

Scission of Dinitrogen by a Molybdenum(III) Xylidene Complex

CHM 5.33

Fall 2004

Outline

- Introduction: basis for the experiment and techniques involved
- Background: the nitrogen molecule and the inorganic chemistry of N_2 in a historical context
- Framework for the synthetic chemistry
- Aspects of bonding and molecular orbital theory
- Conclusions and comments on catalytic nitrogen fixation

Introduction

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

Dinitrogen Cleavage by a Three-Coordinate Molybdenum(III) Complex

Catalina E. Laplaza and Christopher C. Cummins*

Cleavage of the relatively inert dinitrogen (N_2) molecule, with its extremely strong $N\equiv N$ triple bond, has represented a major challenge to the development of N_2 chemistry. This report describes the reductive cleavage of N_2 to two nitrido (N^{3-}) ligands in its reaction with $Mo(NR\text{Ar})_3$, where R is $C(CD_3)_2CH_3$ and Ar is 3,5- $C_6H_3(CH_3)_2$, a synthetic three-coordinate molybdenum(III) complex of known structure. The formation of an intermediate complex was observed spectroscopically, and its conversion (with $N\equiv N$ bond cleavage) to the nitrido molybdenum(VI) product $N\equiv Mo(NR\text{Ar})_3$ followed first-order kinetics at 30°C. It is proposed that the cleavage reaction proceeds by way of an intermediate complex in which N_2 bridges two molybdenum centers.

Science, 268, 1995

Aspects of the Lab

The discovery that $\text{Mo}(\text{NRAr})_3$ could bind and cleave N_2 was adapted to a CHM 5.33 experiment in 1998.

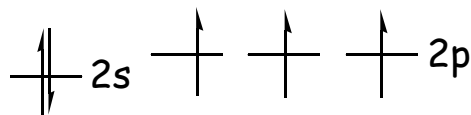
The experiment involves basic organic synthesis and introduces some rudimentary aspects of the manipulation of air and moisture sensitive materials.

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 N₂

N

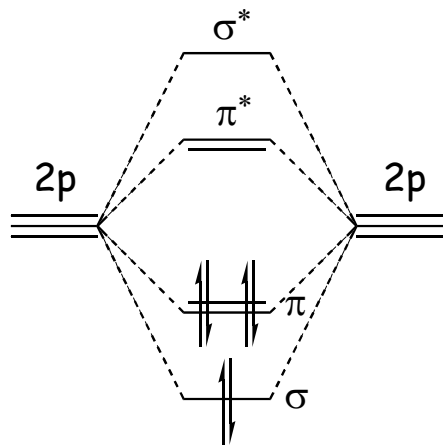


free gaseous atom is a ground-state quartet
(2s²2p³)

nitrogen is trivalent - prefers to form three bonds
(NH₃, HCN, N₂)

“three electron oxidant”

N₂



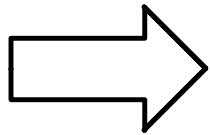
extremely important naturally and synthetically

N₂ (dinitrogen) is the most abundant molecule
in the earth's atmosphere comprising ~80%

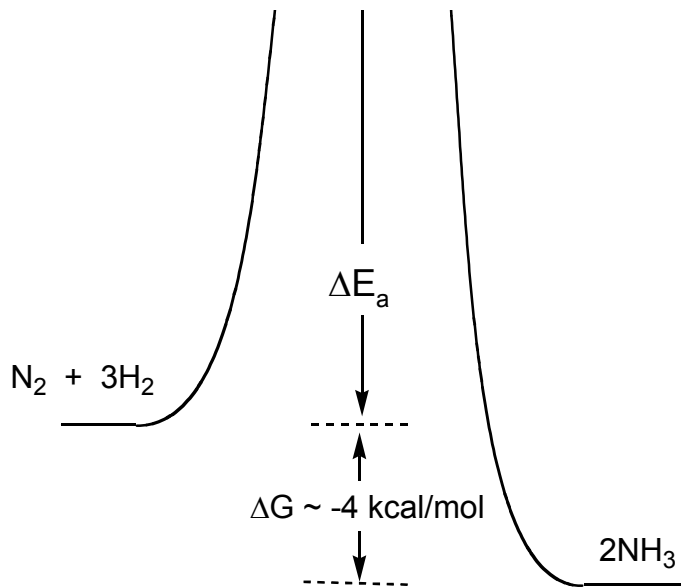
very stable triple bond ($\Delta H_{\text{dis}} = 225$ kcal/mol)
renders N₂ practically inert

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



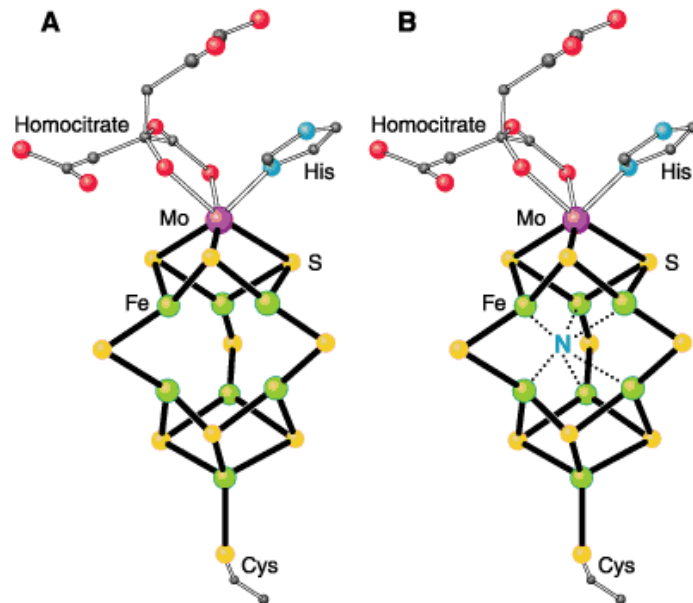
Thermodynamically, the reaction of dinitrogen with H_2 is favorable

The problem lies in overcoming the kinetic barrier

Nitrogen Fixation

In nature, dinitrogen 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).



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

Science, 297, 2002

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

Excerpt from Carl Bosch's 1932 Nobel Prize Lecture

However, as a result of very broadly based series of experiments using our rapidly expanded experimental technique, we succeeded in preparing relatively fast-acting, technically perfect, easily manipulable, stable and inexpensive catalysts, chiefly those with iron as the active substance* which are currently in universal use presumably exclusively for the synthesis of ammonia.

* Molybdenum, particularly in mixtures, was also found to be an excellent catalyst; D.R.P. 246, 377, October 22, 1910.

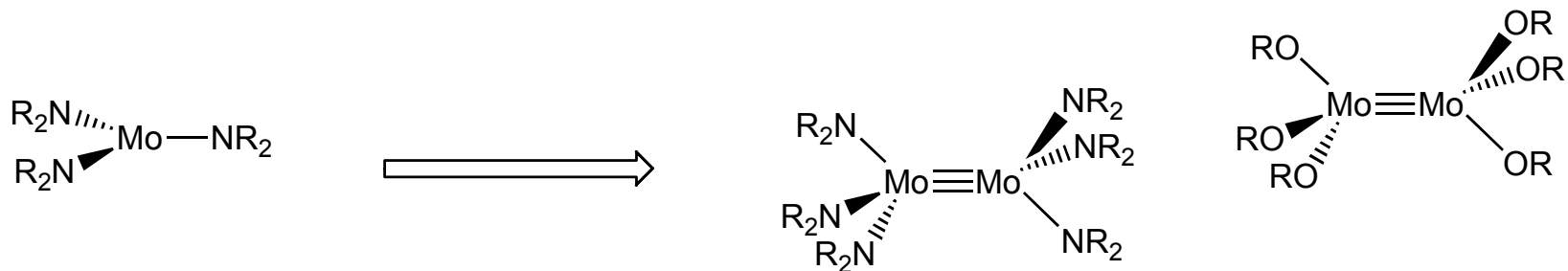
Why Molybdenum?

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

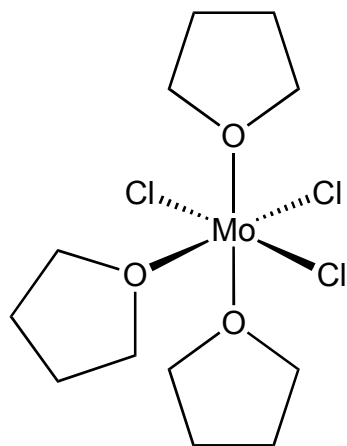
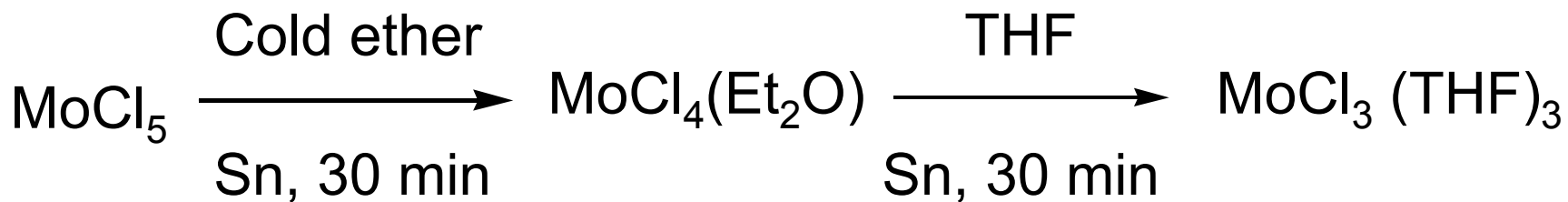
Mo(III) is a three electron reductant (Mo highest ox. state is 6)

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

producing a coordinatively unsaturated Mo(III) complex poses a formidable synthetic challenge
amide and alkoxide ligands have been shown to support three coordinate complexes, but Mo-Mo triple bonds and solvent adducts are a problem



Molybdenum Precursors



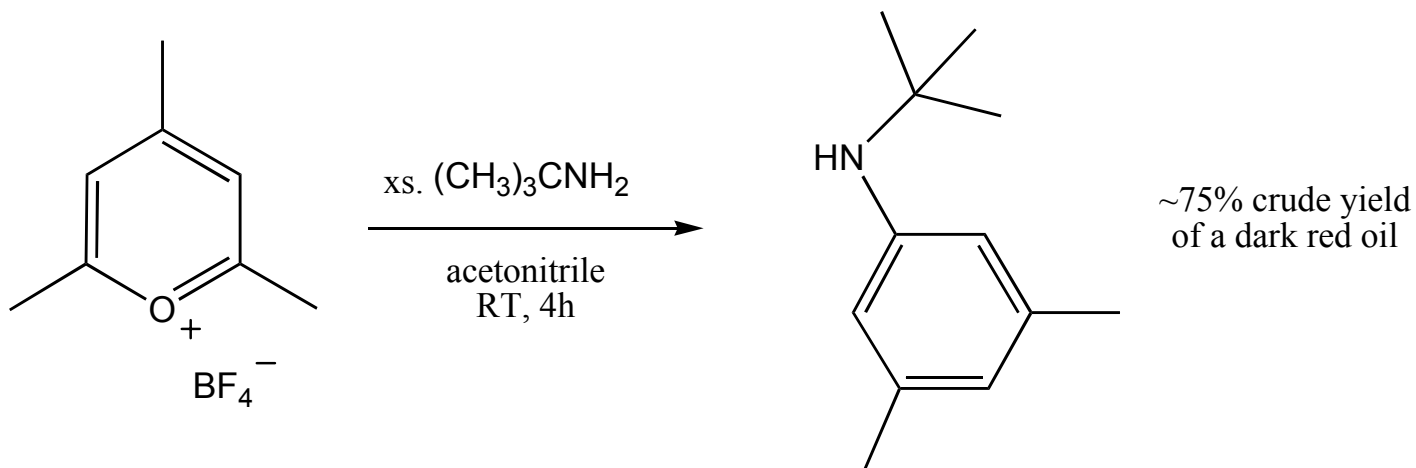
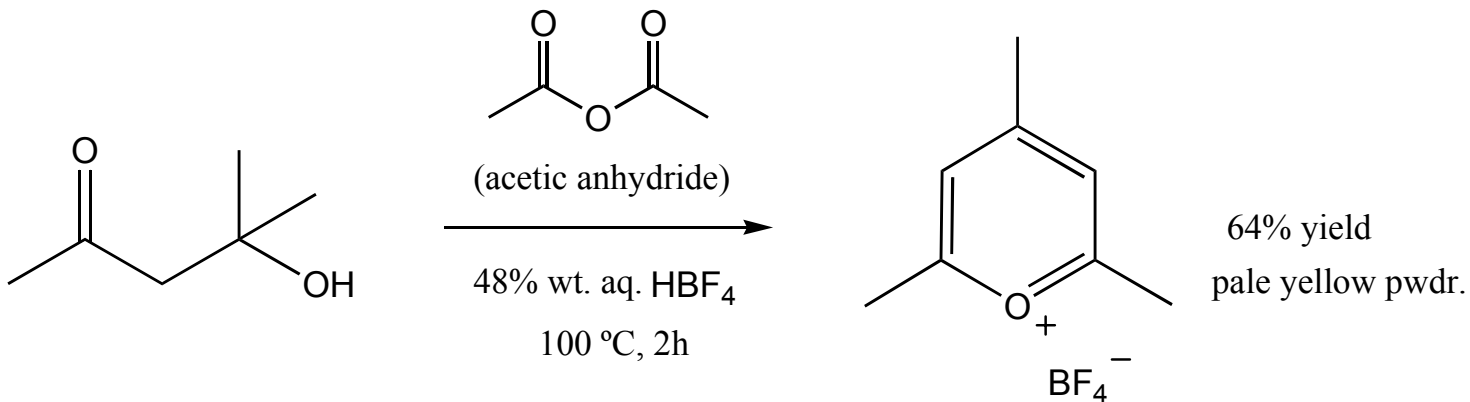
Orange crystalline solid

Solid state structure shows *mer* geometry

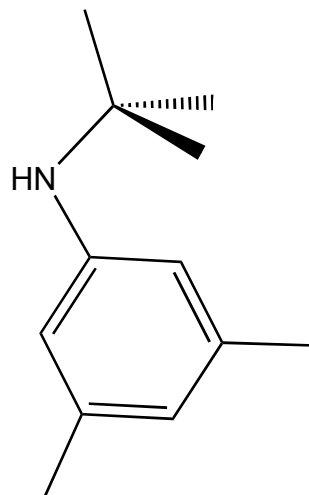
Mo(III) is paramagnetic and contains 3 unpaired electrons

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

Preparation of the *t*-Butyl Xylidene Ligand



Advantages of the Ligand



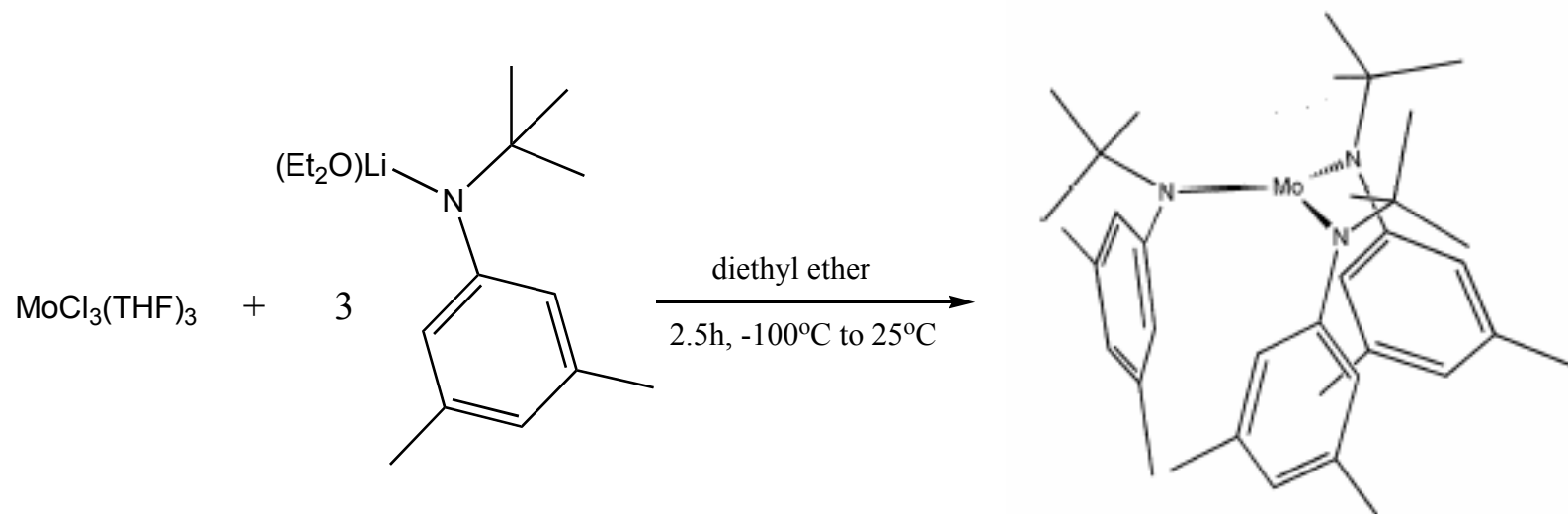
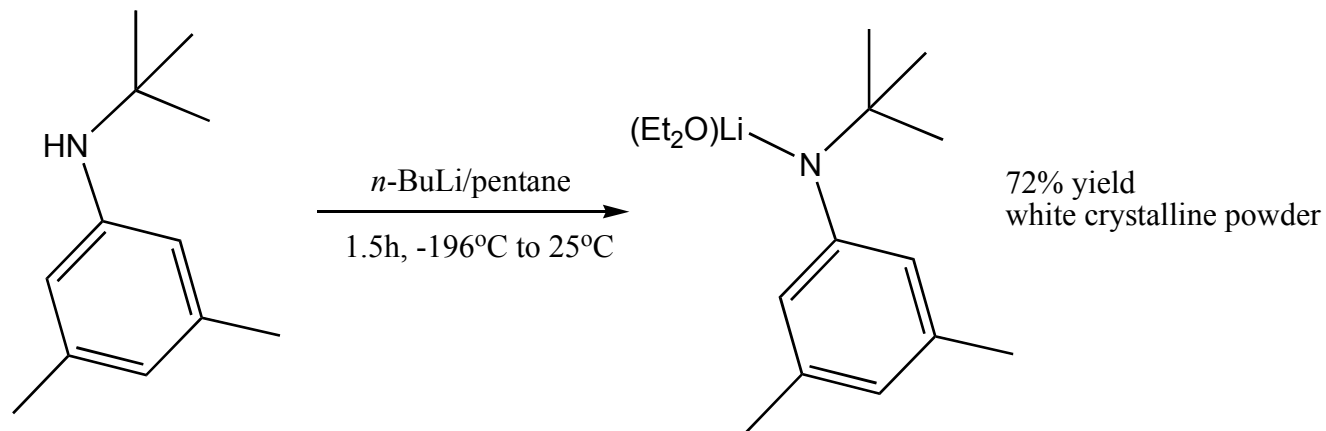
provide steric bulk to discourage metal-metal bonding and only allow access to small molecules

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

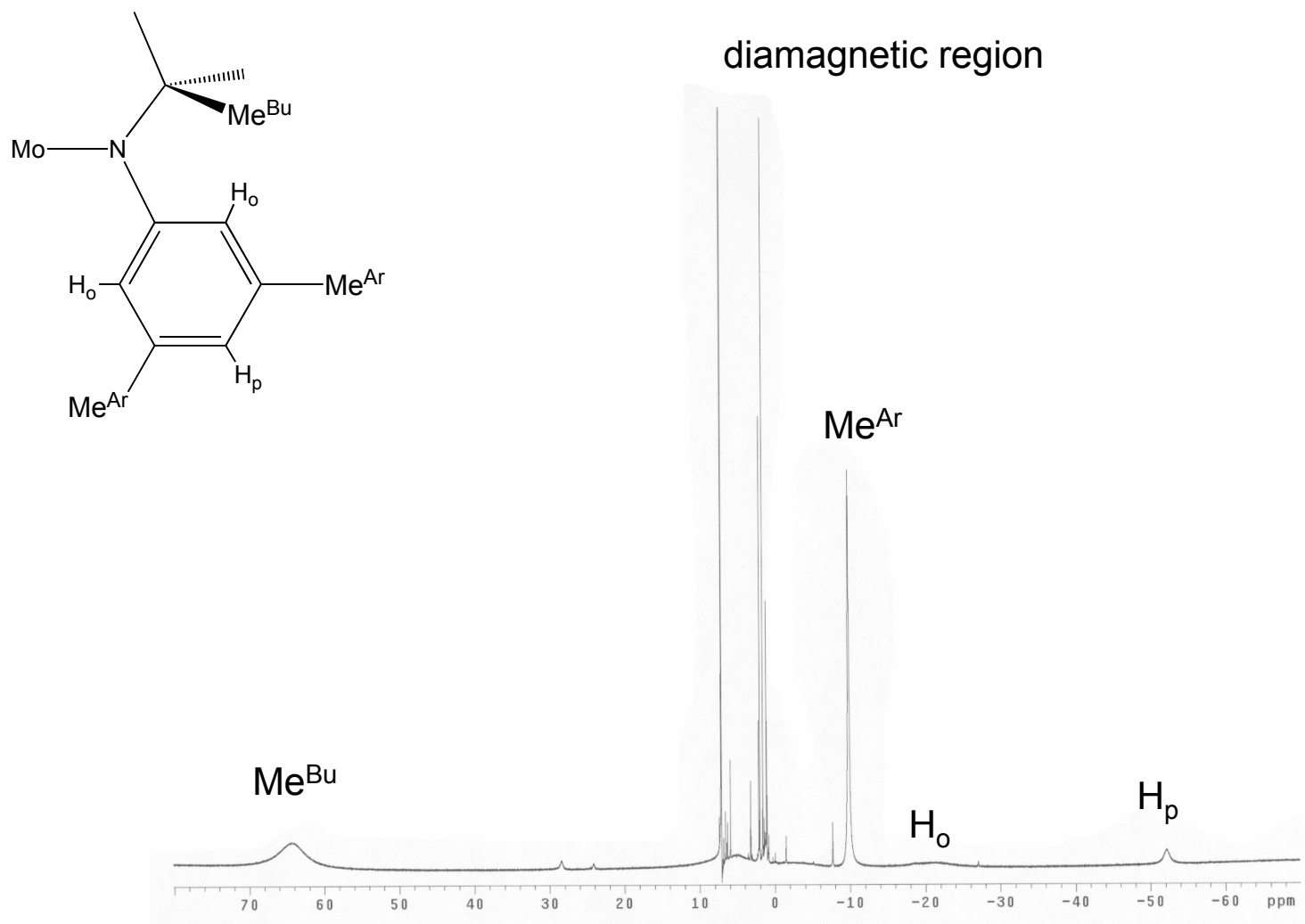
lack β -hydrogens and silyl groups which provide decomposition pathways

amido groups are good π -donors and further stabilize electron deficient metal center

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



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



^1H NMR of Paramagnetic Compounds

Proton spectra of diamagnetic compounds (e.g. organic compounds) typically have very sharp line widths and occur between 0 and 12 ppm.

In contrast, proton spectra of paramagnetic compounds may contain very broad line widths, and occur in a range greater than 200 ppm.

Line broadening is caused by the short relaxation time of the electron (spin-lattice relaxation) and/or hyperfine electron-nuclear coupling.

Paramagnetic chemical shift is a result of two components:

Pseudo-contact shift:

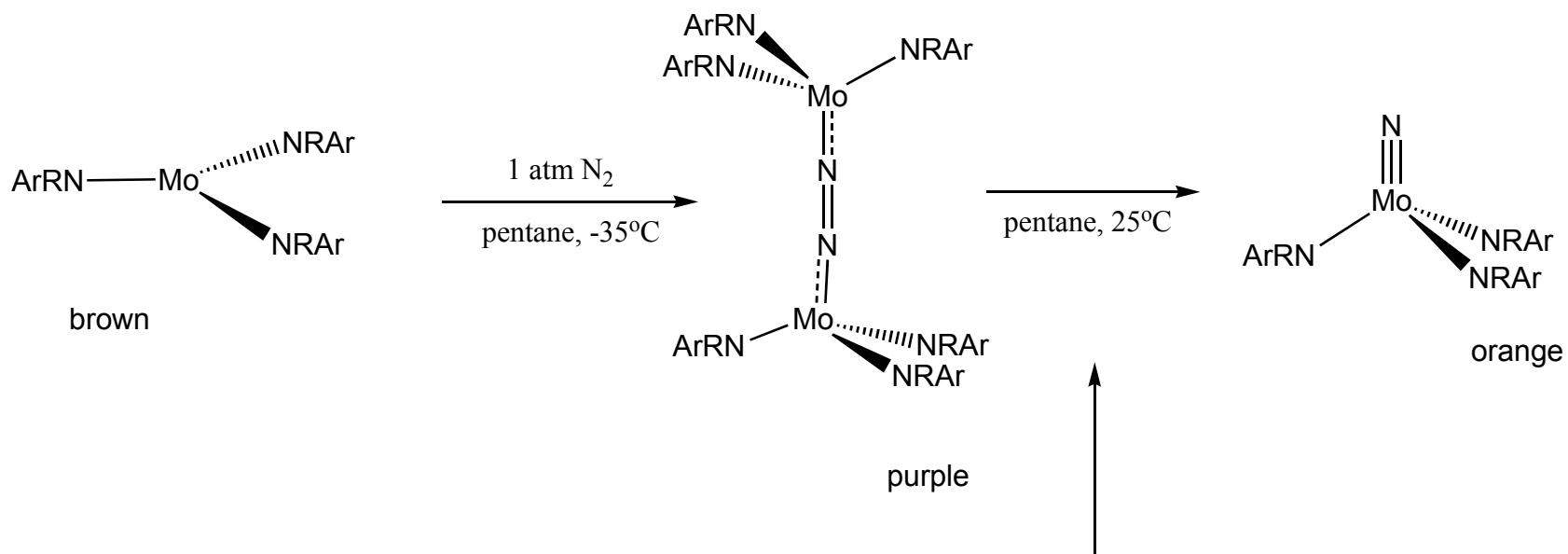
Through space dipolar interaction between the magnetic moments of the nucleus and the electron (small effect)

Contact shift:

Concerns the coupling between the electron and nucleus (large effect)

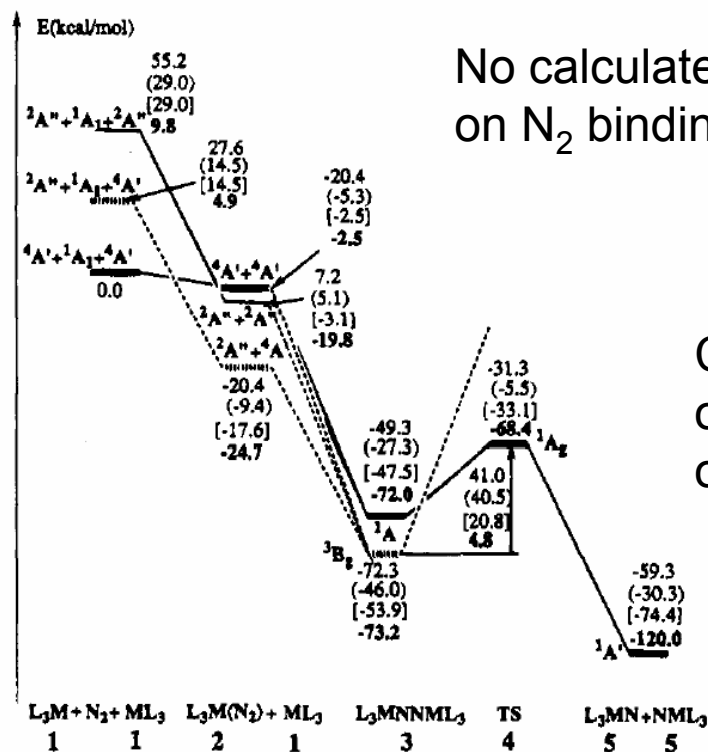
Used as a measure of the unpaired spin density at the nucleus

Scission Reaction



Experimentally measured activation barrier of 23.3 kcal/mol

Theoretical Calculations

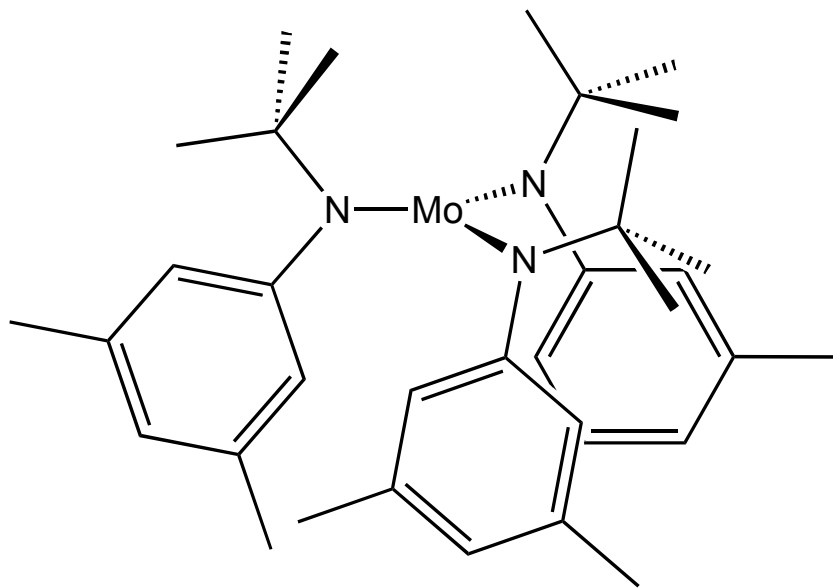


No calculated barrier to end-on N_2 binding

Calculated activation barrier of 20.8 kcal/mol for break up of the μ - N_2 dimer

Figure 1. Calculated relative energies (kcal/mol) of the stationary points on the potential energy surface of the reaction $N_2 + 2ML_3 \rightarrow 2(NML_3)$, where $L = H, Cl$ (in parentheses) and NH_2 (in brackets) for $M = Mo$, and $L = NH_2, M = W$ (bold). The energy scale depicted is for $Mo(NH_2)_3$.

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

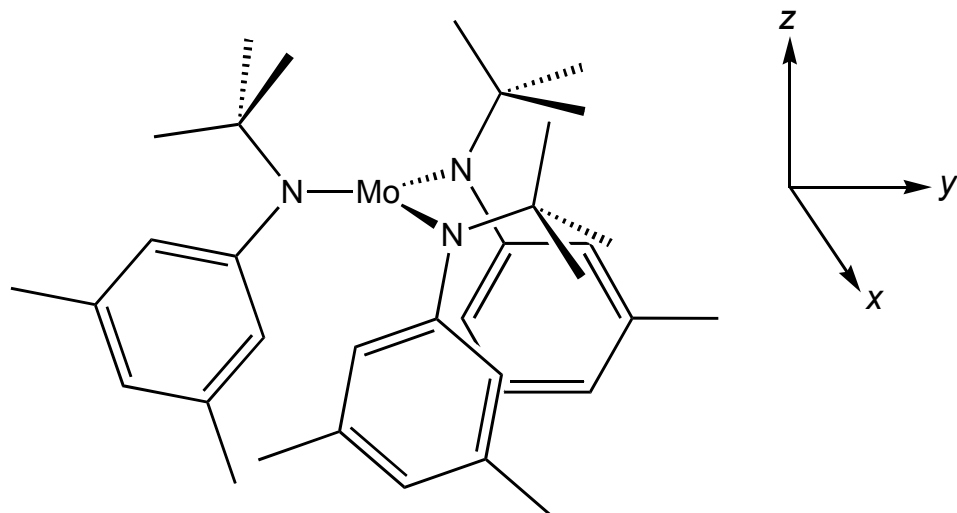


high spin quartet ground state

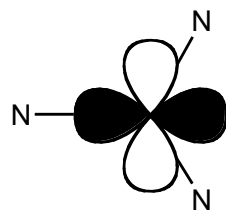
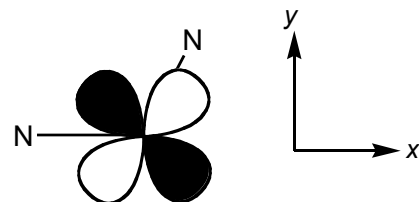
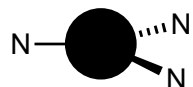
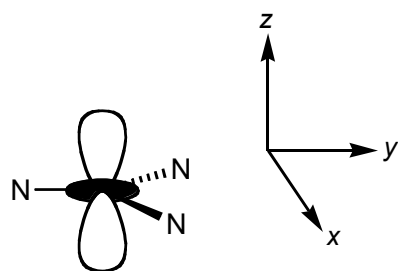
three fold symmetric (C_{3v})

t-butyl groups lie on one side of the MoN_3 face and aryls on the other

Sigma Bonding

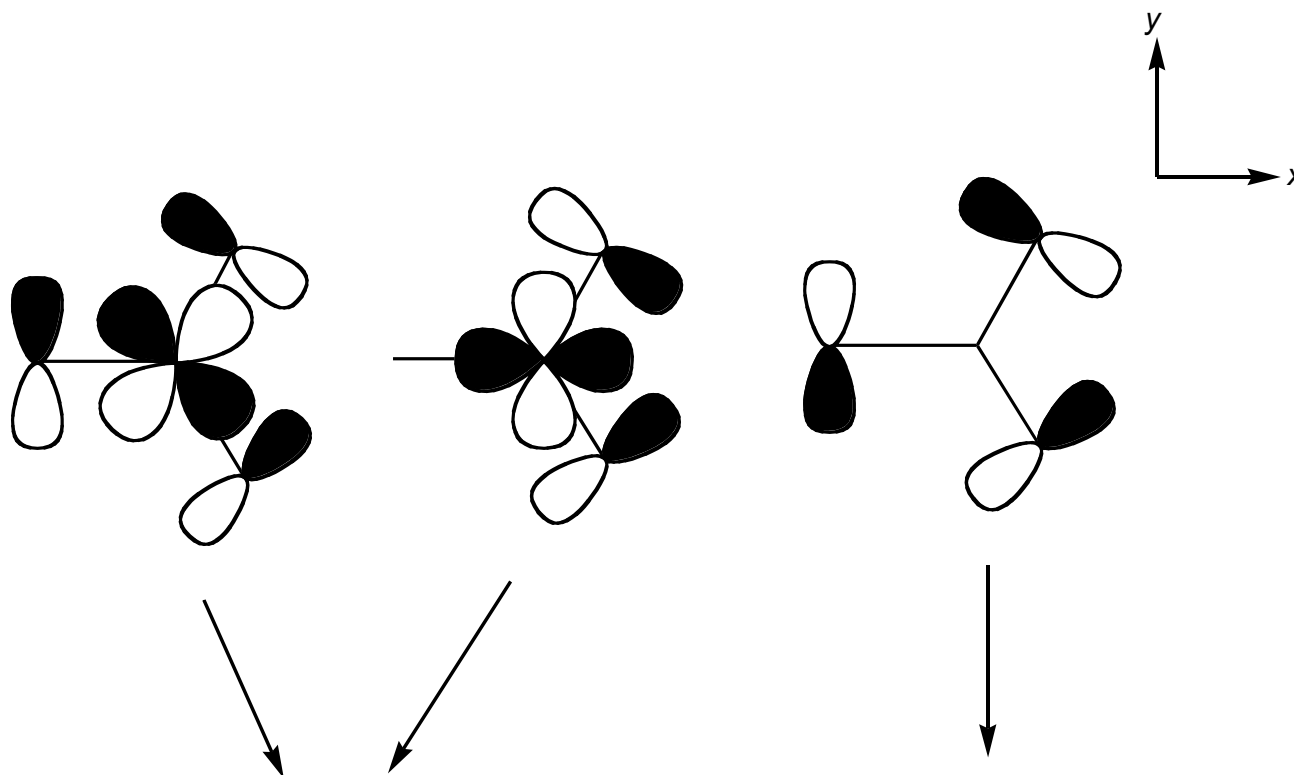


The three nitrogen atoms lie in a plane and direct their σ bonding orbitals at 120° towards Mo.



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

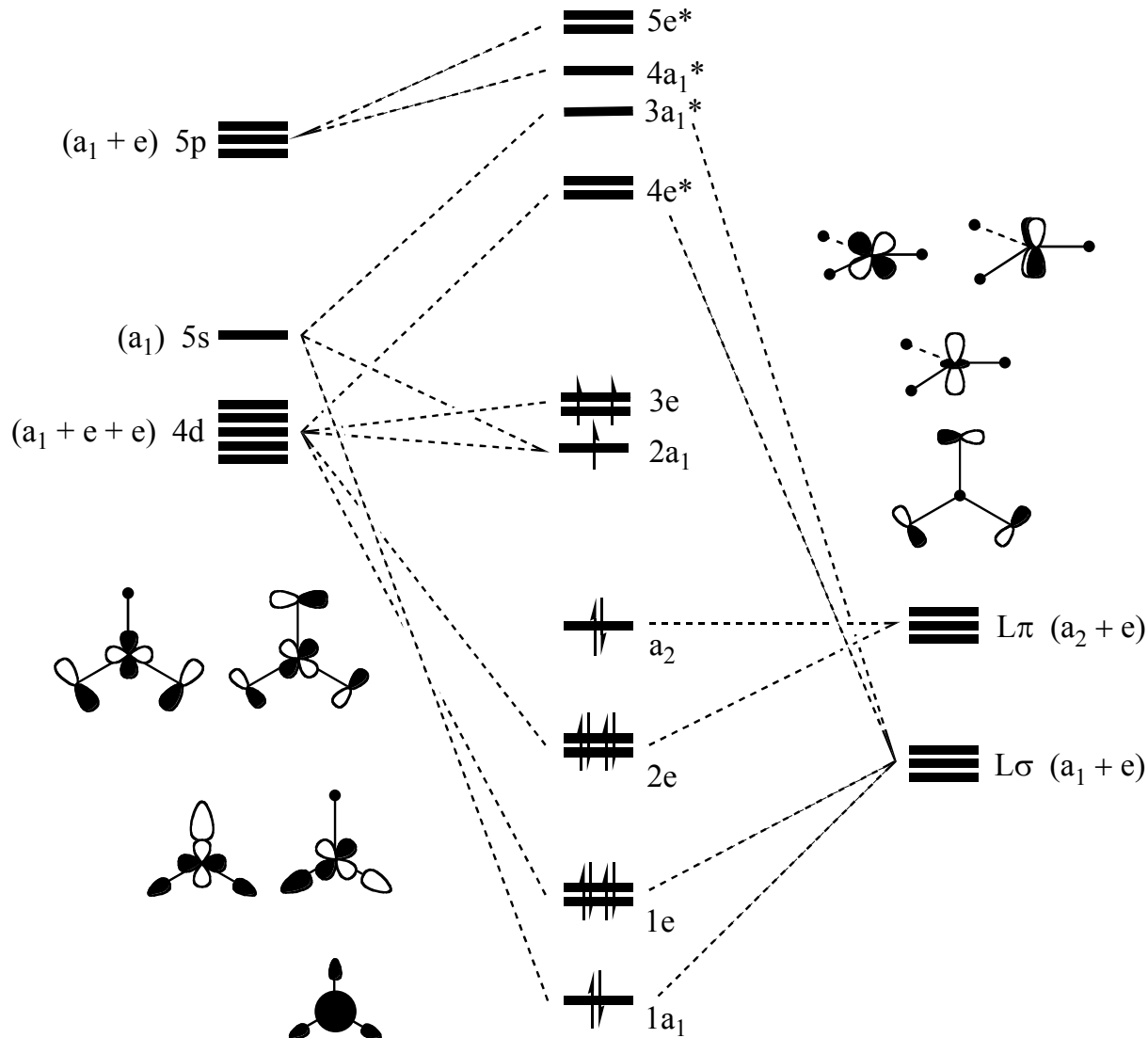
Pi Bonding Contribution



d_{xy} and $d_{x^2-y^2}$ also participate in π bonding with the p orbitals of the amide ligands

this combination of amide p orbitals cannot form π bonds with the metal

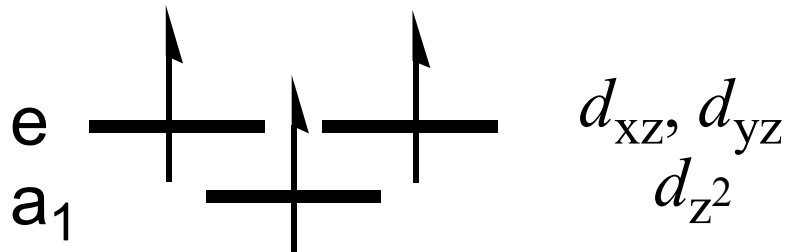
MO Diagram



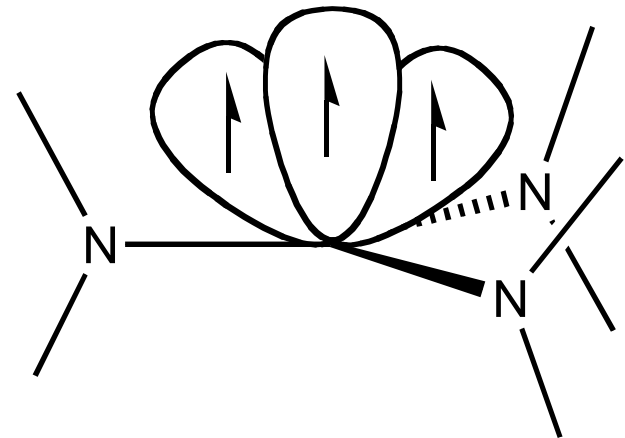
Using ligand field theory, we can develop a MO diagram for the MoL_3 molecule by considering how the ligand orbitals transform in C_{3v} symmetry.

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

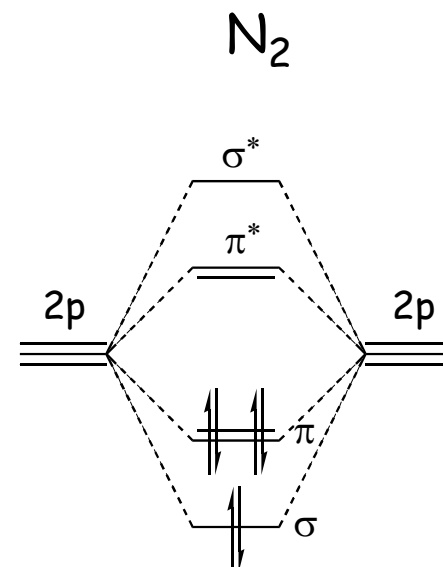
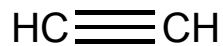
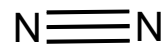
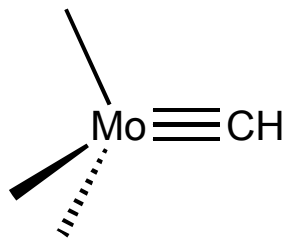
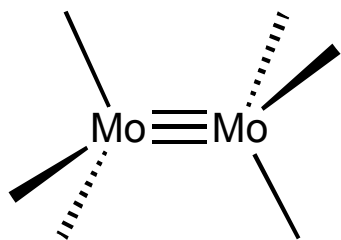
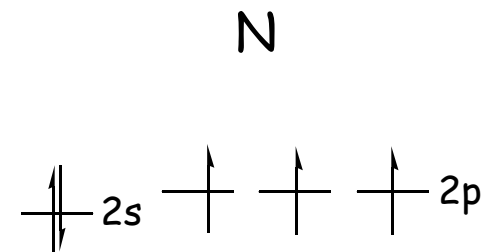
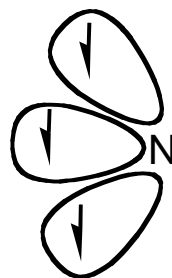
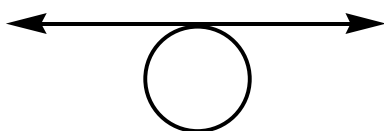
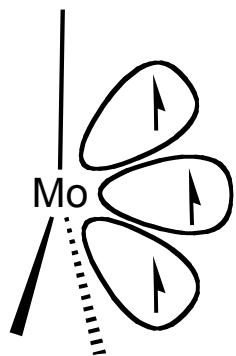
d-Orbital Configuration



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.



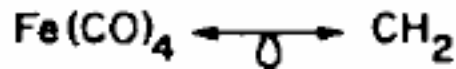
Isolobal Analogy



Roald Hoffmann Nobel Prize



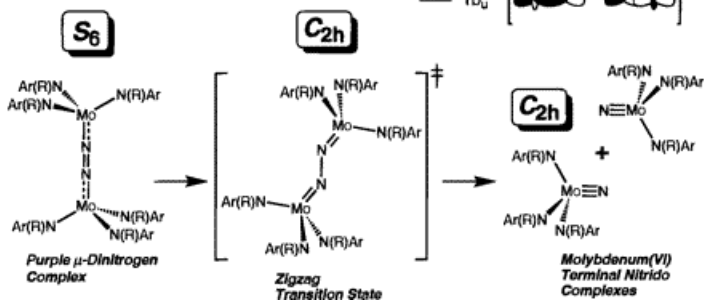
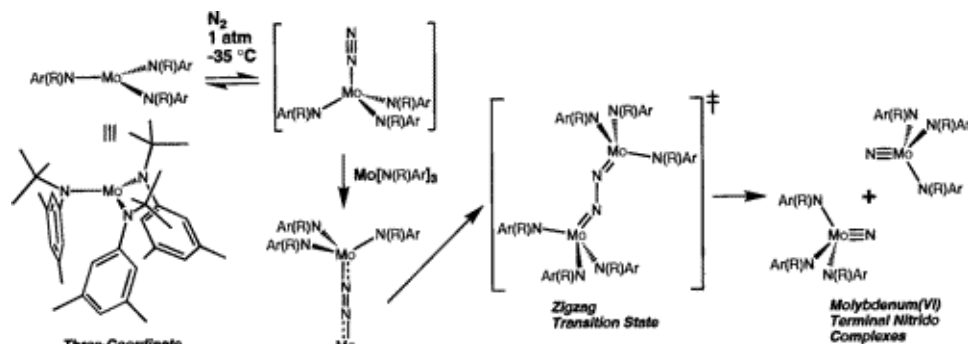
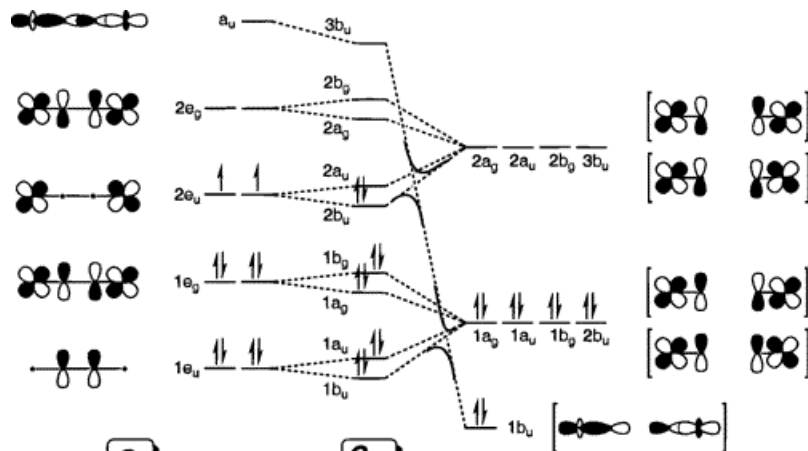
We will call two fragments *isolobal* if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar-not identical, but similar.



Nobel lecture, 8 December 1981

Mechanism of N₂ Binding and Activation

MO diagram



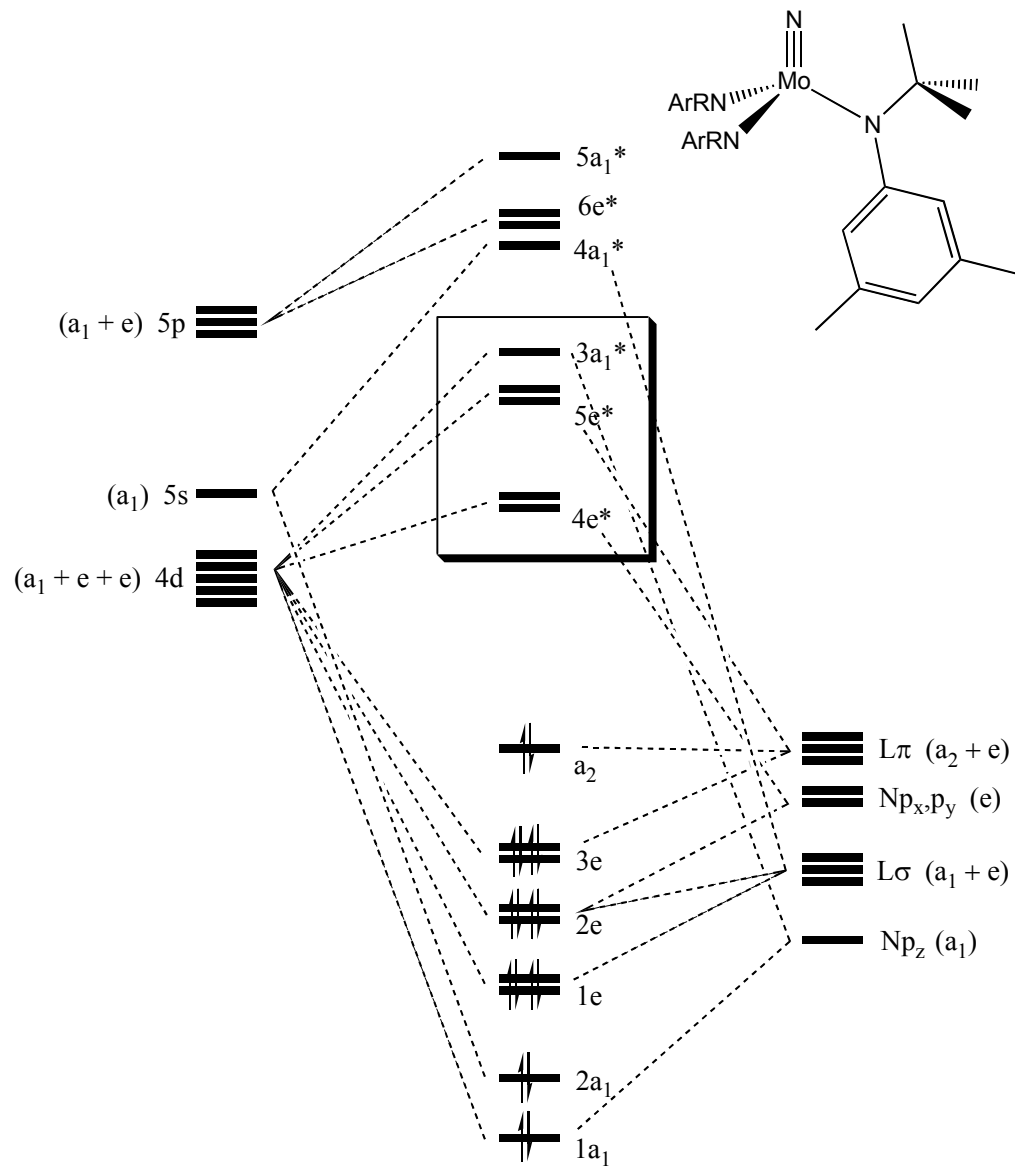
End on binding of N₂

Low temperature encourages N₂ solubility

Only requires 1 atm of pressure

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

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

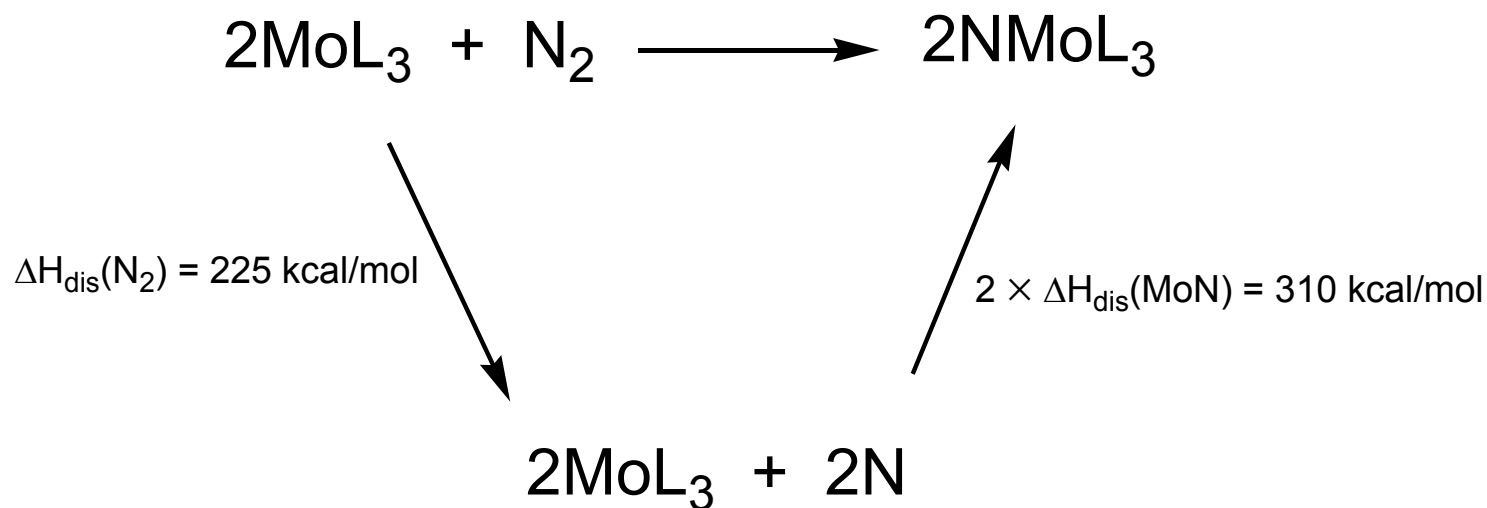


-Mo(VI) d^0

-16e⁻ complex

-1σ and 2π bonds
to N atom

Thermodynamics

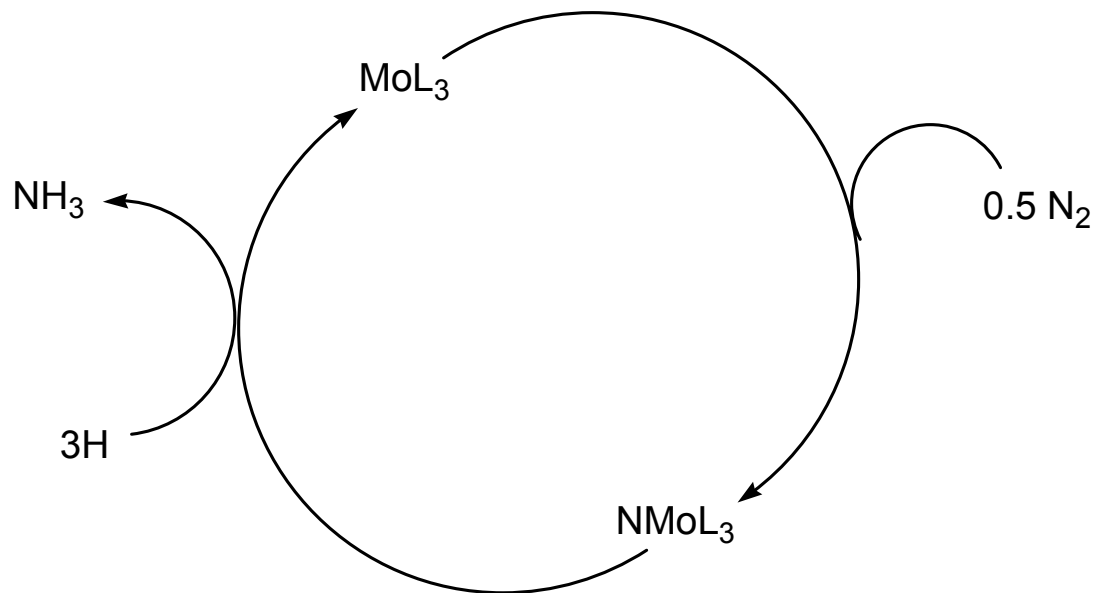


The σ and π components of the Mo-N triple bond result in a very strong bonding interaction. This new interaction compensates for the energy lost in breaking the N_2 triple bond.

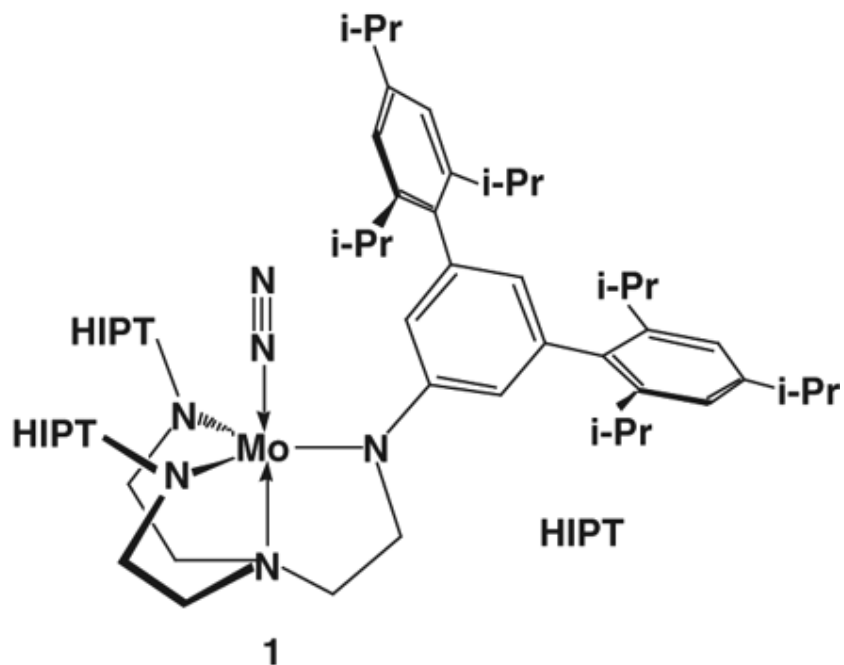
Potential for Catalysis

In order to create a catalytic system, we must regenerate the MoL_3 complex.

Attempts at using MoL_3 as a N_2 to NH_3 catalyst have thus far been unsuccessful.

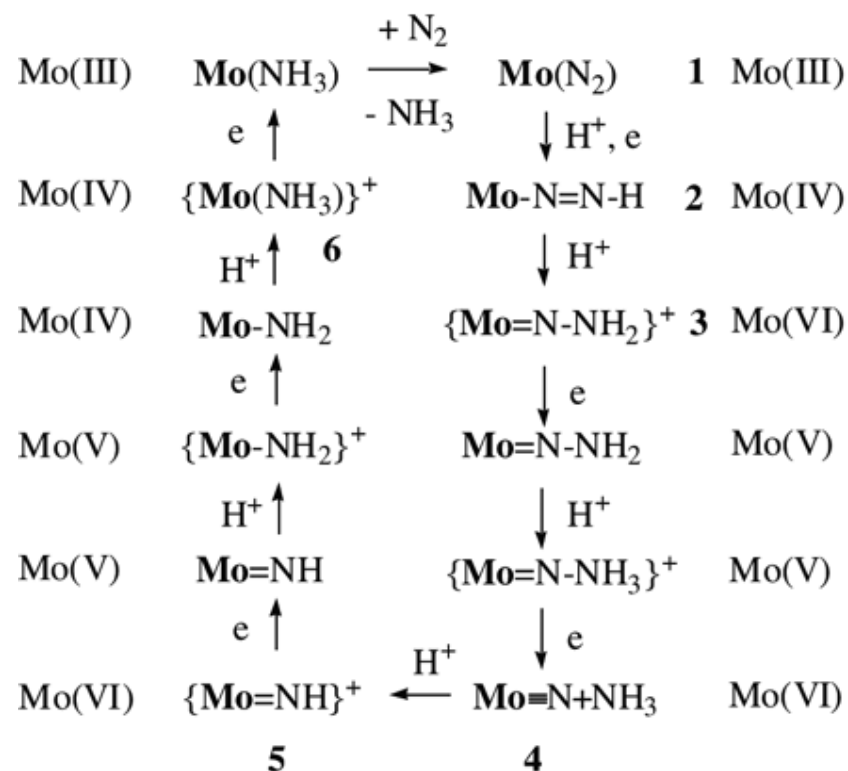


Schrock System



Mo catalyst

Sequential protonation reduction steps



J. Am. Chem. Soc., 124, 2002.

Catalytic Reduction of Dinitrogen to Ammonia at a Single Molybdenum Center

Dmitry V. Yandulov and Richard R. Schrock*

Dinitrogen (N_2) was reduced to ammonia at room temperature and 1 atmosphere with molybdenum catalysts that contain tetradentate $[HIPTN_3N]^{3-}$ triamidoamine ligands {such as $[HIPTN_3N]Mo(N_2)$, where $[HIPTN_3N]^{3-}$ is $[[3,5-(2,4,6-i-Pr_3C_6H_2)_2C_6H_3NCH_2CH_2]_3N]^{3-}$ } in heptane. Slow addition of the proton source $[[2,6-lutidinium]\{BAr'_4\}]$, where Ar' is $3,5-(CF_3)_2C_6H_3$ and reductant (decamethyl chromocene) was critical for achieving high efficiency ($\sim 66\%$ in four turnovers). Numerous x-ray studies, along with isolation and characterization of six proposed intermediates in the catalytic reaction under noncatalytic conditions, suggest that N_2 was reduced at a sterically protected, single molybdenum center that cycled from Mo(III) through Mo(VI) states.

Science, 301, 2003.

Conclusions

- The $\text{Mo}[\text{N}(t\text{-Bu})\text{Ar}]_3$ reacts with N_2 at low temperature to cleave the triple bond and form a pair of Mo(VI) nitride complexes.
- The reactivity of the 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.

