Dinitrogen Scission by a Molybdenum(III) Xylidene Complex

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1. Introduction.

- **Prof. C. C. Cummins**
- **Catalina Laplaza (MIT Undergraduate Research Opportunities Program)**
The main reference:

- **Dinitrogen Cleavage by Three-Coordinate Molybdenum(III) Complexes: Mechanistic and Structural Data**

- Catalina E. Laplaza, Marc J. A. Johnson, Jonas C. Peters, Aaron L. Odom, Esther Kim, Christopher C. Cummins, Graham N. George, and Ingrid J. Pickering;

  *J. Am. Chem. Soc. 1996, 118, 8623-863*
An excerpt from the Kit’s paper references section:

- (1) Dedicated to Professor Alan Davison of the MIT Department of Chemistry on the occasion of his 60th birthday.
Kit’s suggestion (April 1998)
2. About dinitrogen:

On Earth 4/5 of the volume of atmosphere; Titan (moon of Saturn) 82-94%. Bp -195.8 °C (O₂ - 183 °C).

- The triple bond is very strong:
- At 3000 °C do not decompose measurable.
- Bond energy is 225 kcal/mole.
- Combines with other elements only with difficulty. At high temperature combines directly with magnesium, titanium, and aluminum, forming nitrides.
3. Nitrogen fixation (to nif, niffing):

1. Haber-Bosch (1909, 1913)
   (Fe catalyst; 450-650 °C; 200-600 atm):

   \[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

   - Explosives and nitrogen fertilizers.
   - Half of the total nitrogen input to agriculture (the rest comes by biological nitrogen fixation).
   - About 1% of the world’s total annual energy supply.
Nitrogen is not accessible to plants
Nitrogen-fixing bacteria (symbiotic association with legume plants) enzyme (nitrogenase) converts $N_2$ into metabolically ammonia.
Nitrogenase has two component metalloproteins: the Fe-protein (source of electrons) and the MoFe-protein (interprotein electron transfer and catalyst for binding and reduction).
4. Nitrogen binding and scission:

Nitrogen binding and scission involves a process where nitrogen is bound and then scissored under certain conditions. The diagram illustrates the reaction pathway with specific temperature changes and color changes indicating different stages of the reaction.

- At -35 °C in ether, the reaction mixture is orange-red.
- At 25 °C, the color changes to purple, with a shift in infrared spectrum to 1042 cm⁻¹, indicating a change in molecular structure.

The student yield is reported as 75% (76%).

Small substituents allow for metal-metal bonding (NMe₂; OBu¹):

The reaction involves two molecules of molybdenum bound by nitrogen, with specific ligands L, to form a product Mo≡Mo.
Structure:
Mechanism:

end-on binding of N₂

no barrier of activation (theoretical methods)

barrier of activation:
- computed ca. 18 kcal/mol
- experimental 23.3 kcal/mol

Theoretical works (L=NH₂):

Experimental work:
5. Why $\text{N}_2$ is activated by Mo(III) complexes?

- $\text{L}_3\text{Mo}$ is isolobal to nitrogen atom (N) and carbyde (CH), with all three d electrons unpaired (high spin).
- The frontier orbitals $3a^12e^2$ are derived largely from $dz^2$ (3a) and $dxz$ and $dyz$, respectively (2e). (see the pictures on right $dxz$, $dyz$, $dz^2$).
- The NR$_1$R$_2$ substituent is a strong $\pi$ donor into $d_\pi$ orbitals (e MOs) of Mo, increasing the electron density at the metal.
Isolobal analogy (R. Hoffmann, *Angew Chem. Int. Ed. Engl.* 1982, 21, 711) is relating structures of organometallic compounds to organic ones. Two fragments are isolobal “if the number, symmetry properties, approximate energy, an shape of the frontier orbitals and the number of electrons in them are similar.”

**Mo(NRAr)₃** is isolobal with **CH**
There are $\sigma$ and $\pi$ interactions involved in $N_2 \cdot MoL_3$. $N_2$ provides the $\sigma$ electrons to empty $\sigma$ orbitals of Mo (s or d). The $\pi$ component is back-donation from occupied $d\pi$ orbitals to the empty $\pi^*$ of $N_2$. As result Mo-N becomes stronger, the N-N bond weaker and the reaction $L_3MoN_2MoL_3 \rightarrow 2NMoL_3$ more exothermic.

Dissociation energy: $Mo \equiv N$ triple bond = 155 kcal/mol, $N_2$ is 225.7 kcal/mol:

- $2R_3Mo + N_2 \rightarrow 2R_3Mo \equiv N$ is exothermic
6. **Starting materials for MoL$_3$**

- 1. MoCl$_5$
- 2. Ligand from (CH$_3$CO)$_2$O and diacetone alcohol:
7. A. Current version for the synthesis of MoCl$_3$(THF)$_3$


\[
\begin{align*}
\text{MoCl}_5 & \quad \xrightarrow{\text{cold Et}_2\text{O}} \quad \text{MoCl}_4(\text{OEt}_2)_2 \quad \xrightarrow{\text{THF}} \quad \text{MoCl}_3(\text{THF})_3 \\
\text{Sn, 30 min} & \quad \text{Sn, 30 min} \\
\text{black-brown solid} & \quad \text{orange suspension} \quad \text{bright orange powder} \\
\text{brown solution} & \quad \text{in diethyl ether} \\
\end{align*}
\]
Oxidation states of Mo

- Mo: Z=42; Ground state: Kr5s\(^1\)4d\(^5\) (\(^7\)S)

- MoCl\(_5\) (Mo\(_2\)Cl\(_{10}\)): Mo(V) one unpaired electron
  (readily abstracts oxygen from oxygenated solvents)

- MoCl\(_4\)(Et\(_2\)O)\(_2\): Mo(IV) two unpaired electrons

- mer-MoCl\(_3\)(THF)\(_3\): Mo(III) three unpaired electrons
  no fac- MoCl\(_3\)(THF)\(_3\)
7. B. Synthesis of the *m*-xylidine ligand:

\[ \text{BuLi in} \quad \text{thawing pentane} \]

\[ \text{ca. 9-6 equiv. t-BuNH}_2 \]

\[ \text{CH}_3\text{CN/RT} \]

\[ \text{ca } 90^\circ \text{C} \]

student's yield of pyrillium salt: 66% [lit. 72%]


student's yield of *N*-t-Butyl-*m*-xylidene: 62%.

student's yield of *LiN*-t-Butyl-*m*-xylidene*Et_2O: 63% [67%]

Literature data:

Synthesis of Mo[N(t-Bu)Ar]₃

\[ \text{MoCl}_3(\text{THF})_3 + 3 \text{Li}(t-Bu)N \rightarrow \text{MoL}_3 \text{Li} \]

ether, \(-100 \, ^\circ\text{C}\)

L is orange-red, extremely sensitive to moisture and oxygen

Student's yield: 30% (lit. 70%)

8. NMR of paramagnetic compounds

- Diamagnetic compounds (all electrons are paired) display a “normal” NMR, slim signals spread over 0-10 ppm.
- Paramagnetic compounds (unpaired electrons).
  1. NMR signals are broadened proportional to \( \gamma/r^6 \) (\( \gamma \) is the gyromagnetic ratio, \(^1\text{H}: 26.7519 \times 10^{-7}\text{radT}^{-1}\text{s}^{-1}; \)^2\text{H}: 4.1066 \times 10^{-7}\text{radT}^{-1}\text{s}^{-1}).
  2. NMR chemical shifts as result of interaction between electron and nuclear spin is the contact shift (in esr the hyperfine coupling): \( \Delta B/B_0 = (a\gamma^2h)/(4\gamma_p kT) \)
(A) trace: CH$_3$NH$_2$; 
(B) trace Ni(CH$_3$NH$_2$)$_6^{2+}$; Ni$^{2+}$ (d$^8$) is octahedral with 2 unpaired electrons:, t$_{2g}^6$e$_g^2$

$^1$H NMR

![NMR spectra]

9/9/03
The $^1$H NMR of Mo[N(t-Bu)(Ar)]$_3$

t-Bu ca 64 ppm (br); Ar-CH$_3$; -10 ppm
9. Concluding remarks and future developments:

- The 1995 discovery by MIT scientists that the three-coordinate molybdenum(III) complex $\text{Mo[N(t-Bu)Ar]}_3$ reacts readily with nitrogen, became in 1998 an advanced undergraduate experiment.

- The (best) synthesis of the ligand (N-t-butyl-m-xylidine) is performed based on a procedure modified from the literature.

- During the experiment students perform syntheses of diverse organic and inorganic compounds using glove box techniques. Topics like the isolobal concept, $^1\text{H-NMR}$ of paramagnetic species, high spin electronic states are also covered.

- The next version of the experiment will also feature a short cut in the synthesis of $\text{MoCl}_3(\text{THF})_3$, the electronic structures calculated at the DFT level to rationalize the unusual reactivity of $\text{MoL}_3$ and to assess the Mo≡N vibration in $\text{L}_3\text{Mo≡N}$. 