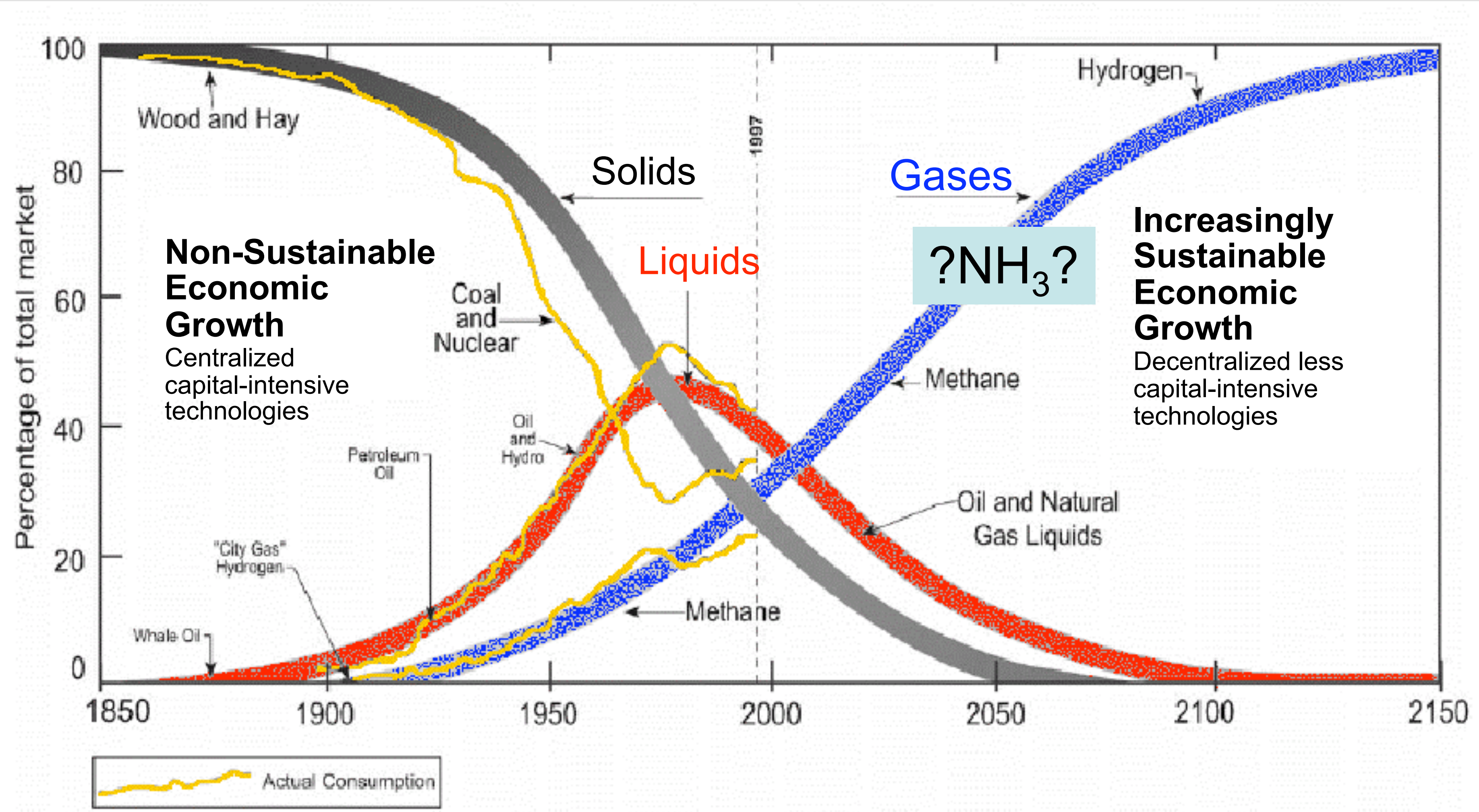
# Reversible surface storage of ammonia

Patrick J. Desrochers
Dept. of Chemistry, University of Central Arkansas, Conway, AR 72035
patrickd@uca.edu

- Transition metal contributions
- Tp*NiBH$_4$ stable H-rich substrate
- Tp*NiX(s) binding of ammonia

AFIII, Golden, CO Oct 2006

# Global transition to energy gases




reproduced from S. Dunn *International Journal of Hydrogen Energy* **2002***, v. 27,* p 235.

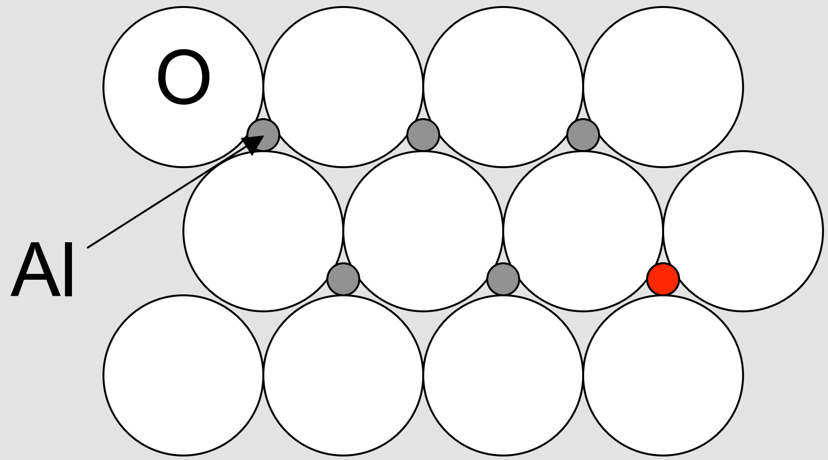
# Transition metals might not make ammonia storage materials, but they might make storage materials better.

- magnetic properties
  probe to monitor, sense ammonia

- electrical (redox) properties
  storage/catalyst/electrode interfaces

- optical characteristics (visible light)
  simple colorimetric sensor/indicator

# Trace transition elements alter properties




aluminum oxide, $Al_2O_3$ ( 99.5%)

0.5% Cr

- optical differences apparent
- new Cr-dependent magnetism

http://www.mineralminers.com/html/rbygems.stm

# Ammonia in general and nickel

$[Ni(NH_3)_6]X_2$ halogen-dependent thermal stability
multi-step thermal decomposition

| X | mass % H | decomposition |
|---|---|---|
| Cl | 7.8 | 3 steps |
| Br | 5.7 | $4NH_3, 2NH_3$ |
| I | 4.4 | ~$6NH_3$ at once |

Flora, T. *Acta. Chim. Acad. Sci. Hung.* **1963**, *37*, 359.

AMMINEX

For comparison
$Mg(NH_3)_6Cl_2$
9.2% H

http://www.greencarcongress.com/2005/09/handheld_hydrog.html

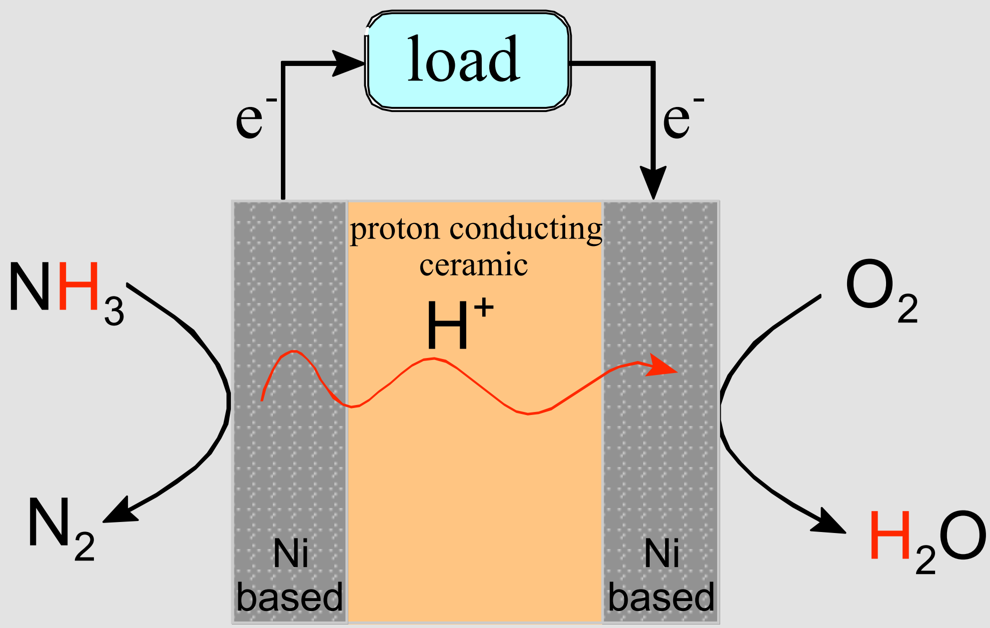
Christensen, C. H.; Sørensen, R. Z.; Johannessen, T. ; Quaade, U. J.; Honkala, K.; Elmøe, T. D.; Køhler, R.; Nørskov, J. K.
*J. Mater. Chem.*, **2005**, *15*, 4106 – 4108.

UCA

# Ammonia in general and nickel

$$NH_3 + \tfrac{3}{4} O_2 \rightarrow \tfrac{1}{2} N_2 + {}^{3}/_{2} H_2O$$

$$\Delta H = -382 \text{ kJ/mol}$$




J. Ganley, Howard University

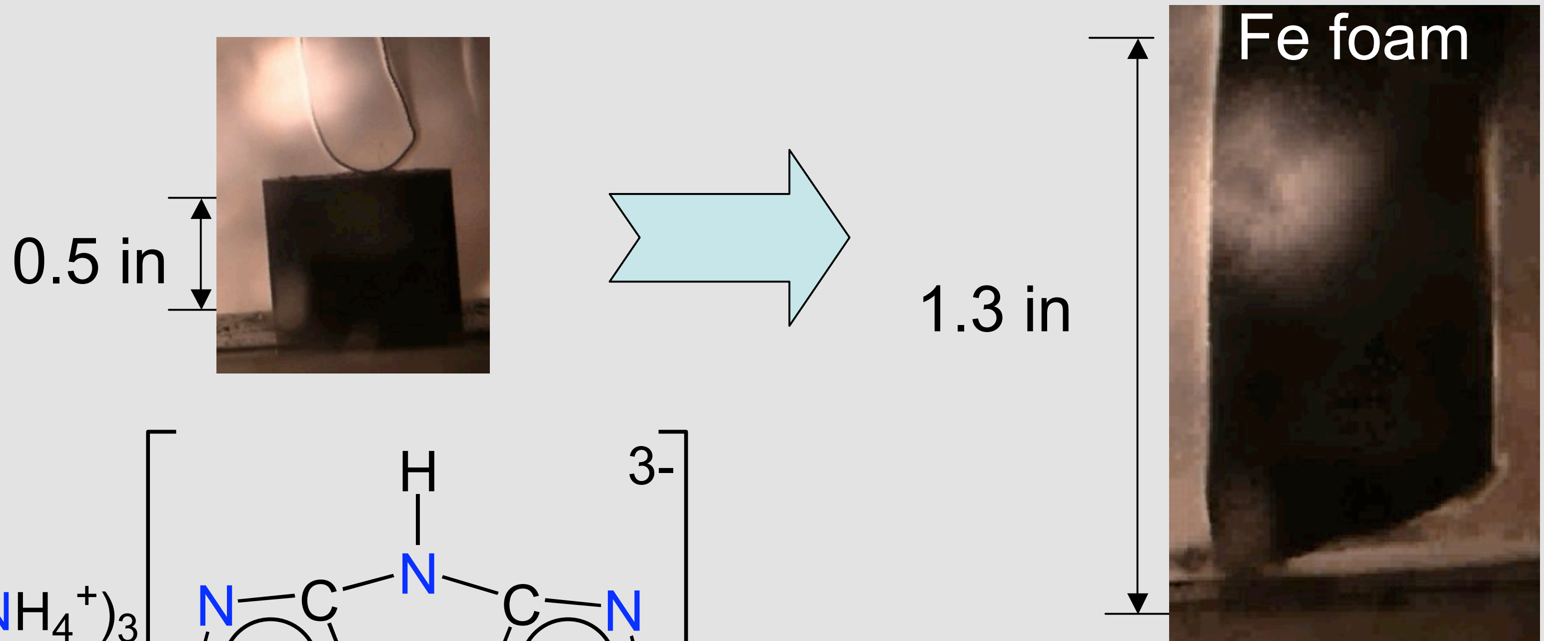
Metal foams

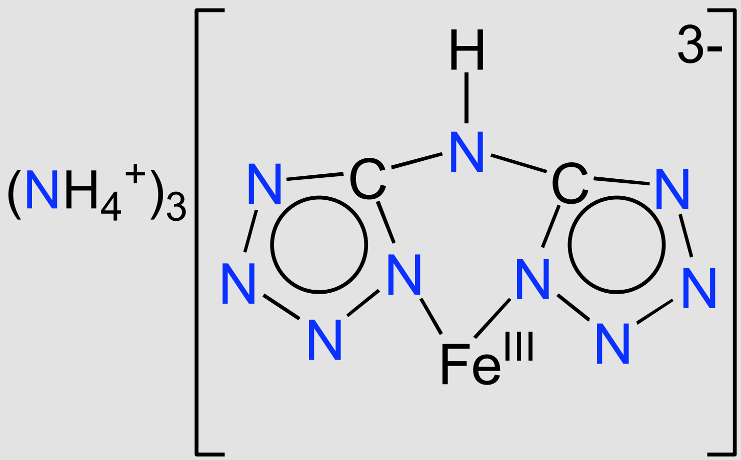
Fe, Co, Cu, Ag

Boisen; Dahl, S.; Nørskov, J. K.; Christensen, C. H. *Journal of Catalysis*, **2005**, *230*, 309–312.

# Metal foams

- *high* surface area, *low* density
- monolithic metals
- possible electrode/catalyst materials




$d$ = 0.011 g/cm$^3$

(Fe $d$ = 7.9 g/cm$^3$)

Tappan, B. C.; Huynh, M. H.; Hiskey, M. A.; Chavez, D. E.; Luther, E. P.; Mang, J. T.; Son, S. F.
*J. Am. Chem. Soc.* **2006**, *128*, 6589-6594.

# Ammonia-derived storage materials

$H_3BNH_3(s)$ 19.7% H

stable up to 100 h @ 60 °C

| | | | |
|---|---|---|---|
| step 1 | $H_3BNH_3 \longrightarrow (H_2BNH_2)_n + H_2$ | | 6.5 % |
| step 2 | $(H_2BNH_2)_n \longrightarrow (HBNH)_n + H_2$ | | 13.1 |
| step 3 | $(H_2BNH_2)_n \longrightarrow (BN)_n + H_2$ | *diamond structure* | 19.7 |

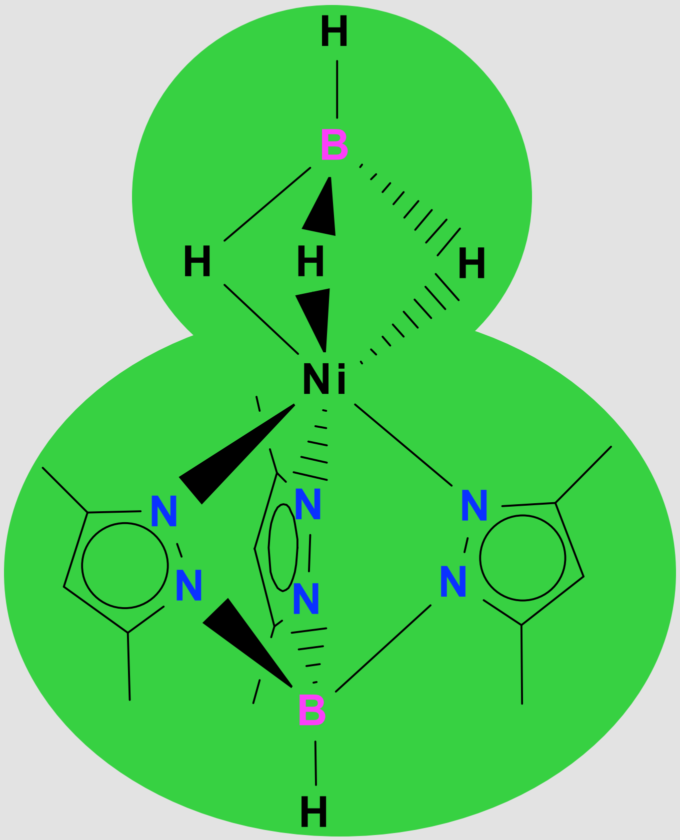
S. D. Rassat, PNNL, 232nd ACS Natl. Mtg., San Francisco, CA Sep. 2006, FUEL 102

$$H_3BNH_3 + 2H_2O \xrightarrow[\text{R.T.}]{\text{T.M. cat.}} NH_4BO_2 + 3H_2$$

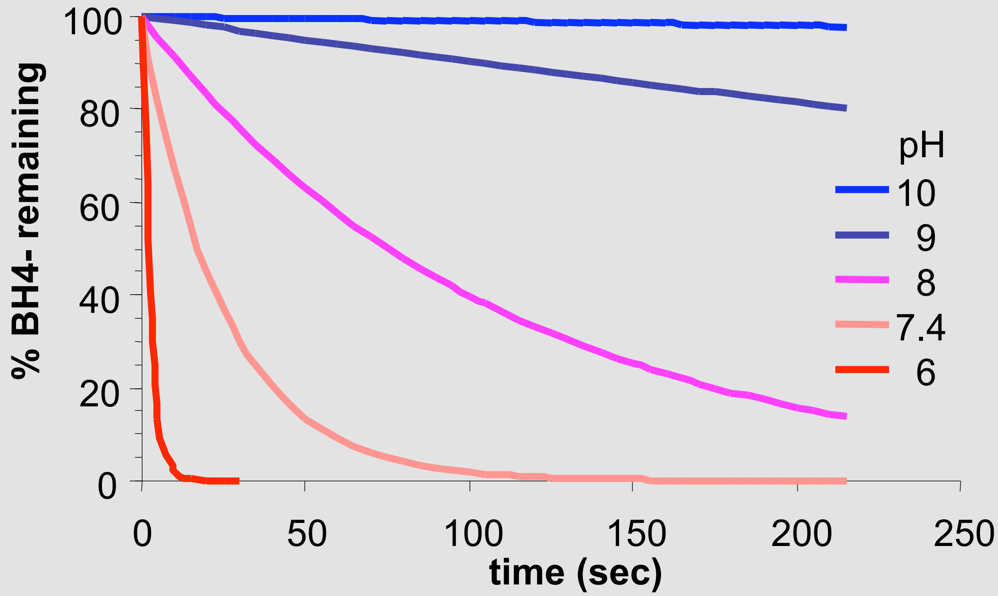
P. V. Ramachandran, 232nd ACS Natl. Mtg., San Francisco, CA Sep. 2006, FUEL 101

Chandra, M.; Xu, Q. *J. Power Sources* **2006**, *156*, 190-194.

# A stable borohydride




Contrasts hydrolysis of $MBH_4$



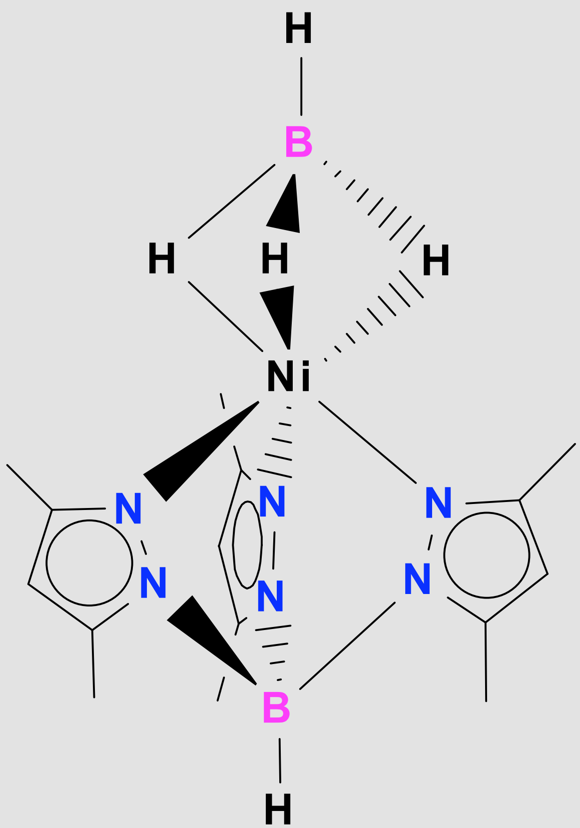

Davis, R. E.; Bromels, E.; Kibby, C. L. *J. Am. Chem. Soc.* **1962**, *84*, 885.

Tp* anchorage tempers reducing power of H-rich substrates

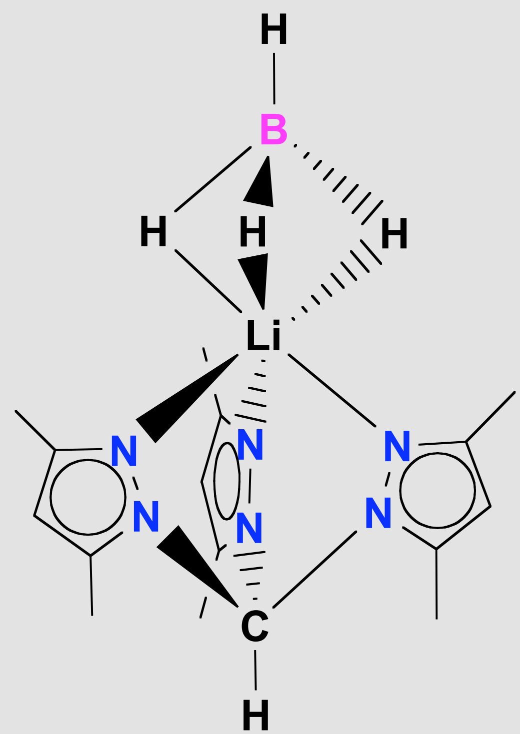
- inert to hot water
- stable in air

Desrochers, P. J.; LeLievre, S.; Johnson, R. J.; Lamb, B. T.; Phelps, A. L.; Cordes, A. W.; Gu, W.; Cramer, S. P. *Inorg. Chem.* **2003**, *42*, 7945.

# A stable borohydride

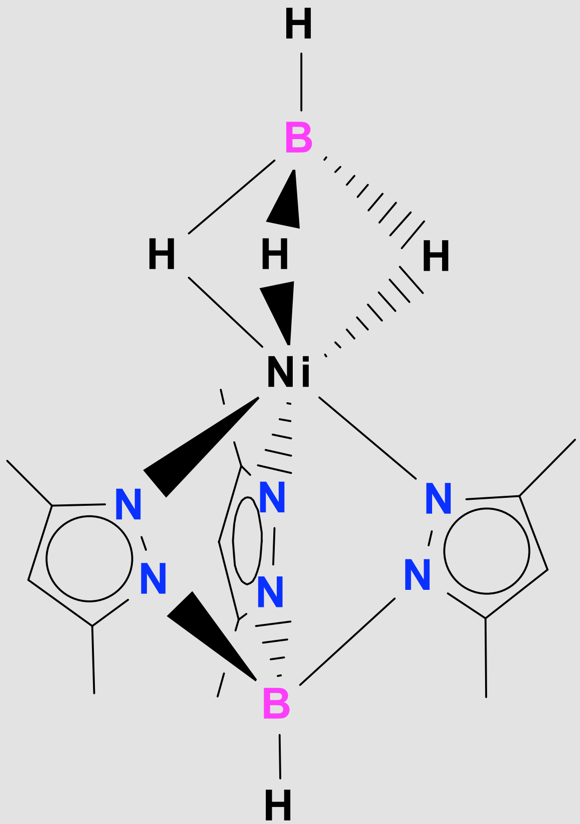


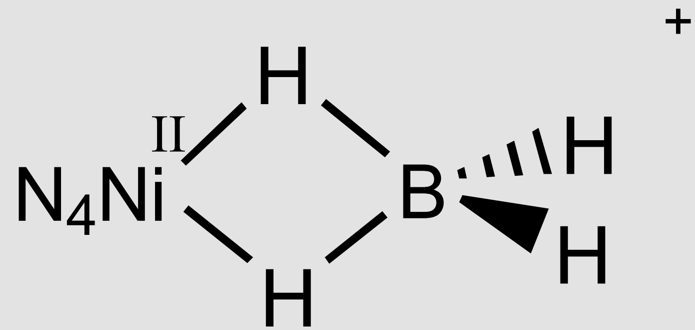

Ligation impedes hydrolysis




Reger, D. L.; Collins, J. E.; Matthews, M. A.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A.; *Inorg. Chem.* **1997**, *36*, 6266.

# Compared to other borohydrides/amines



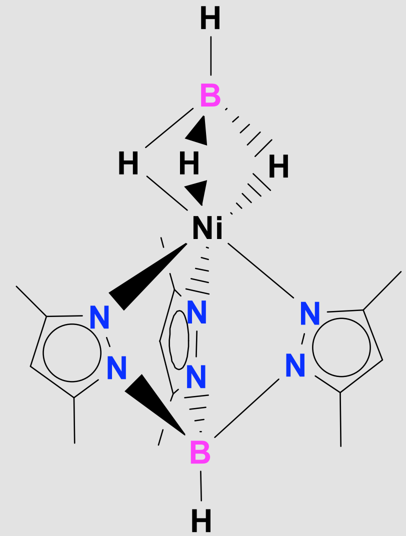



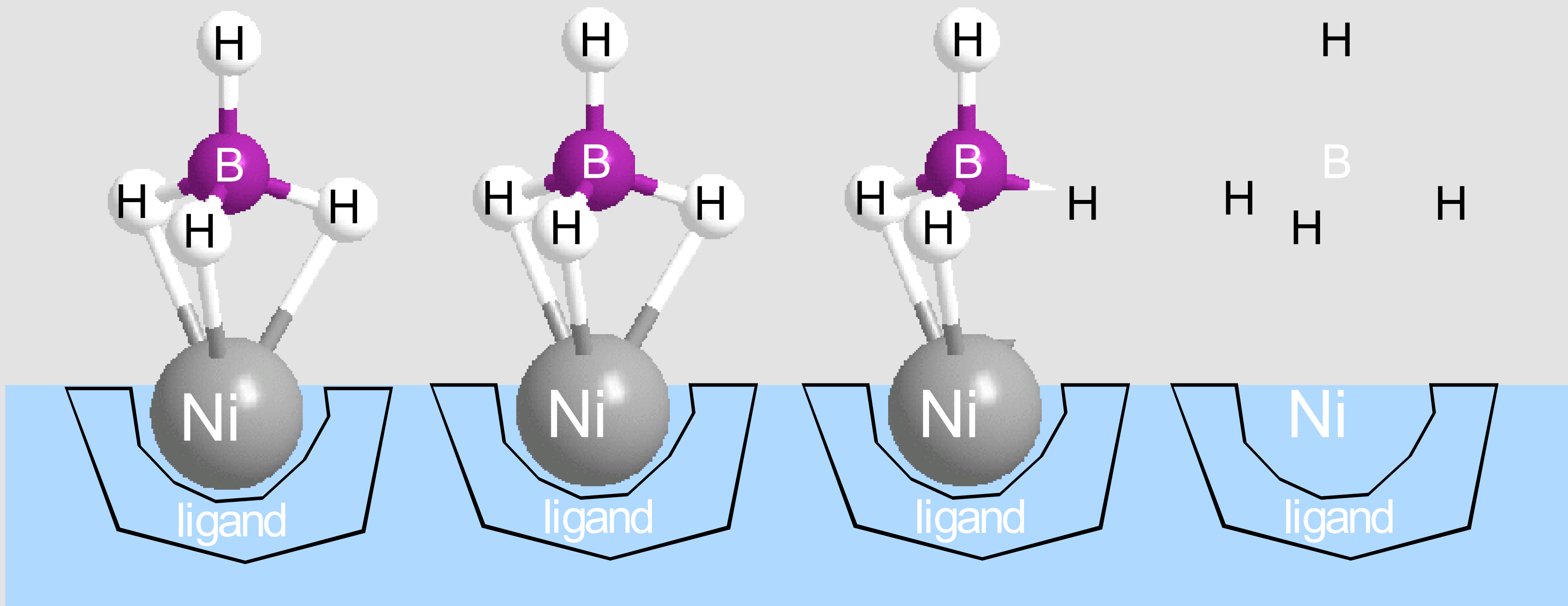

Curtis, N. F. *J. Chem. Soc.* **1965**, 924.

$N_4$ = cyclam

N-rich environments retard reduction


E
F


H
B
H
H
H
Ni
N
N
N
N
N
N
B
H


H
B
H
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Ni
ligand
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B
H
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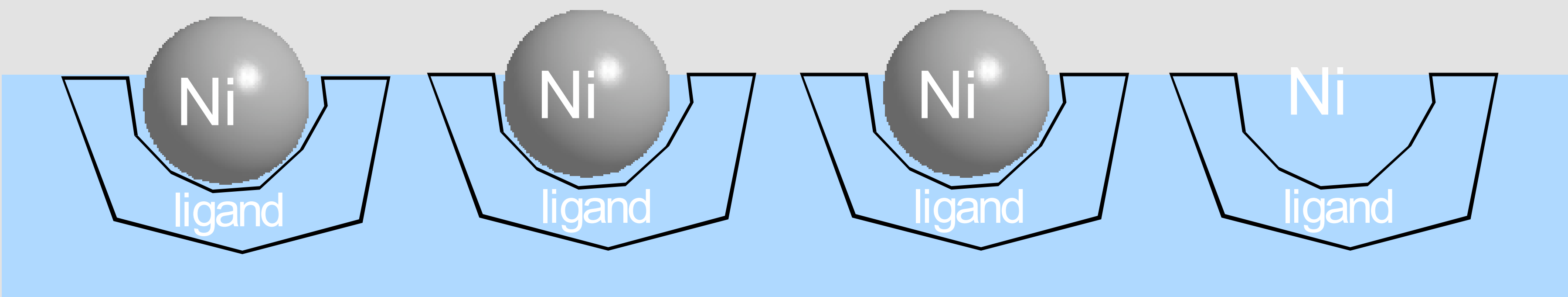
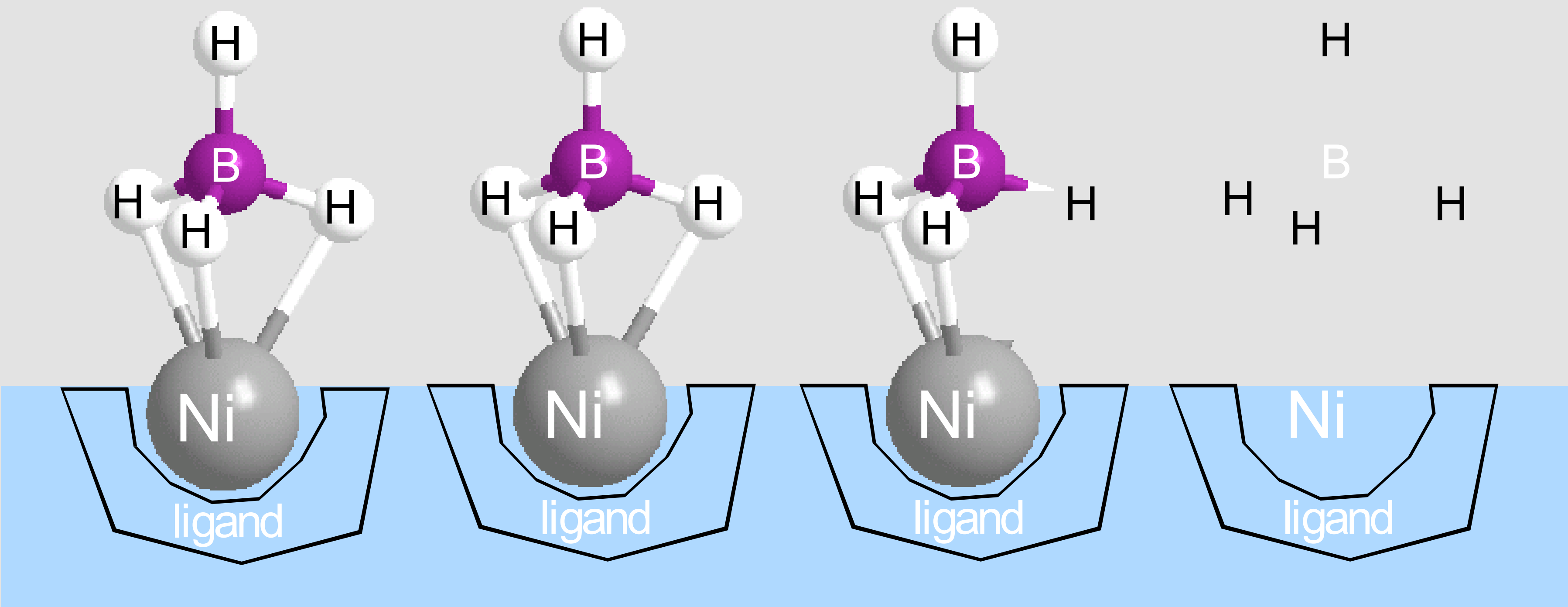
H
Ni
ligand
H
B
H
H
H
Ni
ligand
H
B
H
H
H
Ni
ligand


E
F


Ni
ligand
Ni
ligand
Ni
ligand
Ni
ligand


E
F


H
B
H
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Ni
ligand
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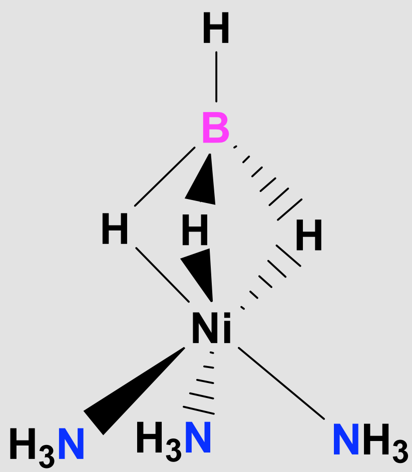
H
H
H
Ni
ligand
H
B
H
H
H
Ni
ligand

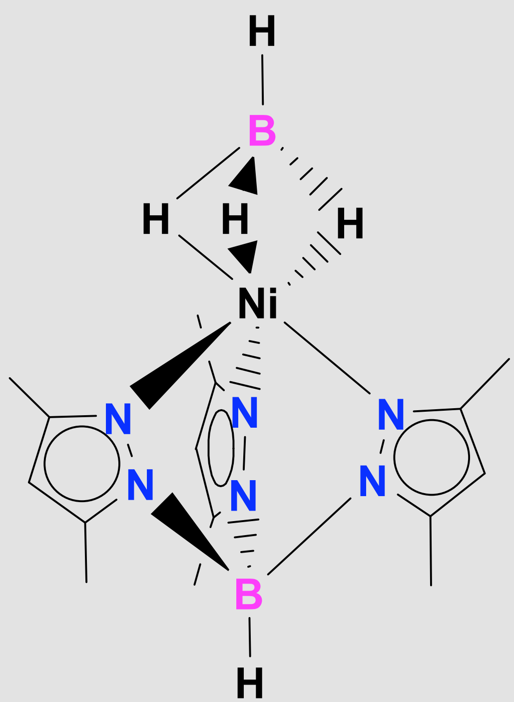
# Nickel anchorages for hydrogen-rich substrates

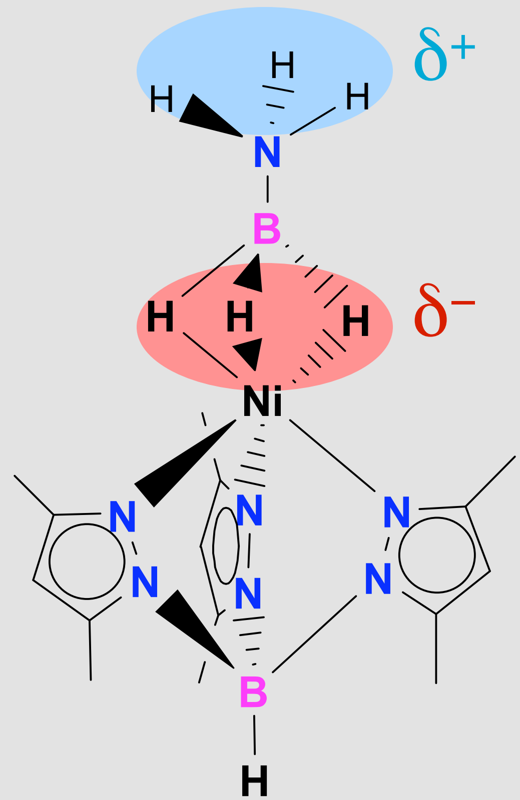
theory: suggests affinity for $H_3N\text{-}BH_3$

exchange Tp*- tripod for $3NH_3$



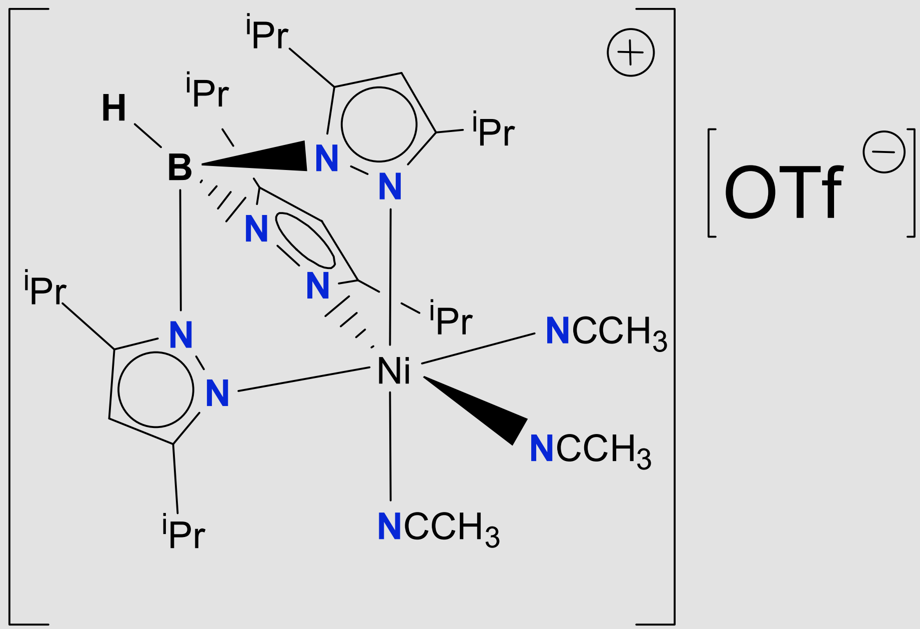

reproduced structural, spectral features for $Tp^{*}NiBH_4$



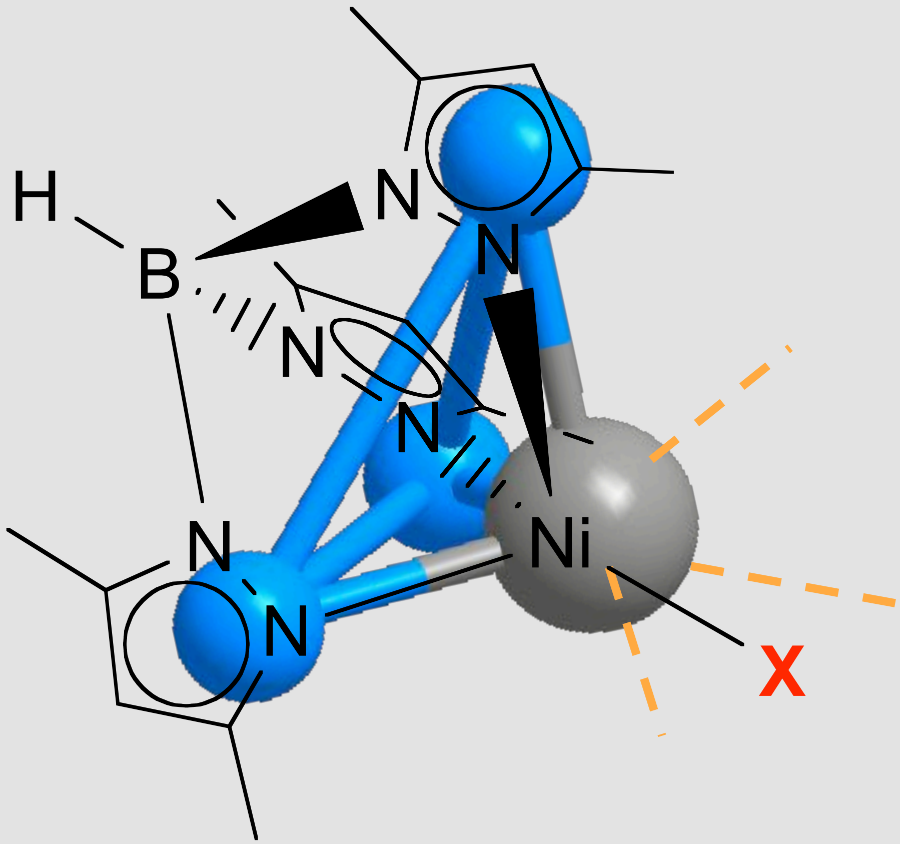
# Nickel has high affinity for nitrogen substrates

Stabilize anchored-nickel in a pliable environment.




Uehara, K.; Hikichi, S.; Akita, M. *J. Chem. Soc., Dalton Trans*. **2002**, 3529.

# Tp*NiX and ammonia




X

Cl $^-$

Br $^-$

I $^-$

$BH_4^-$

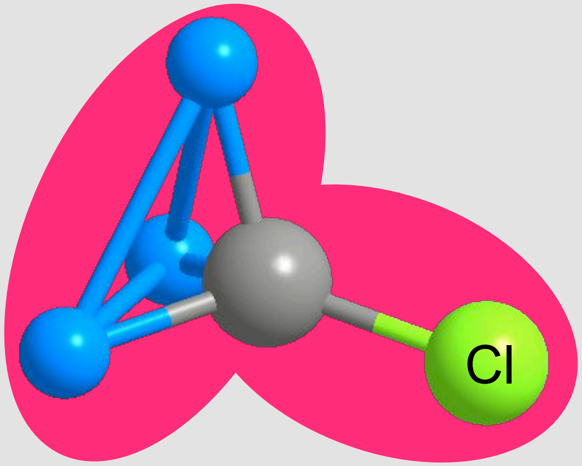
$NH_3$

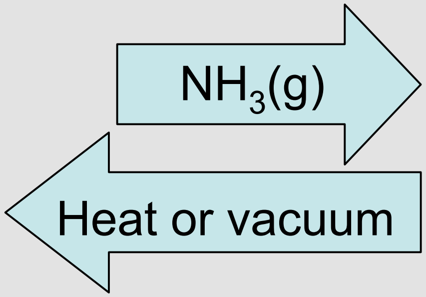
$^-SPh$

$NO_3^-$

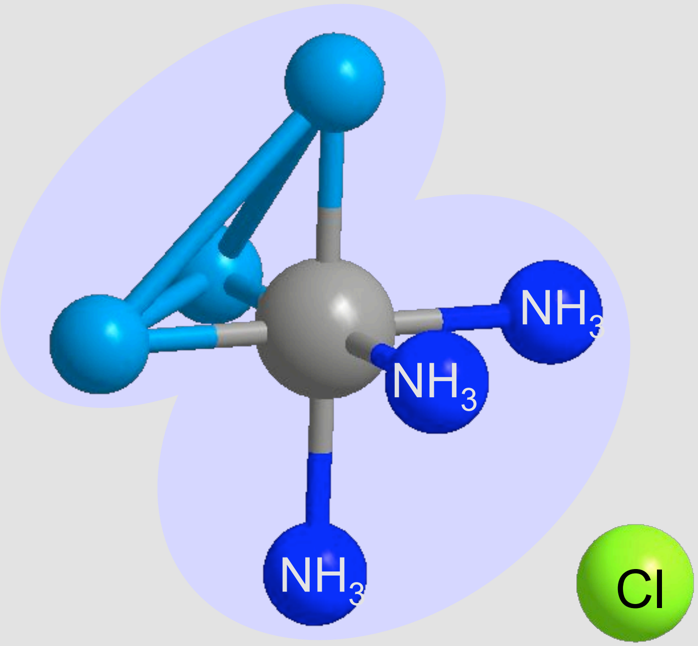
CysR

# Reversible $NH_3$ uptake confirms $3NH_3$:1Ni



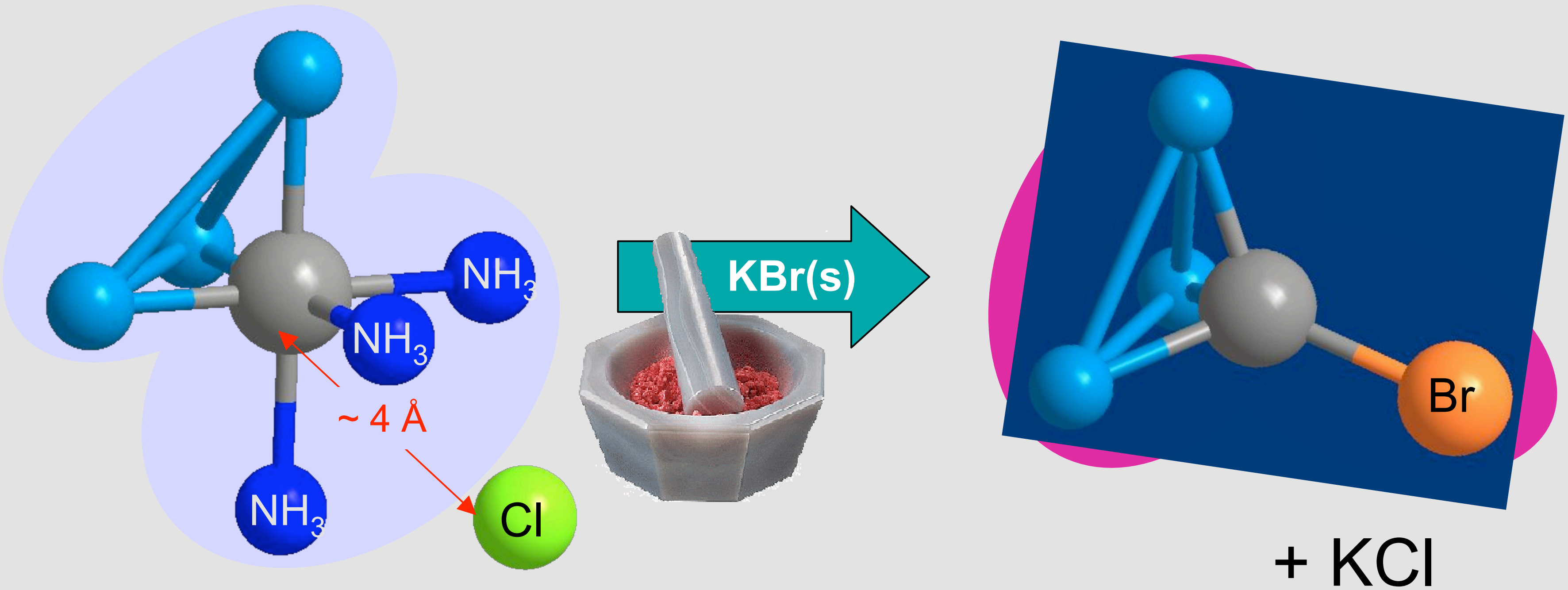

12% loss of mass

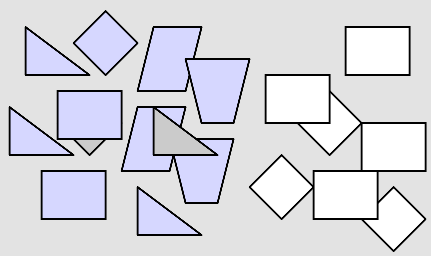



| absorption maxima | absorption maxima |
|---|---|
| 400 nm | 380 nm |
| 800 | 570 |

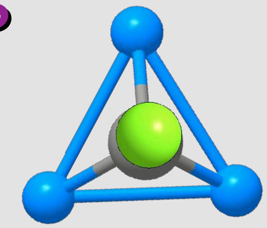
similar to $Ni(NH_3)_6X_2$

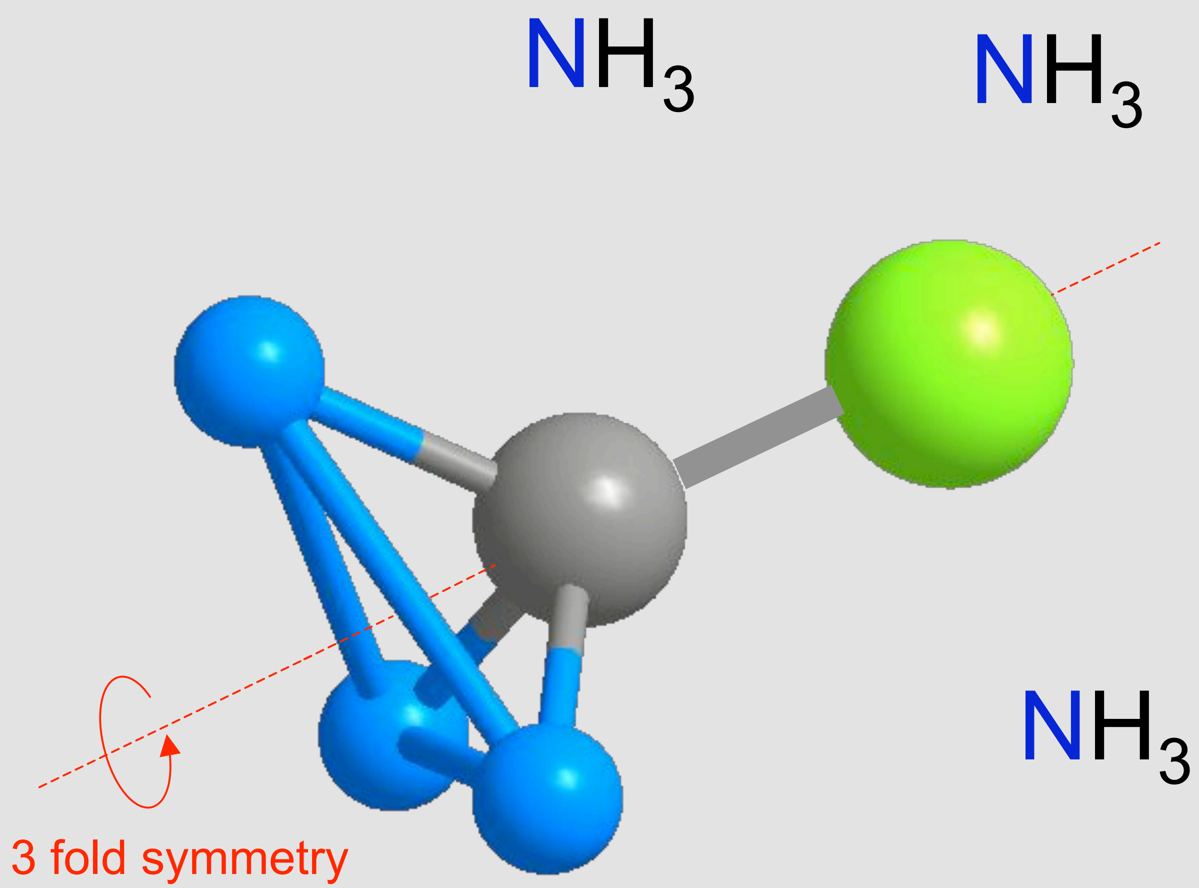
# Nickel-halide weak enough for replacement



# Halogen control may follow three fold axis

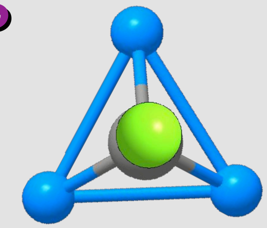


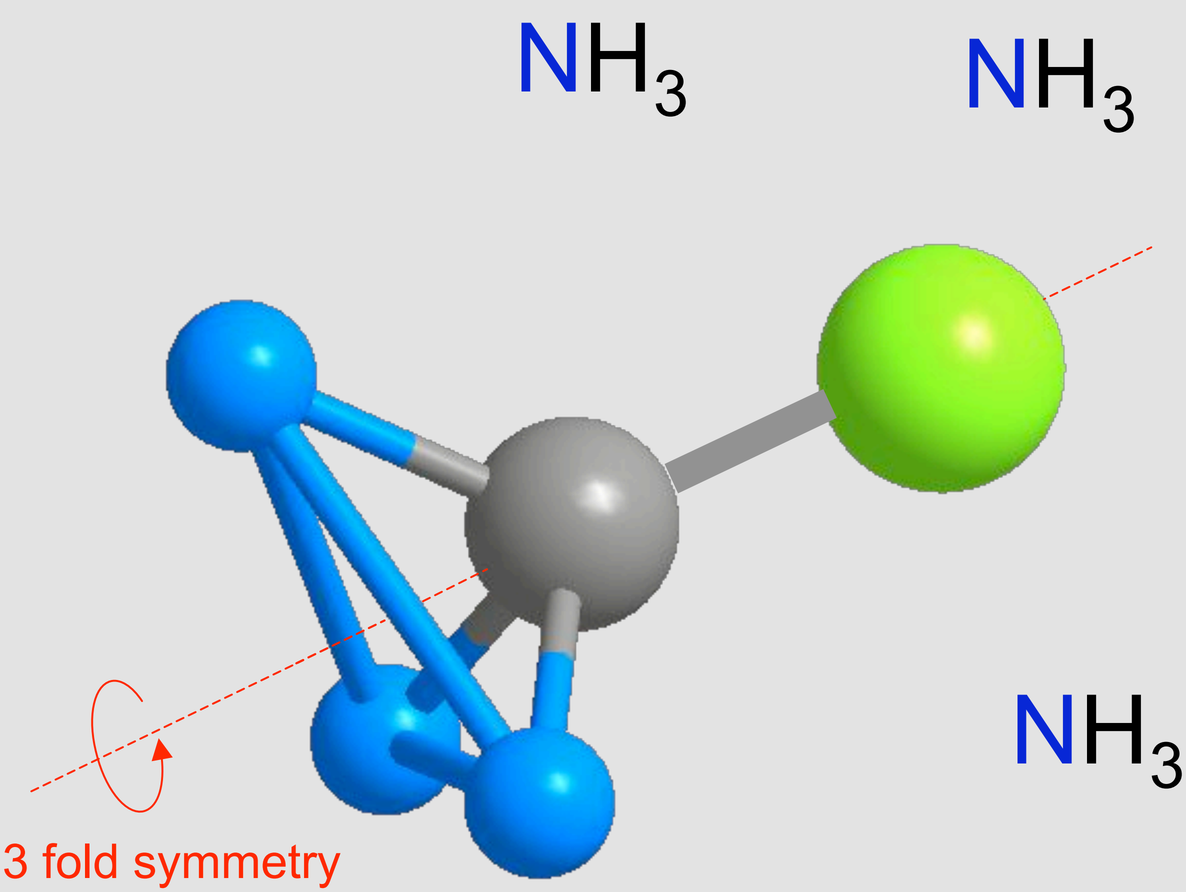



Halide typically along 3-fold axis of metal-ammines.

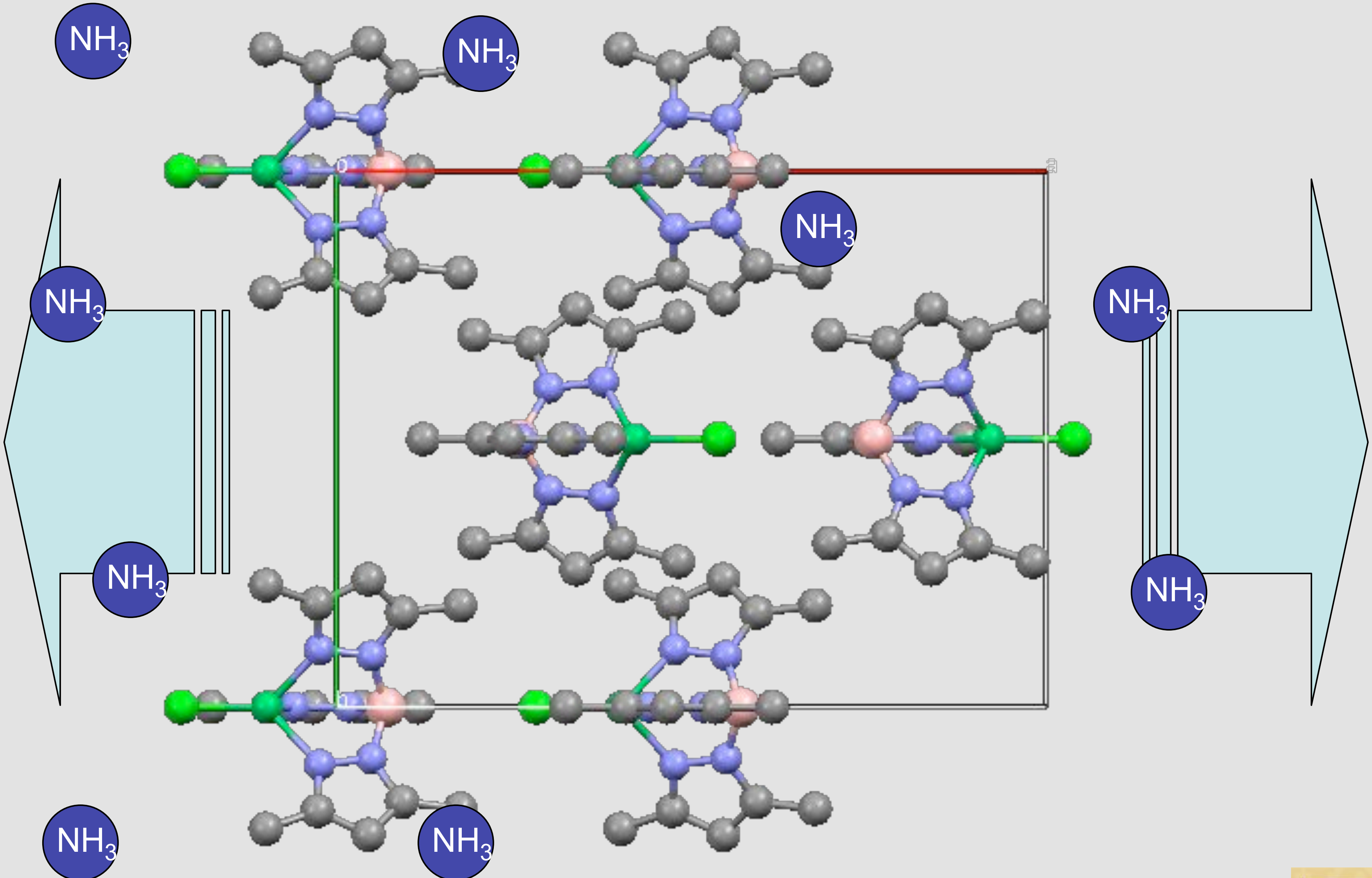

Hwang, I. –C.; Drews, T.; Seppelt, K. *J. Am. Chem. Soc.* **2000**, *122*, 8486.
Scheibel, P.; Prandl, W.; Papoular, R.; Paulus, W. *Acta Cryst* **1996** *A52*, 189.

# Halogen control may follow three fold axis





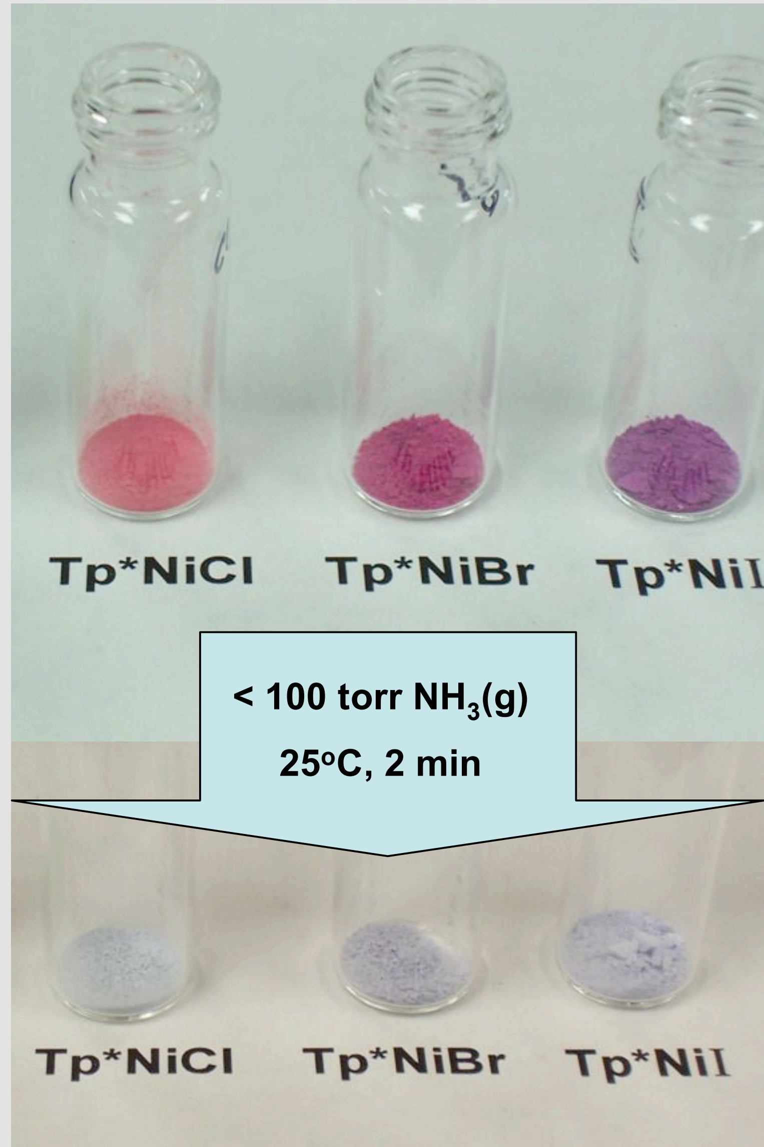
# Directional expansion with ammonia uptake




crystalline $[Tp^{*}Ni(NH_3)_3^{+}][X^{-}]$ ?

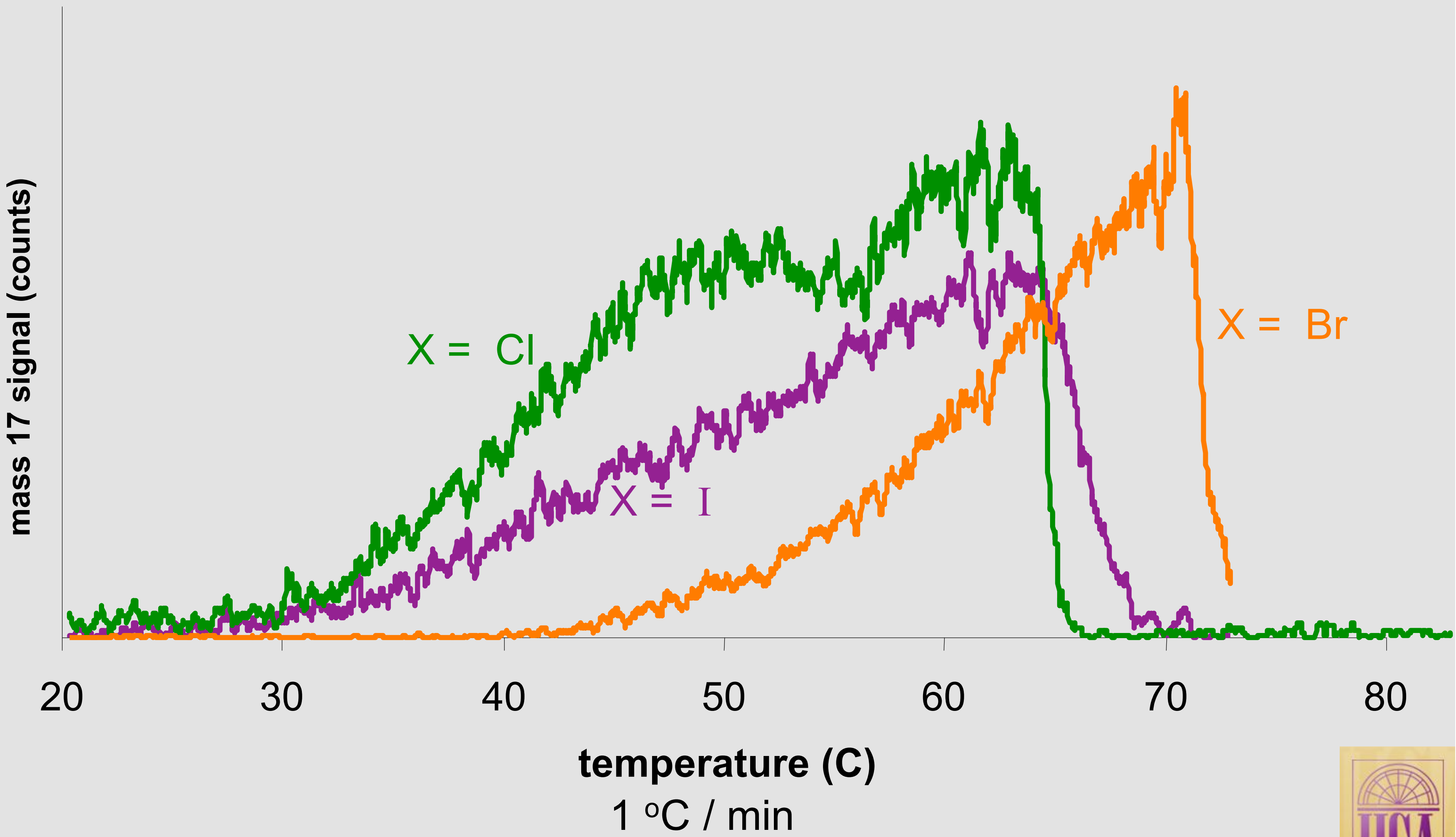
# Rapid, efficient $NH_3$ uptake

- Faster for more dispersed samples
- In solution, instantaneous change
- $H_2O$ vs $NH_3$ discrimination based on high nitrogen-affinity of Ni(II)
- Potential sensor/storage applications

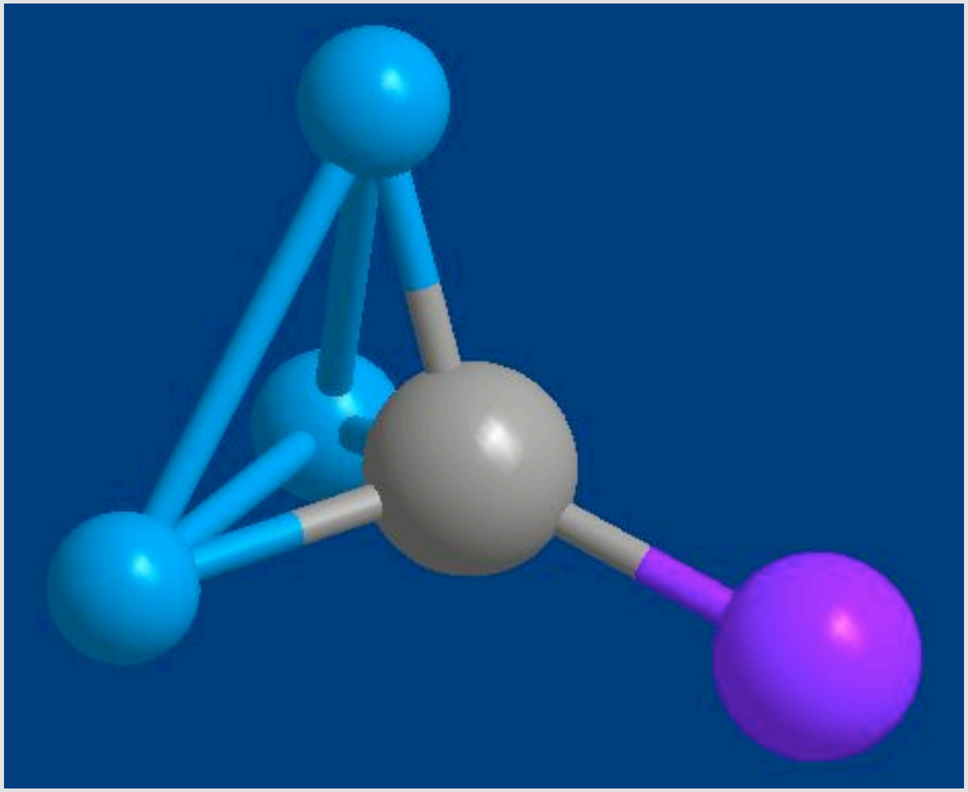


# Workable temperature range

$$[Tp^*Ni(NH_3)_3^+][X^-](s) \xrightarrow{\Delta} Tp^*NiX(s) + 3NH_3(g)$$



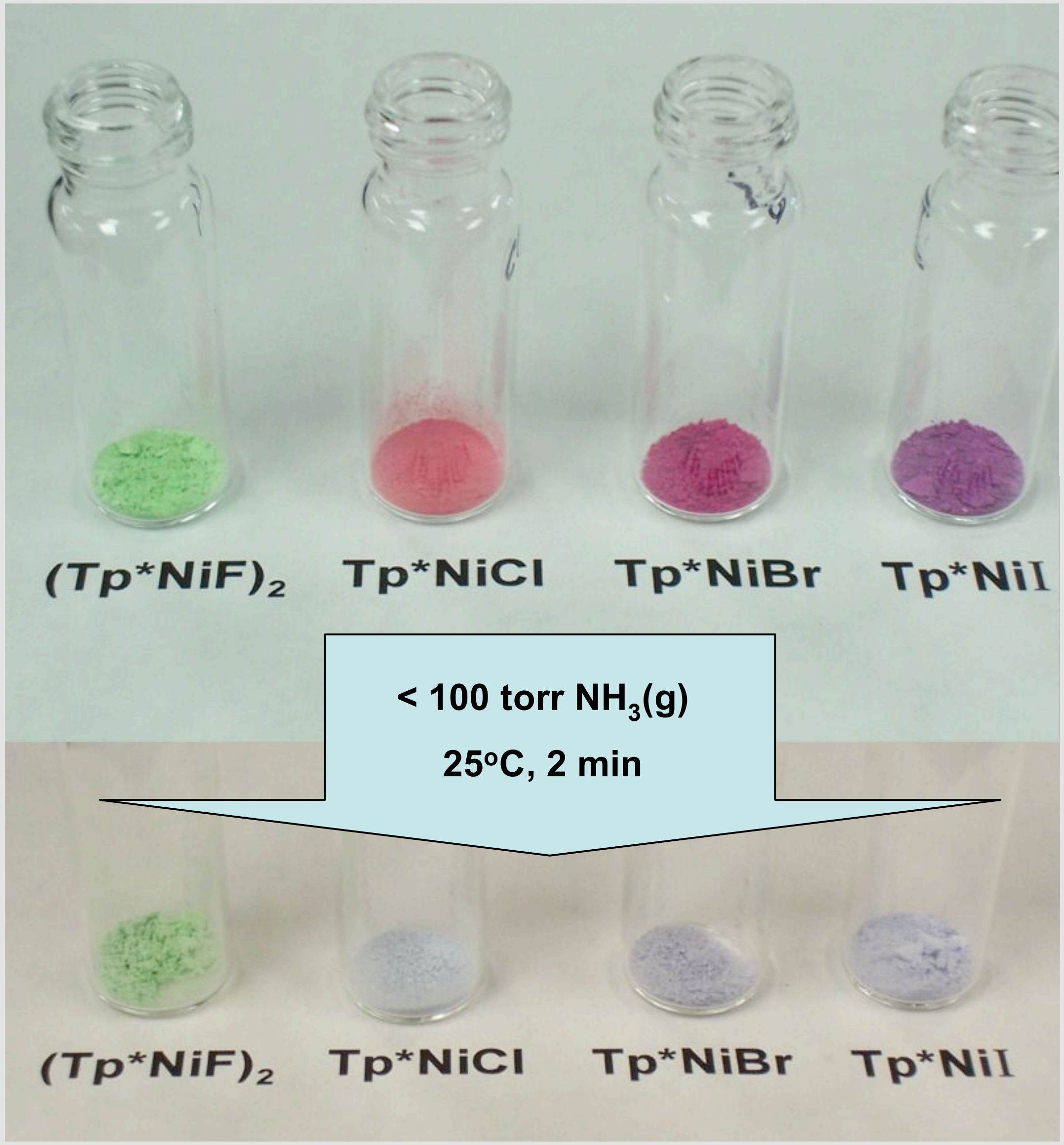
# Tp*NiX, first complete halide series



| X |
| --- |
| **$F^-$** |
| **$Cl^-$** |
| **$Br^-$** |
| **$I^-$** |

Expect *strong* nickel-fluoride bond.

# Strong Ni-F bond impedes $NH_3$ uptake



- $Tp^*NiBH_4$ stable H-rich substrate
  - Tp*- modeled quite well with $NH_3$
  - implications for ammonia-only reactions
  - potential $NH_3BH_3$ interactions
- Tp*NiX(s) binds ammonia
  - reversible, quantitative $3NH_3$:1Ni
  - X-dependent uptake, release; 3-fold axis control
  - colorimetric, magnetic signals, sensor potential
- Combined $NH_3$ storage & decomposition catalyst?
  - porous low-density metal foams
  - carefully chosen metal anchorage


Acknowledgements:

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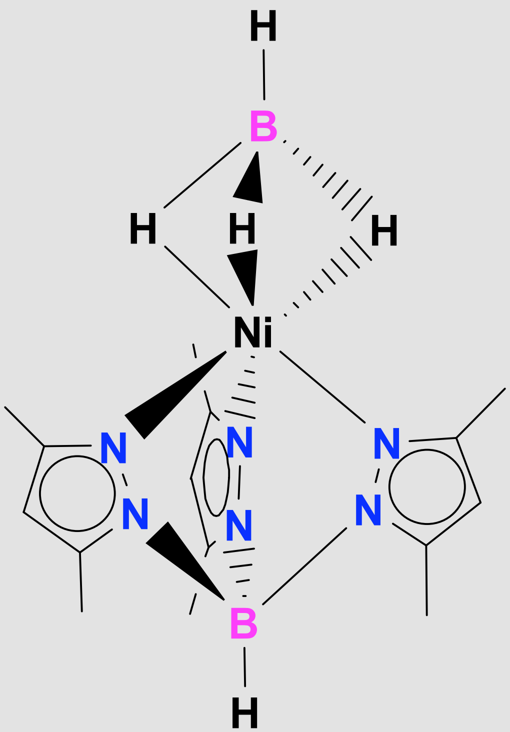
J Krzystek, A. Ozarowski (NHMFL, HFEPR)
M. Abrams (UCA, DFT)
D. Perry (UCA, GCMS)

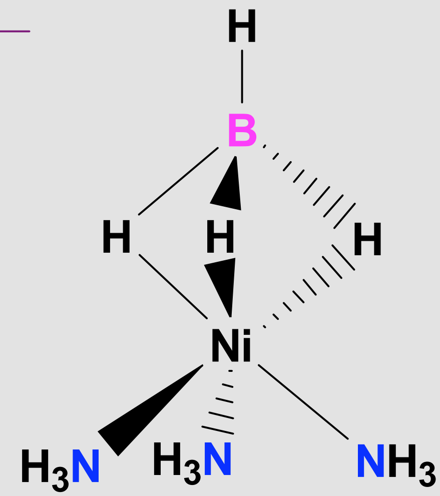
$$ Petroleum Research Fund (Am. Chem. Soc.),
Natl. Sci. Foundation, Nat. High Mag. Field Lab.

# Extra Slides

# A working model for $Tp^*NiBH_4$



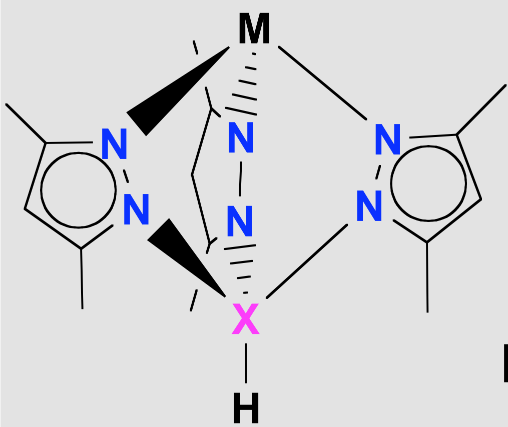

| experiment (XRD) | | theory (DFT) |
|---|---|---|
| 2.048 Å | **Ni-B** | 1.986 Å |
| 1.87 – 1.94 Å | **Ni**-H | 1.864 Å |
| 2.00 – 2.01 Å | **Ni-N** | 2.124 Å |

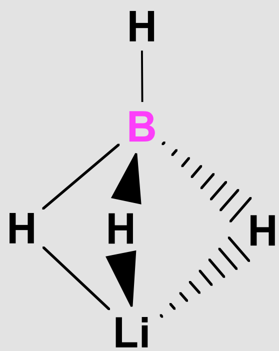
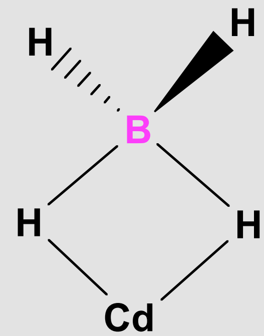
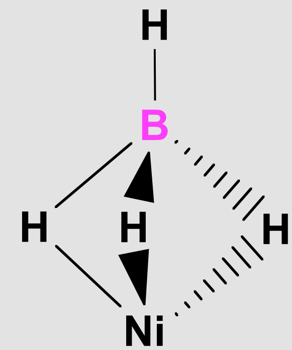



DFT UB3LYP/6-311++G**
geom optimization, freq. calc.

ν(B-H) within 10%

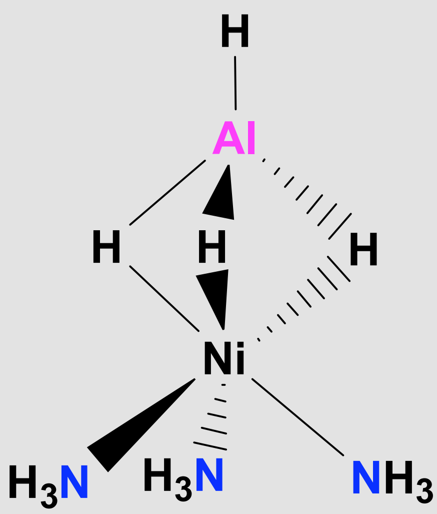
# TpM-$BH_4$: ionic vs covalent interactions




| | $TmLi(\kappa^3-BH_4)$ | $Tp^*Cd(\kappa^2-BH_4)$ | $Tp^*Ni(\kappa^3-BH_4)$ |
|---|---|---|---|
| |  |  |  |
| | X = C | X = B | X = B |
| | Li-B 2.223(7) A | Cd-B 2.423(5) A | Ni-B 2.048(5) A |
| | Li-N 2.038(5) | Cd-N 2.289(3) | Ni-N 1.996(3) |
| | 2.092(5) | 2.246(3) | 2.009(3) |
| Ionic radii (CN = 6) | $Li^+$ 0.76 A | $Cd^{+2}$ 0.95 A | $Ni^{+2}$ 0.69 A |


Ni Desrochers, P. J.; LeLievre, S.; Johnson, R. J.; Lamb, B. T.; Phelps, A. L.; Cordes, A. W.; Gu, W.; Cramer, S. P. *Inorg. Chem.* **2003**, *42*, 7945.
Li Reger, D. L.; Collins, J. E.; Matthews, M. A.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A.; *Inorg. Chem.* **1997**, *36*, 6266.
Cd Reger, D. L.; Mason, S. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 10406.

# Other hydrogen rich substrates?




| theory (DFT) | | theory (DFT) |
|---|---|---|
| 2.304 Å | Ni-E | 1.993 Å |
| 1.861 Å | Ni-H | 1.875 Å |
| 2.129 Å | Ni-N | 2.114 Å |