

# **Scission of Dinitrogen by a Molybdenum(III) Xylidene Complex**

CHM 5.33

Fall 2005

# Introduction

The experiment is based on research performed in the laboratory of Professor Cummins during the early 90's.

Refer to:

Laplaza, Catalina, and Christopher Cummins. "Dinitrogen Cleavage by a Three-Coordinate Molybdenum (III) Complex." *Science* 269 (1995): 861-863.

# Aspects of the Lab

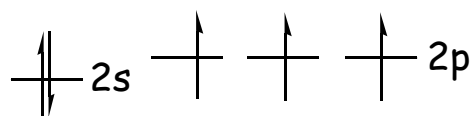
The experiment involves basic organic synthesis and introduces some rudimentary aspects of the manipulation of air and moisture sensitive materials.

In addition, students use GC-MS and NMR to characterize the compounds made during the experiment.

The experiment provides a very good context for the discussion of electronic structure and bonding in transition metal complexes.

# Chemistry of Nitrogen

N



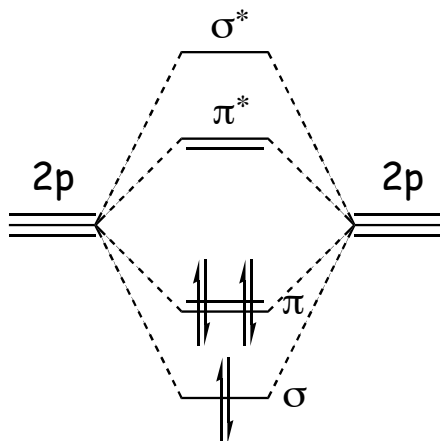
Free gaseous atom is a ground-state quartet ( $2s^2 2p^3$ )

$$2S + 1 \rightarrow 2(3/2) + 1 = 4$$

Nitrogen is trivalent - prefers to form three bonds ( $\text{NH}_3$ , HCN,  $\text{N}_2$ )

“three electron oxidant”

$\text{N}_2$



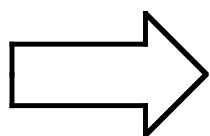
Extremely important naturally and synthetically (amino acids, DNA, polymers, fertilizers)

$\text{N}_2$  (dinitrogen) is the most abundant molecule in the earth's atmosphere comprising  $\sim 80\%$

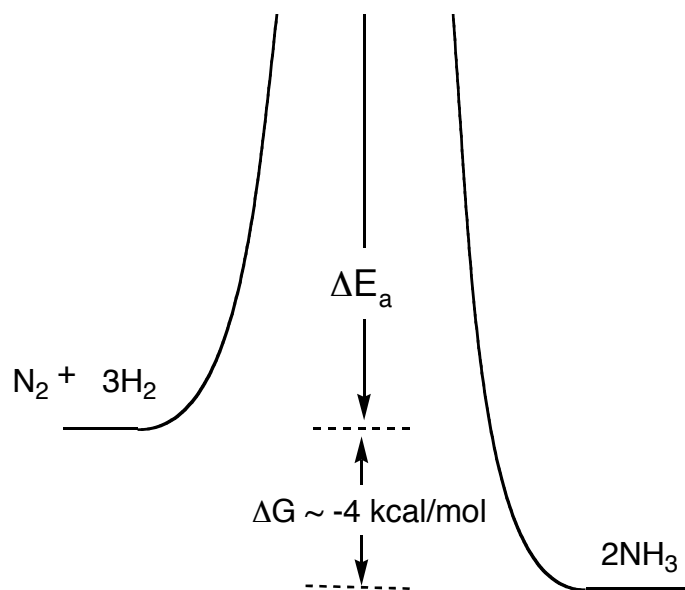
The very stable triple bond ( $\Delta H_{\text{dis}} = 225 \text{ kcal/mol}$ ) renders  $\text{N}_2$  practically inert

$\text{N}_2$  does combine with metals to form nitrides

Nitrogen is a common component of many important natural and synthetic compounds



We need a way to utilize the natural abundance of  $N_2$  as a synthetic feed stock



Thermodynamically, the reaction of  $N_2$  with  $H_2$  is favorable

The problem lies in overcoming the kinetic barrier

# Biological Nitrogen Fixation

In nature,  $N_2$  is converted to ammonia by bacteria which grow in different forms of plant life and algae. These bacteria contain the “nitrogenase” enzyme which catalytically reduces  $N_2$  to metabolically useful  $NH_3$

The enzymes operate anaerobically at ambient temperature and pressure using a two component metalloprotein: the first contains Fe (electron source), and the second contains both Fe and Mo or V (site of binding and reduction).

Image removed due to copyright reasons. Please see:

Einsle, Oliver et al. "Nitrogenase MoFe-Protein at 1.16 Å Resolution: A Central Ligand in the FeMo-Cofactor." *Science* 297 (2002): 1696-1700.

In 2002, Rees reported the 1.6 Å resolution crystal structure of nitrogenase showing the presence of an atom in the center of the FeMo cofactor

# Industrial Production of Ammonia

Haber-Bosch process:

Fritz Haber  
1918

Carl Bosch  
1931



Fe catalyst, 450-650°C and 200-600 atm

This process consumes 1% of the world's total annual energy supply

# Why Molybdenum?

In nature, bacteria are able to "fix" nitrogen at ambient T & P this process is catalyzed by the *nitrogenase enzyme* which contains as part of its structure an Fe/Mo cofactor

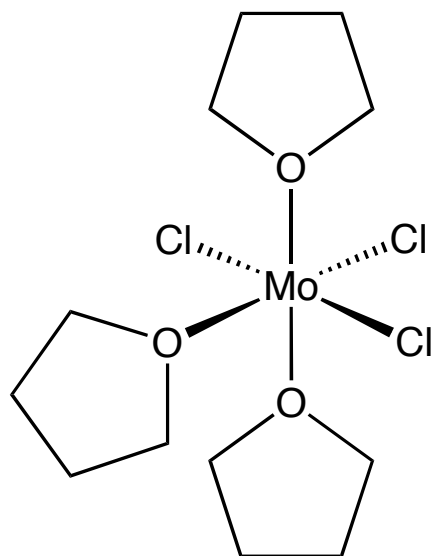
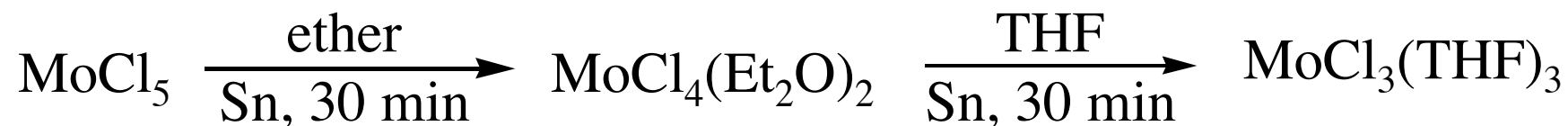
A coordinatively unsaturated Mo(III) compound could presumably bind a small molecule and reduce it by three electrons

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Zr	Nb	<b>Mo</b>	Tc	Ru	Rh	Pd	Ag

Producing a coordinatively unsaturated Mo(III) complex poses a formidable synthetic challenge



# Molybdenum Precursors



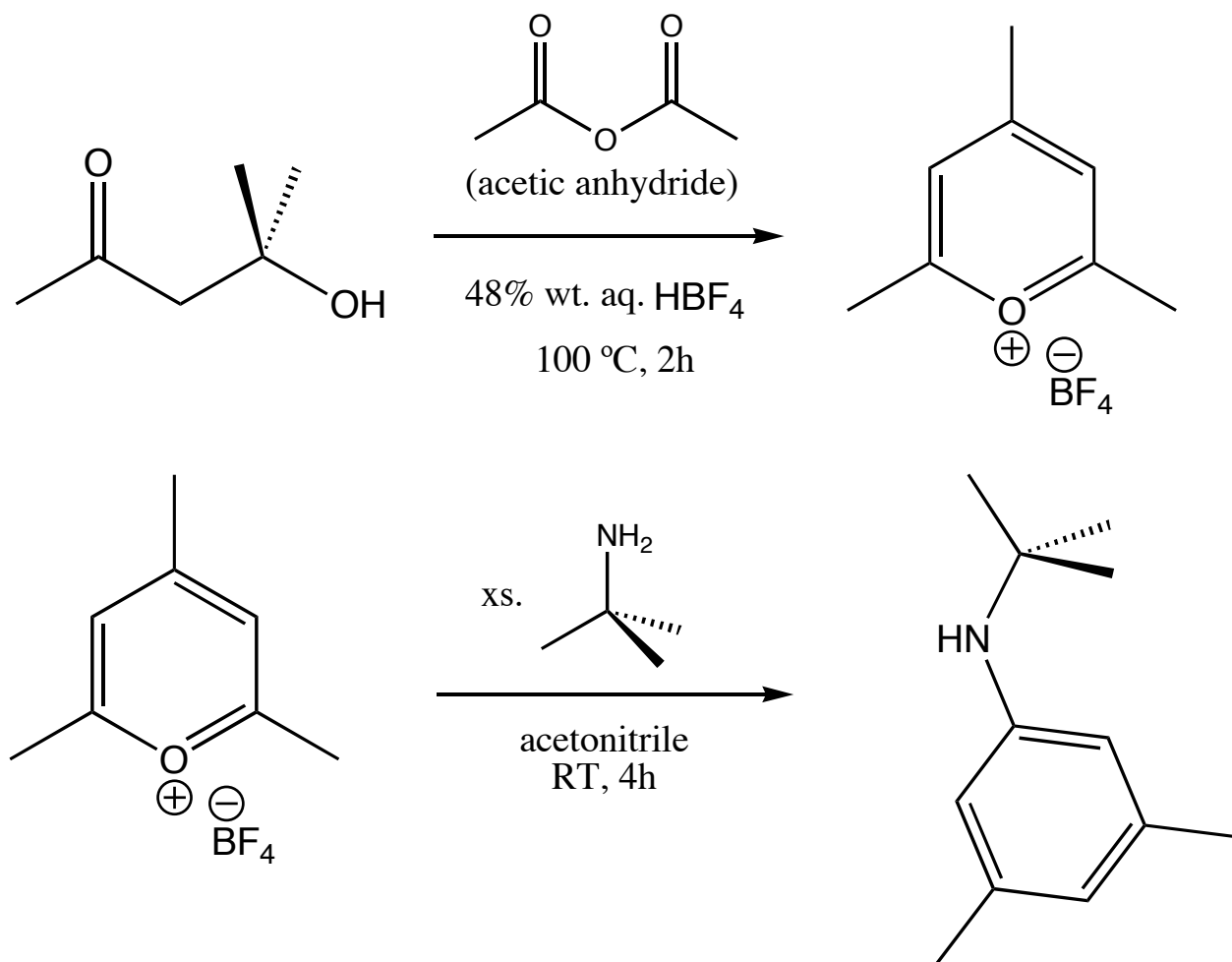
Orange crystalline solid

Solid state structure shows *mer* geometry

Mo(III) is paramagnetic and contains 3 unpaired electrons

*Eur. J. Inorg. Chem.* **2001**, 2699

# Preparation of the *t*-Butyl Xylidene Ligand



*Organometallics*, 22, 2003

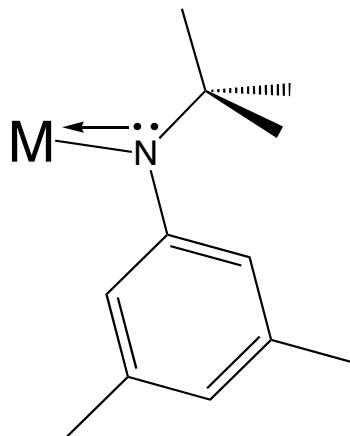
# Advantages of the Ligand

Provide steric bulk to discourage metal-metal bonding and only allow access to small molecules

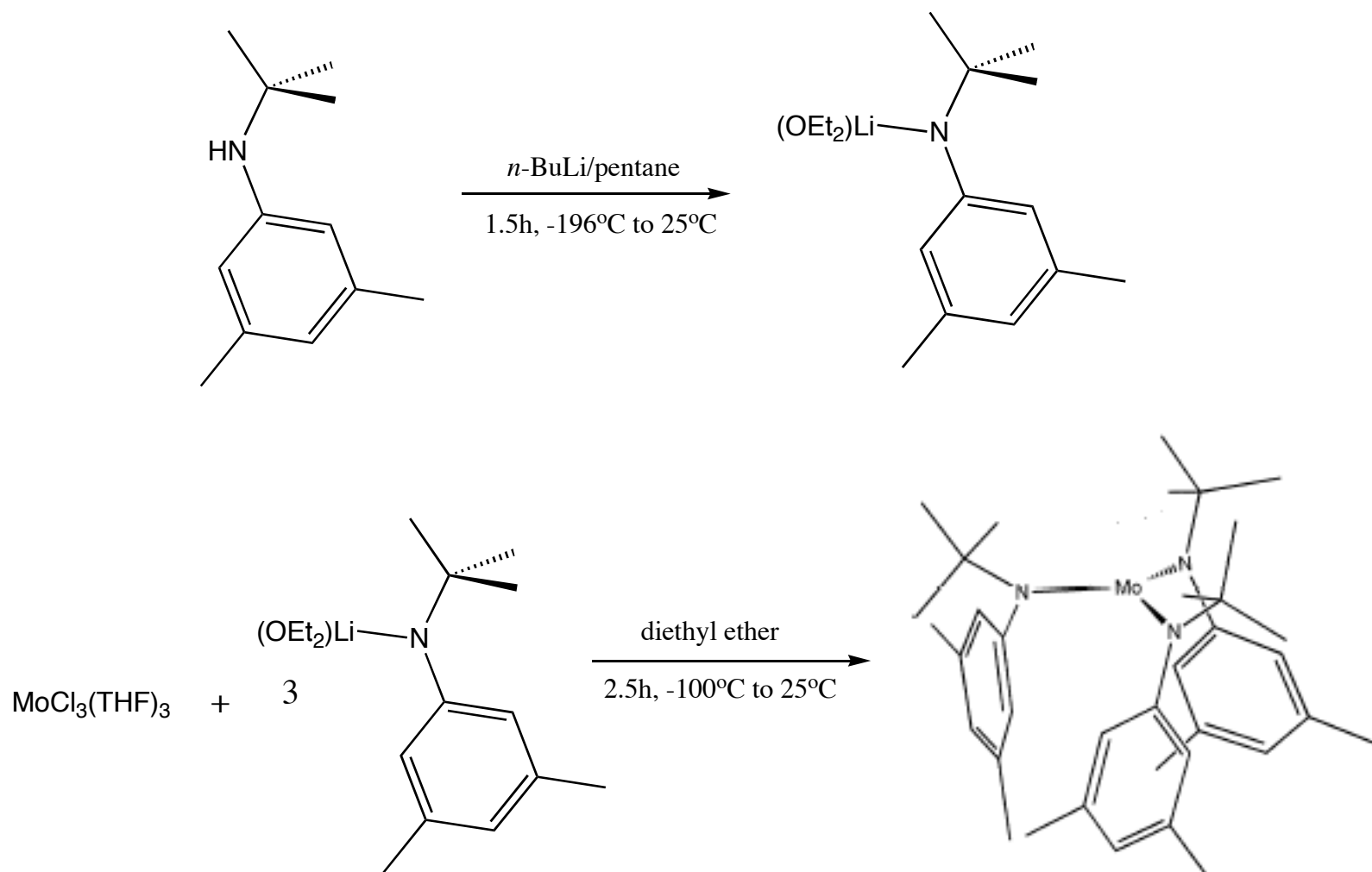
Combine spherical *t*-butyl groups and planar aromatic groups to allow for better crystallinity

Lack  $\beta$ -hydrogens and silyl groups which provide decomposition pathways

Amido groups are good  $\pi$ -donors and further stabilize electron deficient metal center



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



# $^1\text{H}$ NMR of $\text{Mo}[\text{N}(t\text{-Bu})\text{Ar}]_3$

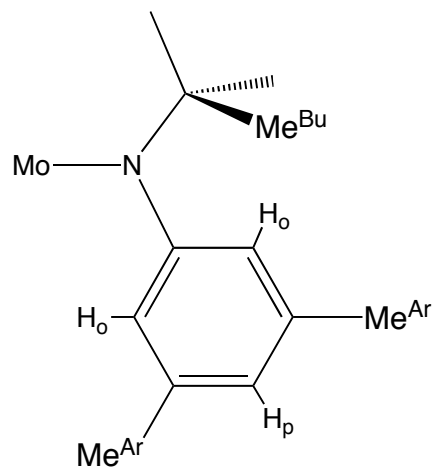
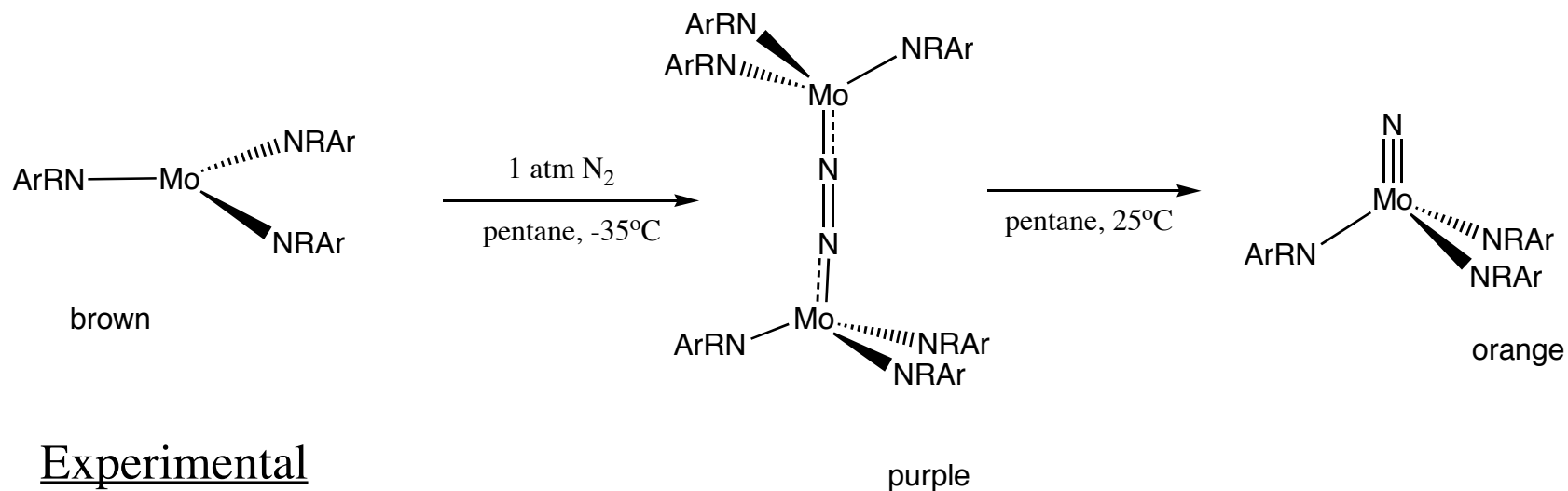


Image removed due to copyright reasons.

# Scission Reaction



## Experimental

Experimentally measured activation barrier of 23.3 kcal/mol

*J. Am. Chem. Soc.*, 118, 1996

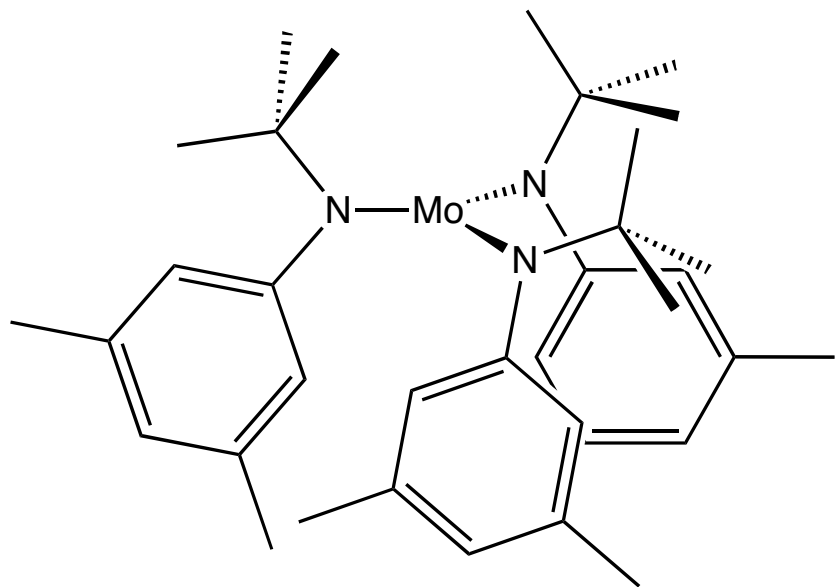
## Theoretical

No calculated barrier to end-on N<sub>2</sub> binding

Calculated activation barrier of 20.8 kcal/mol for break up of the  $\mu$ -N<sub>2</sub> dimer

*J. Am. Chem. Soc.*, 117, 1995

# Electronic Structure of $\text{Mo}[t\text{-Bu}(\text{Ar})]_3$

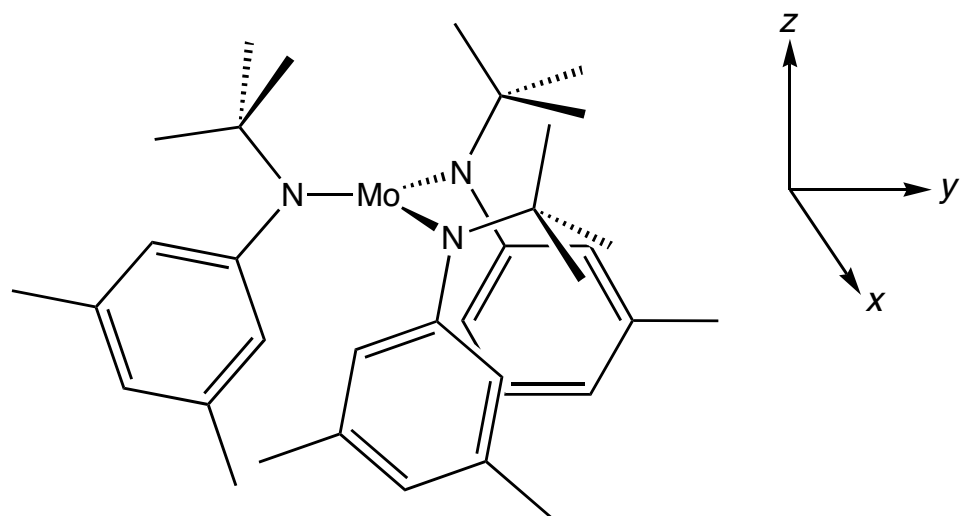


High spin quartet ground state

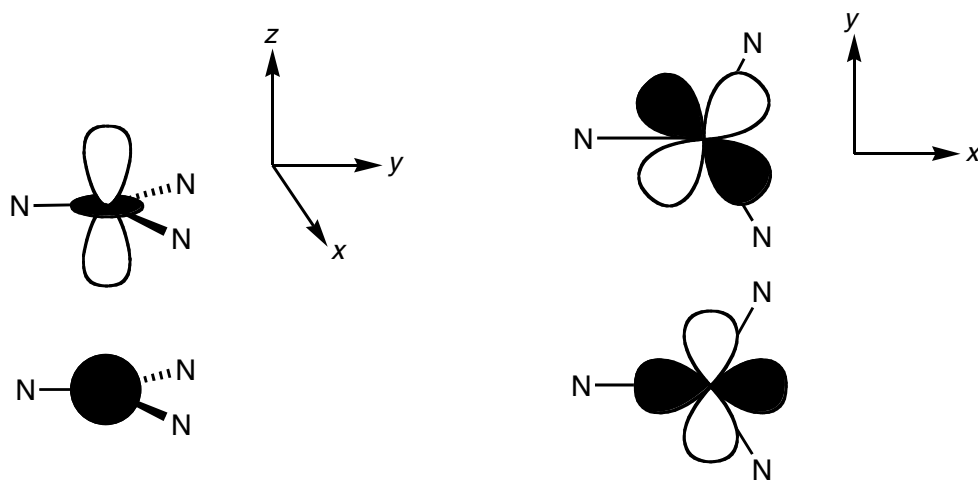
Three fold symmetric ( $C_{3v}$ )

*t*-Butyl groups lie on one side of the MoN<sub>3</sub> face and aryls on the other sterically protecting the metal atom

# Sigma Bonding



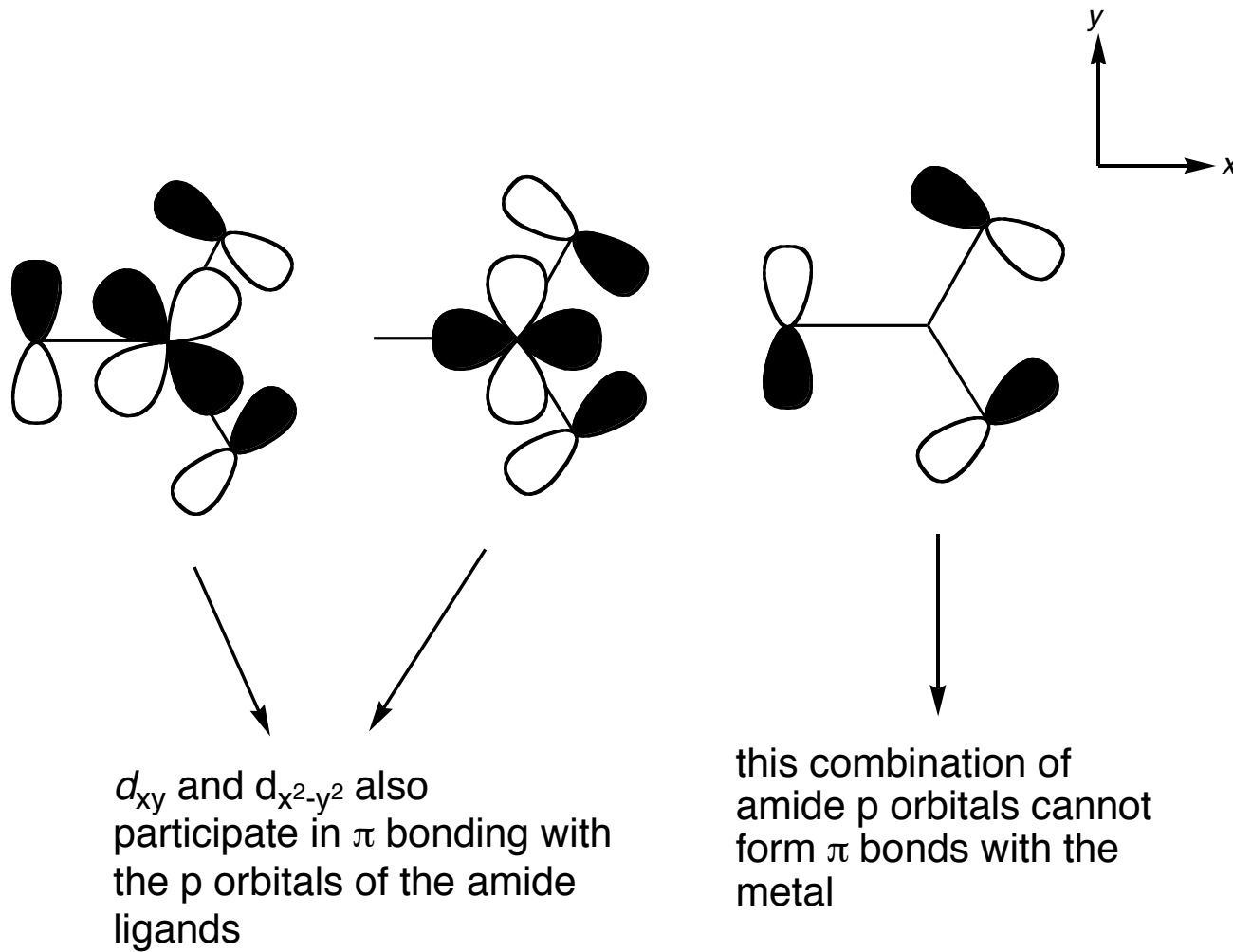
The three nitrogen atoms lie in a plane and direct their  $\sigma$  bonding orbitals at  $120^\circ$  towards Mo.



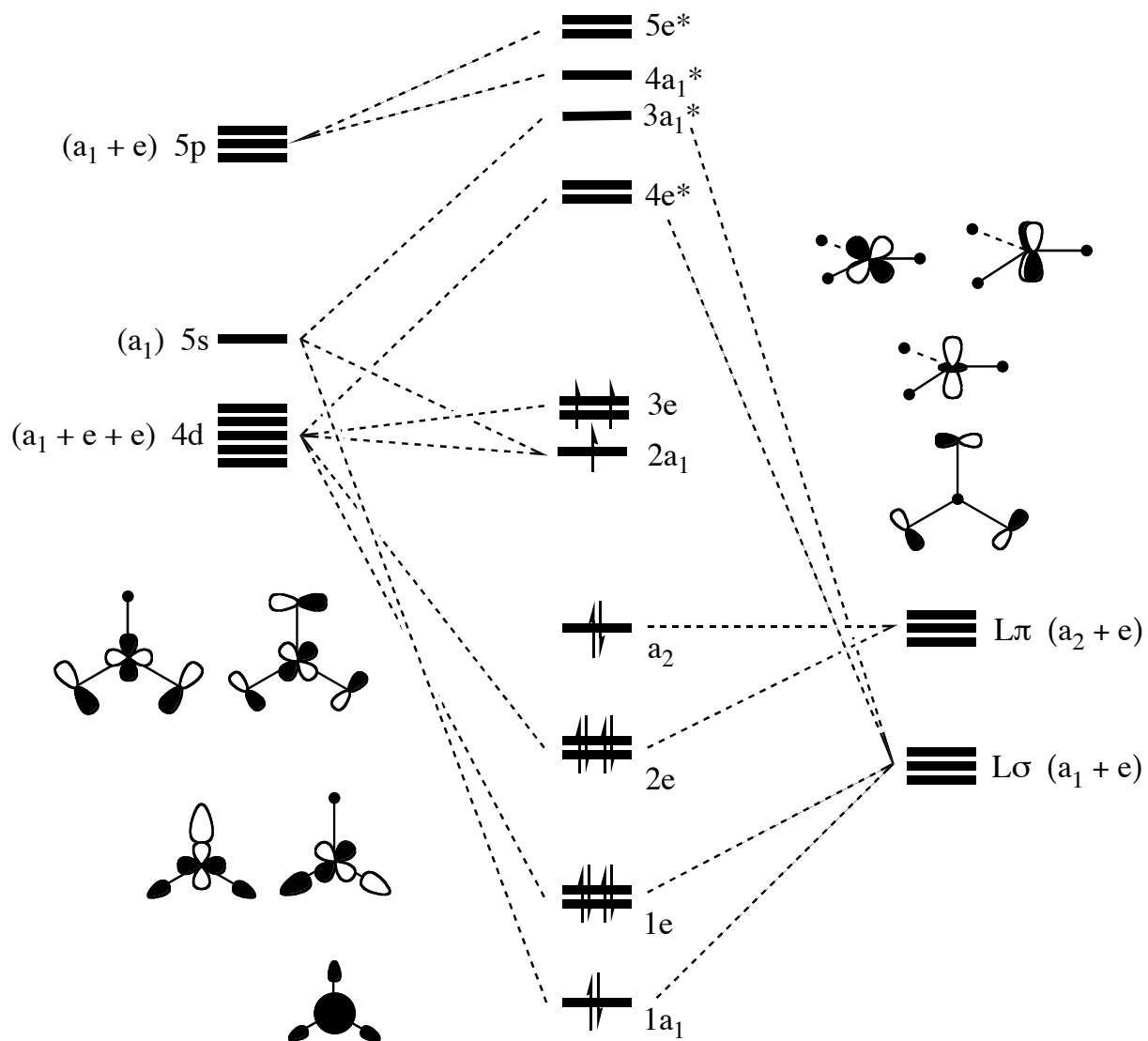
The orbitals on Mo that participate in the  $\sigma$  bonding will be  $s$ ,  $d_{x^2-y^2}$ ,  $d_{xy}$ , and to a smaller extent  $d_{z^2}$ .



# Pi Bonding Contribution



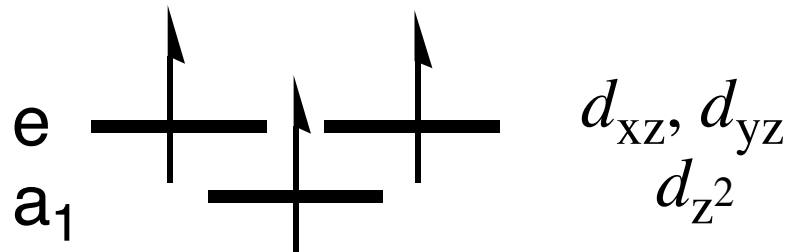
# MO Diagram



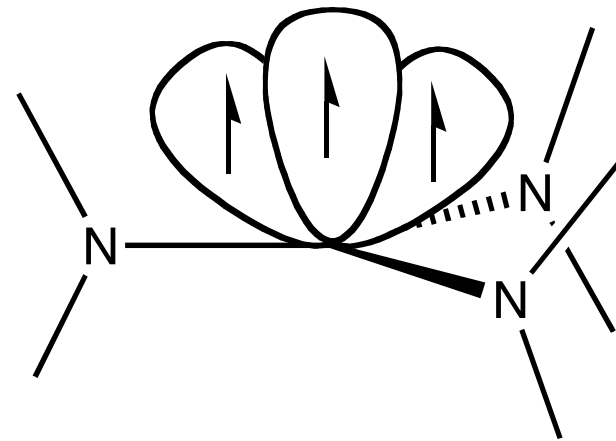
Using ligand field theory, we can develop a MO diagram for the  $\text{MoL}_3$  molecule by considering how the ligand orbitals transform in  $C_{3v}$  symmetry.

We then consider the symmetry allowed interactions with the orbitals on Mo ( $s$ ,  $p$ , and  $d$ ).

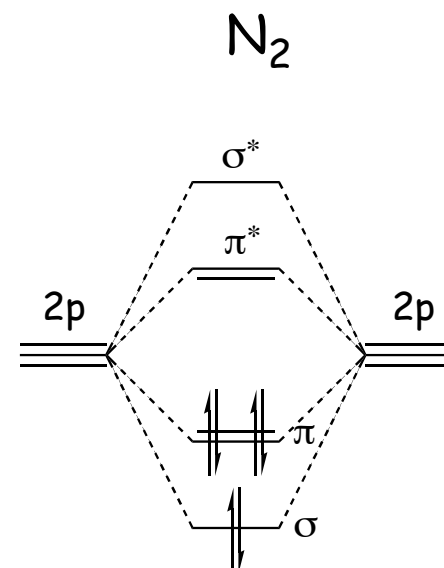
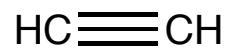
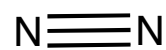
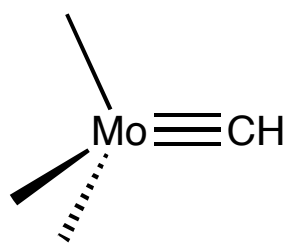
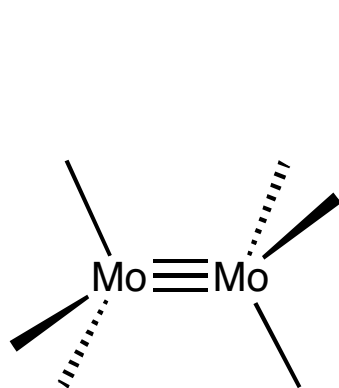
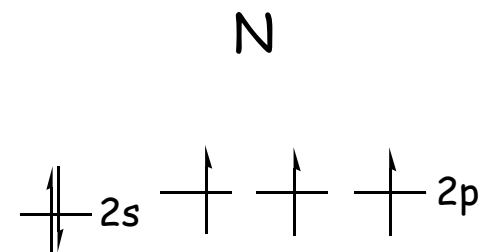
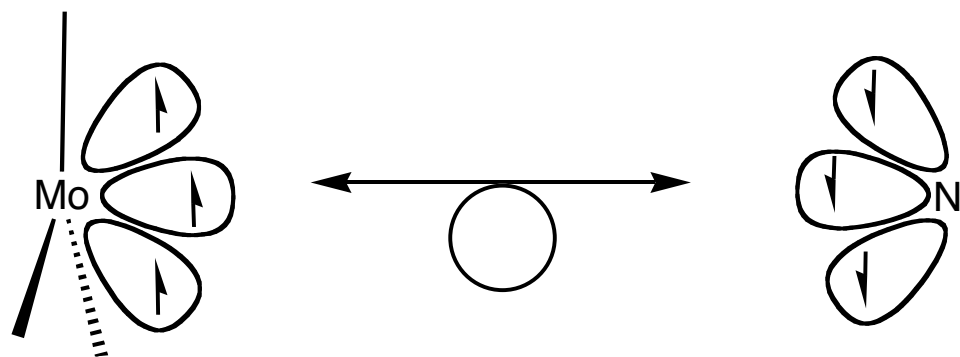
# *d*-Orbital Configuration



Both crystal field theory and ligand field theory result in an orbital picture that places three unpaired electrons in lower lying non-bonding *d*-orbitals

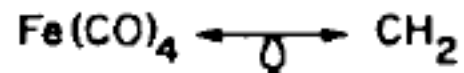


# Isolobal Analogy



# Roald Hoffmann Nobel Prize

We will call two fragments *isolobal* if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar-not identical, but similar.



Nobel lecture, 8 December 1981

# Mechanism of N<sub>2</sub> Binding and Activation

MO diagram

See Scheme 1 in Laplaza, Catalina et al. "Dinitrogen Cleavage by Three-Coordinate Molybdenum(III) Complexes: Mechanistic and Structural Data." *J Am Chem Soc* 118 (1996): 8623-8638.

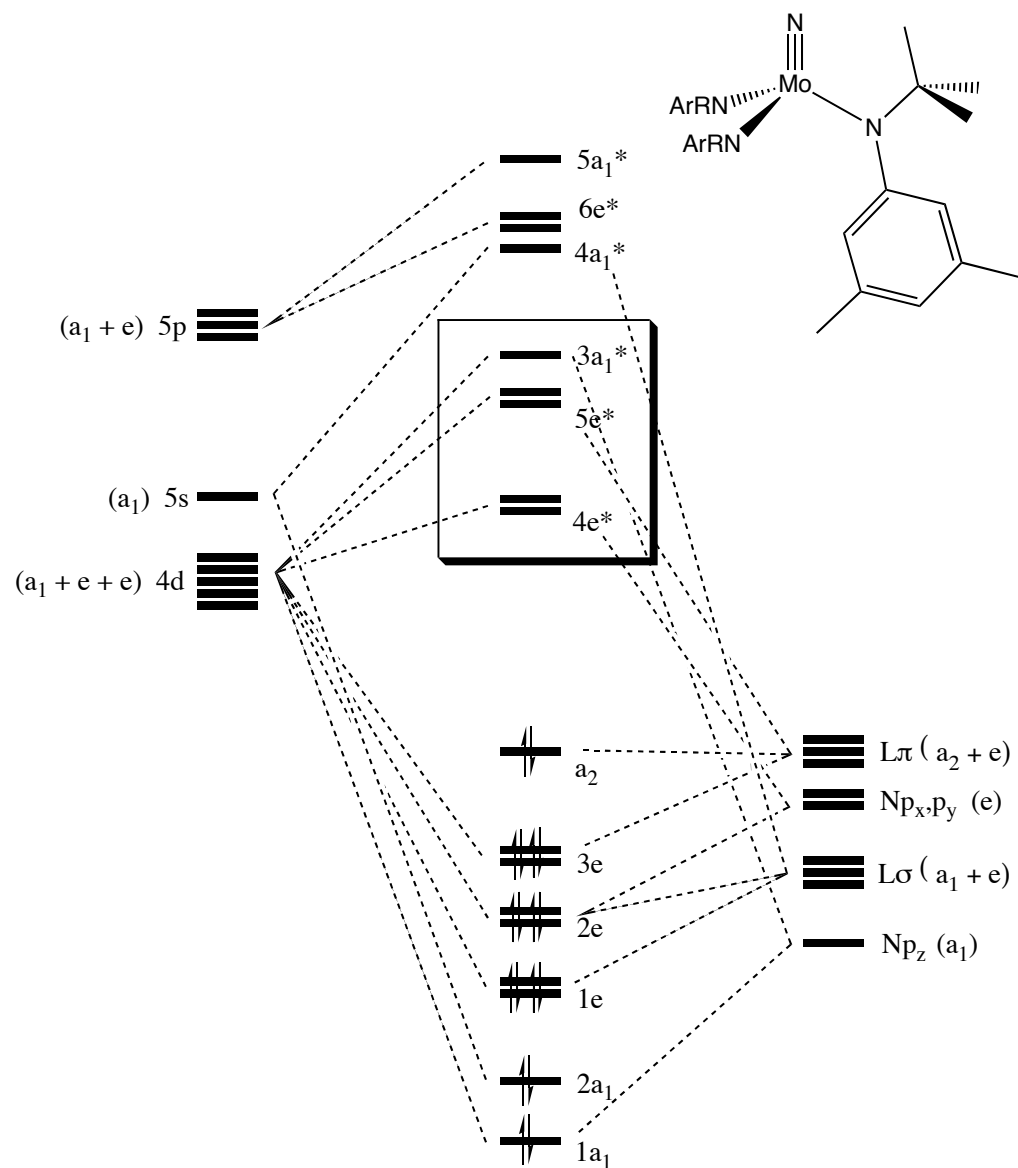
See Scheme 1 in Laplaza, Catalina et al. "Dinitrogen Cleavage by Three-Coordinate Molybdenum(III) Complexes: Mechanistic and Structural Data." *J Am Chem Soc* 118 (1996): 8623-8638.

End on binding of N<sub>2</sub>

Low temperature encourages N<sub>2</sub> solubility

Only requires 1 atm of pressure

# Electronic Structure of $\text{NMo}[\text{N}(t\text{-Bu})\text{Ar}]_3$



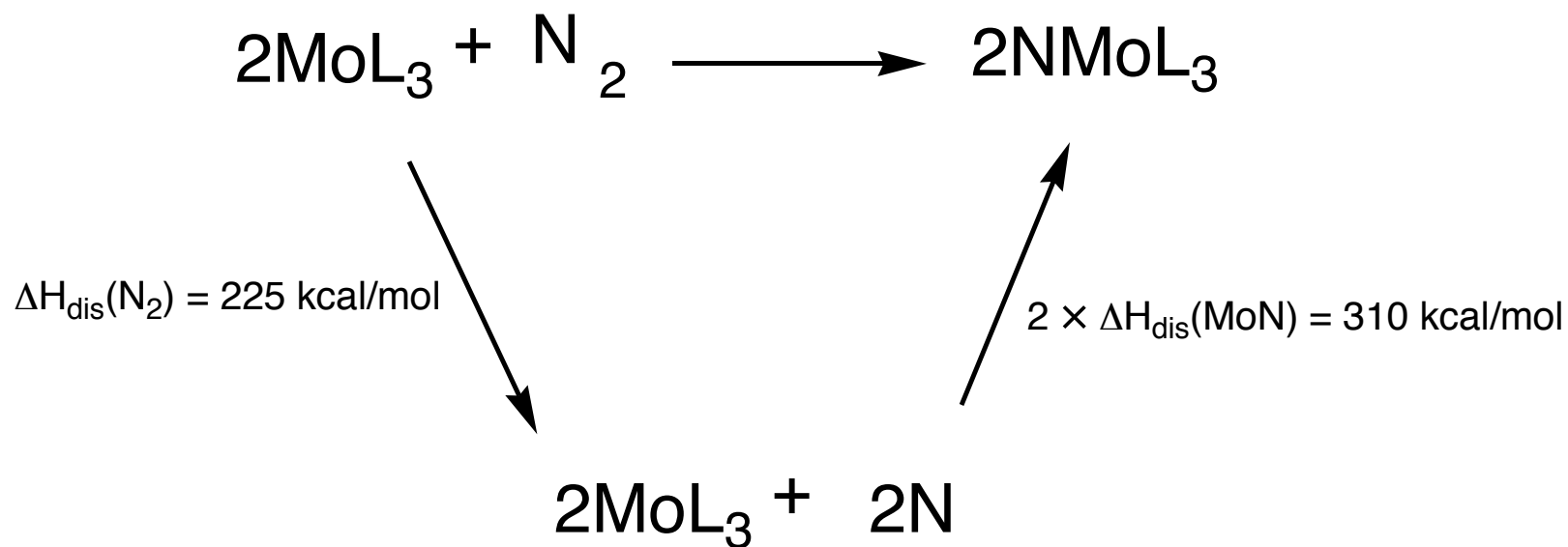
-Mo(VI)  $d^0$

-16e-complex

-1 $\sigma$  and 2 $\pi$

bonds to N atom

# Thermodynamics



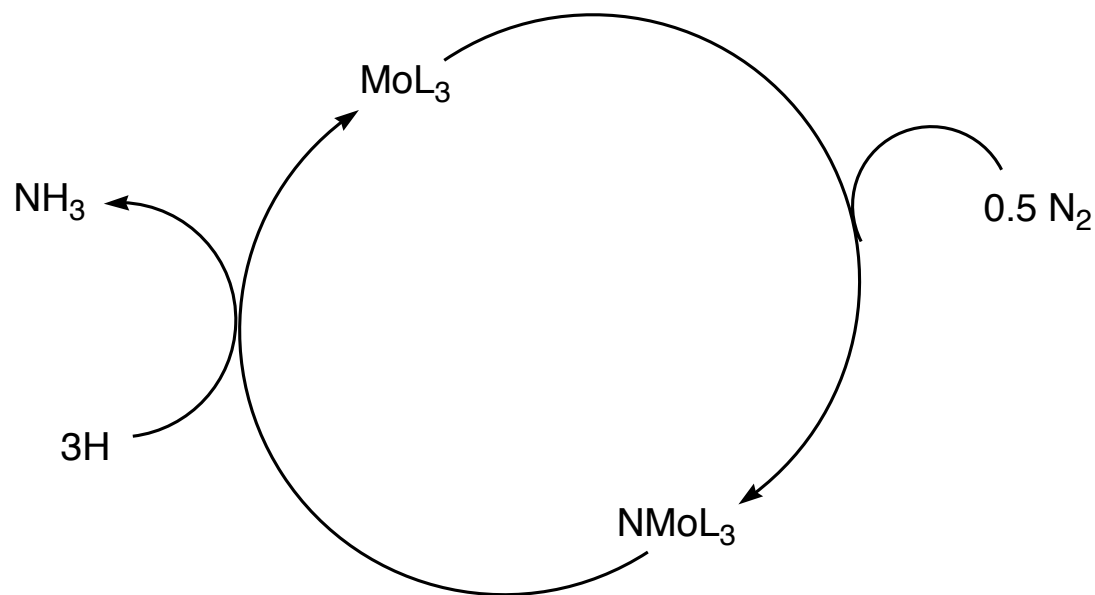
The  $\sigma$  and  $\pi$  components of the Mo-N triple bond result in a very strong bonding interaction. This new interaction compensates for the energy lost in breaking the  $\text{N}_2$  triple bond.



# Potential for Catalysis

In order to create a catalytic system, we must regenerate the  $\text{MoL}_3$  complex.

Attempts at using  $\text{MoL}_3$  as a  $\text{N}_2$  to  $\text{NH}_3$  catalyst have thus far been unsuccessful.



# Schrock System

See:

Yandulov, Dmitry V., and Richard R. Schrock. "Reduction of Dinitrogen to Ammonia at a Well-Protected Reaction Site in a Molybdenum Triamidoamine Complex." *J Am Chem Soc* 124 (2002): 6252-6253.

See:

Yandulov, Dmitry V., and Richard R. Schrock. "Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center." *Science* 301 (2003): 76-78.

# Conclusions

The  $\text{Mo}[\text{N}(t\text{-Bu})\text{Ar}]_3$  reacts with  $\text{N}_2$  at low temperature to cleave the triple bond and form a pair of Mo(VI) nitride complexes.

The reactivity of the  $\text{MoL}_3$  fragment can be rationalized by considering the electronic structure of the molecule and the isolobal analogy.

The CHM 5.33 experiments provides a unique opportunity to explore a recent discovery in the area of inorganic chemistry.