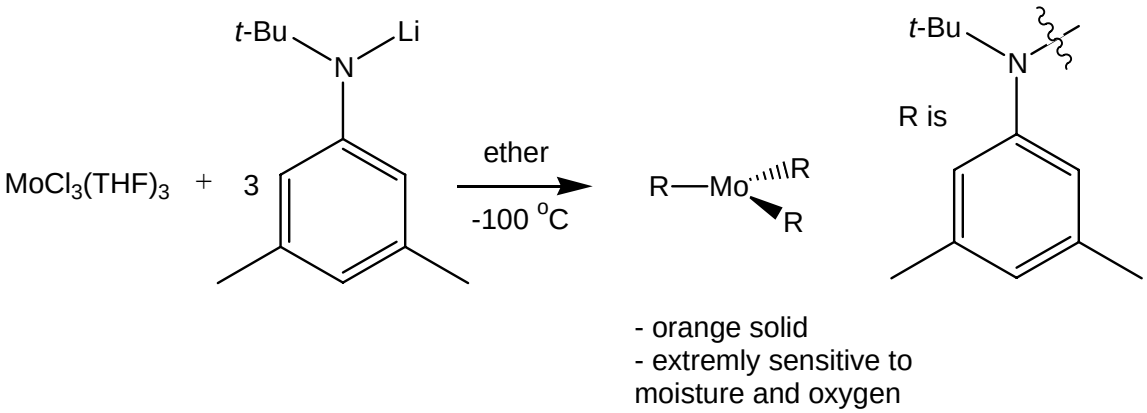
There are three steps employed here to synthesize the lithium salt of the xylidene ligand:

a. Synthesis of 2,4,6-trimethylpyrilium tetrafluoroborate from diacetonalcohol, acetic anhydride and 40% aqueous solution of fluoroboric acid.
b. Synthesis of HN[*t*-Bu]Ar from the pyrilium salt and *t*-butylamine in anhydrous acetonitrile.
c. Synthesis of LiN[*t*-Bu]Ar·OEt_2 from HN[*t*-Bu]Ar using *n*-BuLi.



3. Synthesis of the molybdenum xylidene complex.

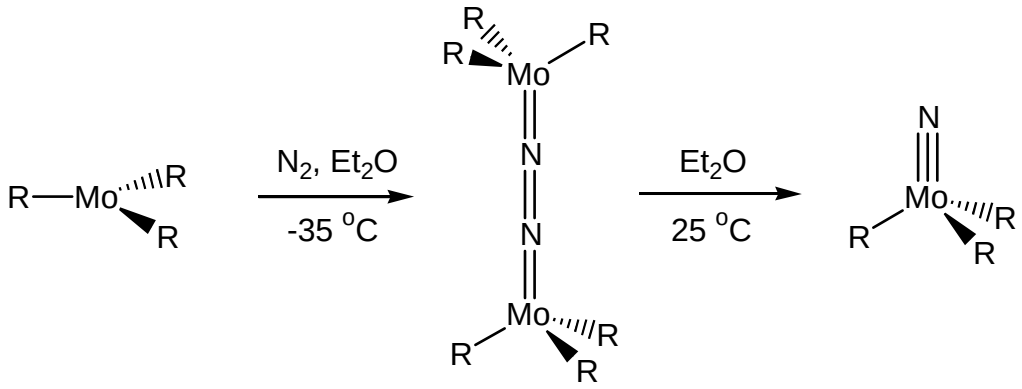
Starting from low temperature, the reaction between the lithium salt of the ligand and the molybdenum-containing starting material generates the desired three-coordinate molybdenum (III) *tris*-amide.



- orange solid
- extremly sensitive to moisture and oxygen

4. Nitrogen scission by the molybdenum *tris*-amide complex.

The amber nitrido complex $NMo(N[t\text{-}Bu]Ar_3)_3$ results cleanly by warming to room temperature the $(\mu\text{-}N_2)[Mo(N[t\text{-}Bu]Ar)_3]_2$. The latter is obtained from $Mo(N[t\text{-}Bu]Ar_3)_3$ and dinitrogen at -35 °C.



II. Experimental

Before starting the experiment on the syntheses of LiN[*t*-Bu]Ar·OEt_2 and $MoCl_3(THF)_3$ read carefully the following comments on the use of glove boxes.

A. Use of Glove Boxes

You will use a glove box (GB) for the air sensitive reactions in this lab. The nitrogen gas that fills the glove box is relatively dry and oxygen-free. (*Question*: Why is this important? Give specific examples relevant to this chemistry. Write chemical equations where it is appropriate.) It is tempting to believe that all your reactions will work because they are done in the GB, but the GB is not magic! The atmosphere is only as good as you make it! This means you will need to dry your glassware in the oven, use dried and degassed solvents, and purge the glove box atmosphere periodically.

Your TAs will demonstrate the use of the glove boxes including the use of the pressure regulation gauges, the pedal to increase the pressure, the chambers, the cold well, and the catalysts. Before you begin working in the glove box, please remove watches, bracelets, and rings that might snag and tear the gloves. White cotton gloves will be provided and they are to be worn while working in the glove box. Latex gloves should not be worn at any time in the glove box. Long sleeves are recommended while working in the glove box. When beginning your use of the glove box, adjust the pressure regulation gauge to the working level and then insert your arms slowly. The pumps regulating the pressure can only work so fast to compensate for the volume of gas you are displacing with your arms! While in the glove box, use care not to damage the gloves. This includes sharp instruments (watch out for broken pipettes!) and spilling solvent or grease. Please open and close the refrigerator door gently, since your labmates may have products crystallizing inside.

B. Equipment in the Glove Box.

It takes time to bring things into and out of the glove box. One of the glove boxes that will be used in 5.33 is conveniently equipped with a small chamber that only needs to be pumped out for 5-10 minutes, which is convenient for bringing NMR tubes in and out of the glove box. The large chamber, which is necessary for large amounts and larger pieces of glassware, needs to be pumped out for a minimum of 45 minutes. Because both chambers are on the same pump, they cannot be evacuated at the same time. It is also important that all glassware has been dried overnight in the oven above 100 ºC before being introduced into the GB. This includes NMR tubes, stir bars, and spatulas, but does not include septa or NMR caps. Plan ahead!

It is important to make sure that all of the equipment that you need is in the GB BEFORE you begin working. This will make your time in the GB much more efficient. Included in the procedures are lists of all of the equipment you will need. While your TA will maintain many of these supplies, make sure they are there before you start. Also, if you use up the last of a common supply, make sure that you replenish it or ask your TA to do so! There are some materials that cannot be brought into the GB. For example, it is not possible to dry cork rings sufficiently to be able to bring them into the GB. You should find in the glove box: **balance**, **stir plates** and **clamps**, **weigh boats** (it is necessary to pump on these for longer than other items), **vials** and **pipettes** (these are heated overnight), **pipette bulbs**, **Kimwipes** (predried, and

then pumped on overnight), **neoprene vacuum adaptors**, **rubber stoppers**, **Celite** (dried under vacuum at 200 °C overnight), and **vacuum connections**. Please conserve weigh boats and Kimwipes. You do not need to use a new Kimwipe every time!

The solvents that we are using in the GB have been collected from a solvent still and brought into the GB in a closed vessel with a stopcock. Many of the solids that we are using as starting materials are air sensitive and therefore come packed under nitrogen or argon. These bottles can be brought directly into the box. **BE VERY CAREFUL ABOUT WHAT YOU BRING INTO THE BOX**. If in doubt, ask your TA.

C. Use of the Vacuum.

There are two vacuum pumps used with this GB. The first is used to evacuate the chambers and to control the pressure inside the box. The second is an external pump that can be used to remove solvents inside the box. This second pump will be used in conjunction with an external liquid nitrogen trap to prevent solvents from entering the pump oil. **BE VERY CAREFUL WITH THE LIQUID NITROGEN TRAPS. THEY SHOULD NOT BE SET UP OR TAKEN DOWN WITHOUT THE DIRECT SUPERVISION OF YOUR TA. IF THEY ARE NOT CARED FOR PROPERLY, OXYGEN CAN CONDENSE AND CAUSE AN EXPLOSION!**

The solvent pump has a valve in the back of the GB, as well as a stopcock on each connection hose inside the box. These should all be closed when not in use. Open valves will cause air to leak into the box when the pump is off, and will continually evacuate the box when the pump is on.

When filtering, it is important that you put a rubber stopper on top of the filter as soon as the solution has been completely transferred, and make sure that it has made a tight seal. Otherwise, you will hear the solenoid that controls the pressure inside the box constantly clicking as it seeks to continuously replace the removed nitrogen. Also, it is very important to be careful not to allow solvents to "bump." Solvents that "bump" into the vacuum lines will clog the lines. To avoid bumping while pumping on a reaction, stir your solvent on the stir plate using a Teflon-coated stir bar.

D. Time and courtesy

Make sure that before you start a reaction you have allowed enough time to both complete the reaction and purge dichloromethane from the atmosphere. If next group will be doing the same reaction, it will not be necessary to purge. A glove box is a closed system, therefore every solvent that is in the box atmosphere remains in the atmosphere until it is removed. ***For example, CH_2Cl_2 will destroy $Mo(N[t\text{-}Bu]Ar)_3$ and is bad for the catalyst.***

You MUST keep the glove box clean. This means that if you have a spill, sweep it up using the little brush in the glove box. Place all garbage in the waste bin near the large chamber door. You are responsible for disposing of any vials you make dirty in the glove box, and you MUST clean all of your glassware within one lab day of having it removed from the glove box. Be sure to return any frits to the stockroom at the end of this lab so the next rotation can use them.

1. Synthesis of the Molybdenum Precursor

1. Synthesis of trichloro-*tris*(tetrahydrofuran)molybdenum(III), $MoCl_3(THF)_3$[6]

Materials: One 250 mL round-bottom flask, three 150 mL (or larger) filter flasks, three stir bars, two frits, waste bottle or other container to hold waste solvent, spatula, stir plate, clamp, balance, weigh boat, neoprene vacuum adapter, rubber stopper, septum, pipettes and pipette bulb, Celite.

Time: The reaction time is VERY important. If you allow the reaction to go too long, the product will begin to decompose. Make sure that you have all the glassware in the box and cool before you begin the reaction. You will need 1 hour + 30 minutes to purge, and then 30 minutes later in the afternoon to collect the product.

Procedure:

- Weigh out 5 g of powder molybdenum pentachloride and cool in the cold well.
- Measure 3-5 equivalents (make a decision!) of tin powder and cool in the cold well for at least 8 minutes.
- Using the cold well, 60 mL of diethyl ether (in a 250 mL RB flask) is chilled for at least 6 minutes. (*Note*: Just estimate the amount of solvent you are using. You do not need to use a graduated cylinder to measure it.)

$MoCl_5$ is then suspended in cold diethyl ether. The resulting solution is placed in the cold well for several minutes. To the cold solution of $MoCl_5$ is added cold tin powder while maintaining rapid stirring. The mixture is stirred at room temperature for 30 minutes (note any color change). Place the RB flask in the cold well for about 5 minutes allowing the solids to settle. Once the solids have collected at the bottom of the flask, quickly decant the supernatant solution of diethyl ether away from the solids, leaving a small amount of ether in the RB flask. Keep the diethyl ether slurry cold before adding 40 mL of freshly thawed THF while stirring rapidly. Continue rapid stirring for 10 minutes (shake the reaction vessel if necessary) before filtering through celite. However, if the reaction mixture takes on a purple tint (it should look green!) before 10 minutes has elapsed, immediately filter the mixture through a bed of celite on a sintered glass frit. Discard the filtrate. Into a clean filter flask containing 15 mL THF, wash the $MoCl_3(THF)_3$ away from celite using the ***minimal amount*** of CH_2Cl_2. **DO NOT** stir the celite, as the tin powder may penetrate the coarse frit. Immediately check your filter flask for solids. If any tin made its way trough the frit, immediately filter the solution through celite (with a clean frit). Concentrate on the vacuum to roughly 10-20 mL. Collect $MoCl_3(THF)_3$ by filtration as a salmon- or orange-colored compound. Wash solids with small amounts of THF then diethyl ether and dry under vacuum. The complex is stored in a freezer and in the dark. Care should be taken, since the product is extremely moisture sensitive. Record the yield and color of obtained product.

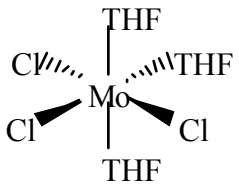
WASTE DISPOSAL: **Tin is EXTREMELY TOXIC.** The tin waste should be removed from the glove box, and the tin and celite transferred to the flask. Concentrated HCl should then be

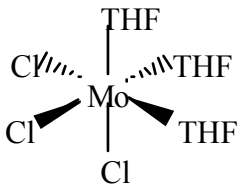
[6] Adapted from: Stoffelbach, F.; Saurenz, D.; Poli, R. *Eur. J. Inorg. Chem.* **2001**, 2699.

added slowly and carefully to the stirring suspension. This should be stirred overnight and then disposed of in the proper waste bottle.

Properties:

The complex $MoCl_3(THF)_3$ is crystallized as pale orange needles from dichloromethane/tetrahydrofuran solution. The IR spectrum of the pure complex is free of intense bands in the 900-1000-cm^{-1} region, which is characteristic of molybdenum oxo species. The single-crystal X-ray structure supports the meridional (*mer*) positioning of the THF units, and not a facial (*fac*) configuration. [7]





mer-$MoCl_3(THF)_3$ *fac*-$MoCl_3(THF)_3$

[7] Hofacker, P.; Friebel, C.; Dehnicke, K.; Bäuml, P.; Hiller, W.; Strähle, J. *Z. Naturforsch.* **1989**, *44b*, 1161-1166.

2. The ligand HN(*t*-Bu)Ar (Ar = 3,5-$C_6H_3Me_2$) Synthesis[8]

2A. Synthesis of the 2,4,6-trimethylpyrylium tetrafluoroborate

Diacetone alcohol: Irritant
Acetic anhydride: Corrosive; Lachrymator
Fluoroboric Acid (48% wt solution in water): Corrosive; Lachrymator

Reagent	FW	bp (°C)	mp (°C)	density g/mL	amount	mmole
Diacetonalcohol 99% (2-methyl-2-hydroxypentanone) [123-42-2]	116.16	166	-	0.931	10 mL	80
Acetic anhydride 99%+ [108-24-7]	102.09	138-140	-73	1.082	75 mL 81 g	800
Fluoroboric Acid 48% wt sol in water [16872-11-0]	87.81 (HBF_4)	-	-	1.4	10.4 mL	80

Procedure:[9]

Note: Grease and clip all joints. Thoroughly clamp your reaction set-up before adding reagents.

Attach a Vigreux column topped with a water condenser to the central neck of a 250-mL three-neck (14/20) round bottom flask containing a 1" stir bar. On one of the side necks, attach a thermometer. Be sure that the bulb of the thermometer is below the level of the reaction mixture. On the remaining neck, attach a pressure-equalizing dropping funnel. Charge the flask with 75 mL acetic anhydride. Cool the flask in ice water. At *ca*. 5 °C, add 10 mL of diacetonalcohol in three portions through the top of the condenser while stirring. Stir for an additional 5-10 minutes to ensure the temperature has equilibrated. Remove the ice water bath. Wipe the bottom of the flask and attach a heating mantle connected to a Variac (keep Variac *off* for the time being). Using the dropping funnel, start adding the HBF_4 (1 drop each 10 to 20 sec). The temperature should not exceed 95 °C. When all of the HBF_4 has been added, start the heating and keep the temperature at 95-100 °C for an additional 30 minutes. Then cool the RB flask to 0-5 °C. When this temperature is reached add 100 mL ether through the top of the condenser. Keep stirring for an additional 10 min. Filter the pyrilium tetrafluoroborate through a fritted (25-50 μ) Buchner funnel without suction. Wash the brownish precipitate with 3x10 mL of ether, stopping when the precipitate becomes white or pale yellow. Apply short suction to remove all the solvent.

[8] For additional details see: Tsai, Y.-C.; Stephens, F. H.; Meyer, K.; Mendiratta, A.; Gheorghiu, M. D.; Cummins, C.C. *Organometallics,* **2003**, *22*, 2902-2913.
[9] Adapted after: Vernaudon, P; Rajoharison H. G.; Roussel, C. *Bull. Soc. Chim. Fr*. **1987**, 205-211.

Dry the pyrilium salt in a petri dish overnight in the hood. You should get 8-10 g of 1,3,5-trimethylpyrilium tetrafluoroborate, mp 218-220 °C (decomp). Take a ^{1}H NMR in CD_3CN. Signals are at δ (ppm): 2.75 (3H, s); 2.9 (6H,s); 7.66 (2H, s). Record the yield, melting point, and NMR data.

WASTE DISPOSAL: **The filtrate is EXTREMELY acidic.** Before disposing the filtrate **you must neutralize** the acid. Transfer the filtrate into an erlenmeyer flask of capacity equal 2-3 times larger than the volume of transferred liquid. When still empty add a 1" magnetic bar, than pour the filtrate into the Erlenmeyer. Put the erlenmeyer over a magnetic stirrer. Start the stirring. Add solid Na_2CO_3 carefully (avoiding extensive foaming). When the CO_2 has ceased take the pH (with a pH paper). If is still acidic add more Na_2CO_3. If it is neutral discard the solution into the ligand waste jar.

2B. Synthesis of the N-*t*-butyl-*m*-xylidene.

t-Butylamine: Highly toxic flammable liquid
Acetonitrile: Flammable liquid, toxic.

Reagent	FW	bp (°C)	mp (°C)	density g/L	amount	mmole
t-Butylamine [75-64-9]	73.14	46	-67	0.696	21 mL (14.6 g)	200.0
2,4,6-Trimethylpyrilium Fluoroborate	209.98		204-6		8.400 g	40.00
Acetonitrile	41.05	81-82	-48	0.786	100 + 150 mL	80

Note: This reaction takes at least 4 hours. You must arrive promptly at the beginning of lab to finish this experiment during the laboratory hours! The extraction step can be completed the following day if the reaction mixture is placed into the refrigerator in a sealed, labeled container.

Set up the same apparatus as for experiment **2A** (except using a 500 mL RB flask). Charge the 500-mL three-neck (14/20) round bottom flask with 100 mL anhydrous acetonitrile, and 21 mL of *t*-butylamine. Add into the dropping funnel a solution of 8.4 g of trimethylpyrilium tetrafluoroborate in 150 mL of anhydrous acetonitrile. (All of this solution may not fit in the dropping funnel. It is acceptable to add portions to the dropping funnel as it empties.) Start the magnetic stirring and, under nitrogen, begin adding the pyrilium solution dropwise such that complete addition takes approximately 4 hrs (1 drop every 2 to 5 seconds). Transfer the contents of the flask into a RB single neck 500-mL flask. Remove the acetonitrile via rotary evaporation. Dissolve the resulting oil in *ca*. 100 mL of petroleum ether (**PE**). Wash the **PE** with ca 100 mL of water. Dry the **PE** layer over anhydrous $MgSO_4$. Filter the solution over a fritted Buchner filter, and rotavap away the **PE**. Record the yield, GC/MS and NMR (C_6D_6) for your crude product. With at least one other group, vacuum distill the ligand. (Some of the extraction solvent may remain in the oil you are distilling. Therefore, begin the distillation slowly and

include a stir bar to help avoid bumping as this solvent is pumped away. (Remember, the numbers on the Variac are not temperatures!). At **15 mT,** which is highly recommended in order to obtain a colorless xylidine distillate, the bp is 45 °C.

3. Synthesis of the Molybdenum *tris*-Amide Complex

3A. Preparation of LiN[*t*-Bu]Ar ·Et_2O (Ar = 3,5-dimethylphenyl).

Materials: 100-mL round bottom flask, stir bar, graduated cylinder, frit, filter flask.

The HN[*t*-Bu]Ar (4.00 g, 22.6 mmole) is dissolved in 50 mL of pentane and the solution is frozen in the glove box cold well. Measure the BuLi (1.6 M in pentane, 14.8 mL, 23.7 mmole, 1.05 equiv) into a syringe at room temperature. Transfer the solution to a vial, and briefly cool (in the cold well) before adding to the frozen n-pentane solution of amine. Then remove the frozen amine solution (in pentane) and the BuLi (in pentane) from the cold well and mix them. The solution is allowed to stir for 2 hours, at which time it is concentrated to 20 mL. Subsequently, diethyl ether (25 mL, *ca*. 10 eq) is added. Place the reaction flask into the cold well for 10 to 15 minutes. White crystals should begin precipitating. These are collected on a frit and dried under vacuum. A second crop can be collected by cooling the mother liquor to -35 °C and allowing it to stand overnight in the refrigerator. Record the yield.

3B. Synthesis of $Mo(N[t\text{-}Bu]Ar)_3$.

Materials: 200-mL round bottom flask, stir bar, 1 frit, 1 filter flask, 50-mL Schlenk tube, glass stopper.

mer-$MoCl_3(THF)_3$ (1.743, 4.164 mmol) and Li[N(*t*-Bu)Ar](OEt_2) (2.190 g, 8.315 mmol) are added to 70 mL of cold (-100 °C) diethyl ether. The reaction mixture is stirred for 3 h after being warmed to 28 °C. Filter the reaction mixture through celite to remove LiCl and the excess *mer*-$MoCl_3(THF)_3$. The filtrate is then concentrated to dryness. Redissolve the residue in the *minimum amount* of diethyl ether and transfer the solution into a Schlenk tube. Close the Schlenk tube using a glass stopper (grease!) and quickly evacuate to remove all the nitrogen by rotating the stopcock rapidly several times. Store in the -35°C refrigerator, being careful to keep the tube somewhat upright so the grease does not dissolve. After one or two days, collect the solid and characterize by color and ^{1}H NMR (C_6D_6). $Mo[N(t\text{-}Bu)Ar]_3$ is extremly oxygen- and moisture sensitive, but also decomposes in an inert atmosphere (< 5% left after 24 hrs at 25 °C in solution).
^{1}H-NMR (C_6D_6): ca 64 (br, *tert*-butyl), -9.6 (ArC***H*****$_3$**). Broad peaks at ca. 23 ppm and ca. –51 ppm are due to an impurity ($ClMo(N[t\text{-}Bu]Ar)_3$).

4. Nitrogen Scission with the Molybdenum Xylidene Complex

Synthesis of $NMo[N(t\text{-}Bu)Ar]_3$ from $Mo[N(t\text{-}Bu)Ar]_3$ and Dinitrogen.

By storing a solution of $Mo(N[t\text{-}Bu]Ar)_3$ (300 mg, 0.467 mmol) in diethyl ether (6 mL) at -35 °C under nitrogen (*ca*. 1 atm in a glove box) for 70 to 100 h, a purple solution of (μ-

N_2)[Mo(N[*t*-Bu]Ar)$_3$]$_2$ is formed. After this time, the reaction mixture is allowed to warm to room temperature (28 °C) for ca. 5 h, during which the mixture turns into an amber nitrido complex NMo(N[*t*-Bu]Ar)$_3$. Remove the solvent. Record the ^{1}H-NMR (C_6D_6).
^{1}H-NMR (C_6D_6): 6.83, 5.98, 2.21, 2.04 ppm.

III. Report

Your report for this laboratory consists of a long abstract and a fifteen-minute poster presentation followed by questions from your TAs. It is important to be able to introduce this chemistry and to put the material in context, as well as to present the results you obtained in the laboratory. While you should understand the background of the molybdenum chemistry, you should focus on YOUR results and how YOU interpret these results.

You should prepare a set of data summary sheets on your poster. These sheets should include the following items: (*1*) Pyrilium salt — yield and ^{1}H NMR (in CD_3CN); (2) HN[*t*-Bu]Ar — reaction conditions, purification procedure, GC/MS data, ^{1}H NMR results. For all reaction steps, you should demonstrate an understanding of the basic reaction mechanism, product workup and purification, why and how side products are formed, and how to minimize the formation of side products. Report atom economy ratios and your experimental E-factors for each reaction step.

Here are some other questions to think about which may be helpful as you prepare:

1. What are the advantages of the ligand you synthesized?
2. What are the reducing agents that are used to transform Mo^V into Mo^{III}?
3. What is the glove box used for, and why is it important in this synthesis?
4. $LiNMe_2$ is a commercially available amide. Why don't we use this instead of LiNRAr, which we have to synthesize? [*Hint*: what is the product of the reaction between $MoCl_3(THF)_3$ and 3 $LiNMe_2$?]
5. What are the limitations that prevent $Mo(NRAr)_3$ from being an efficient nitrogen fixation system? Is the system catalytic? What type of molecule would you use in trying to generate a catalytic nitrogen fixation system?