Reusable Nickel-Based Materials for Small Scale Ammonia Storage

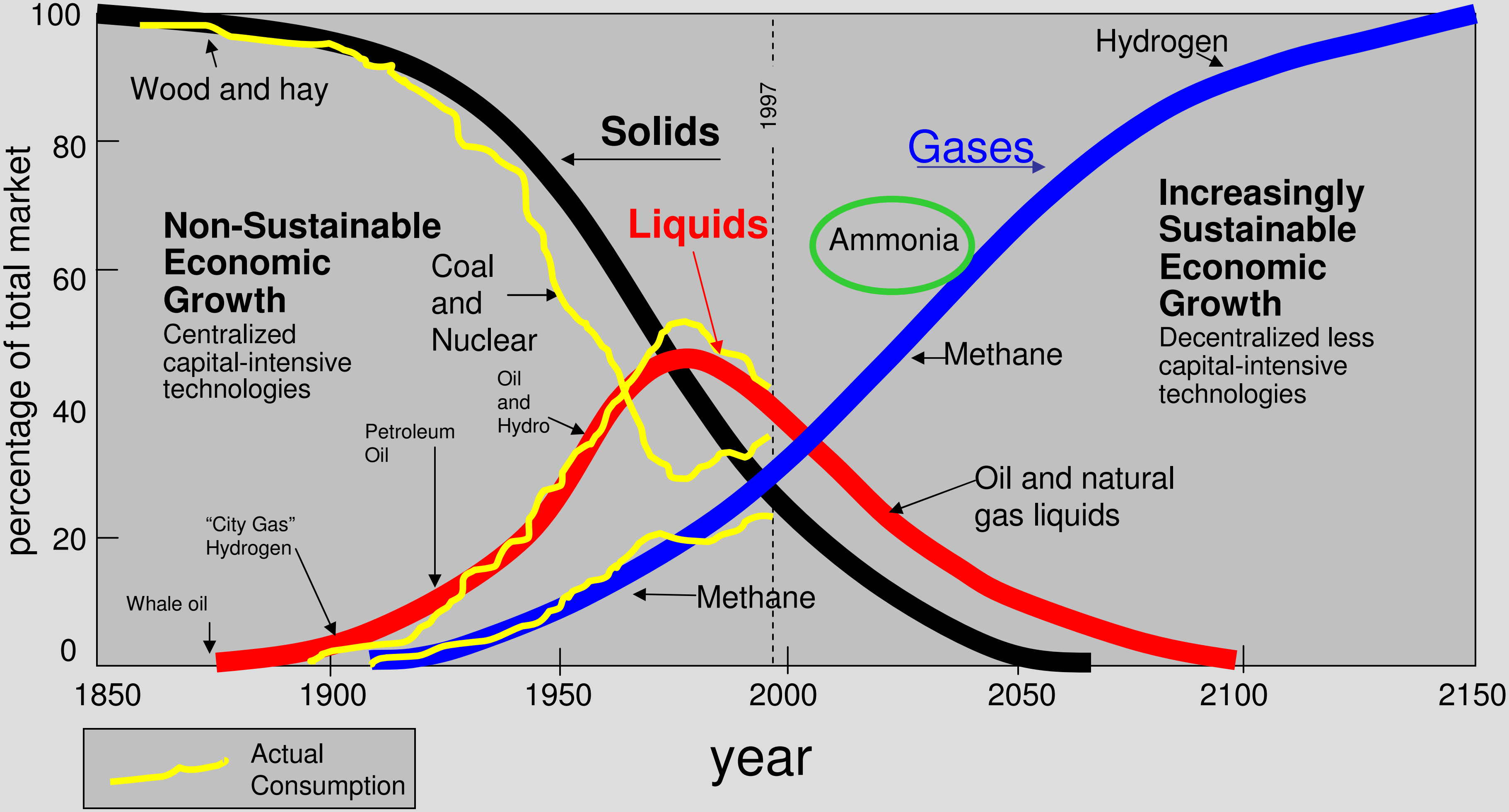
Patrick J. Desrochers
Dept. of Chemistry, University of Central Arkansas, Conway, AR 72035
patrickd@uca.edu

AFV, Minneapolis, MN Sep 2008

- Global energy gases—ammonia in context
- Tp*NiX(s) binding of ammonia
- Advantages of the organic anchorage
- Tp*NiBH$_4$: ammine-borane hybrid

Global transition to energy gases

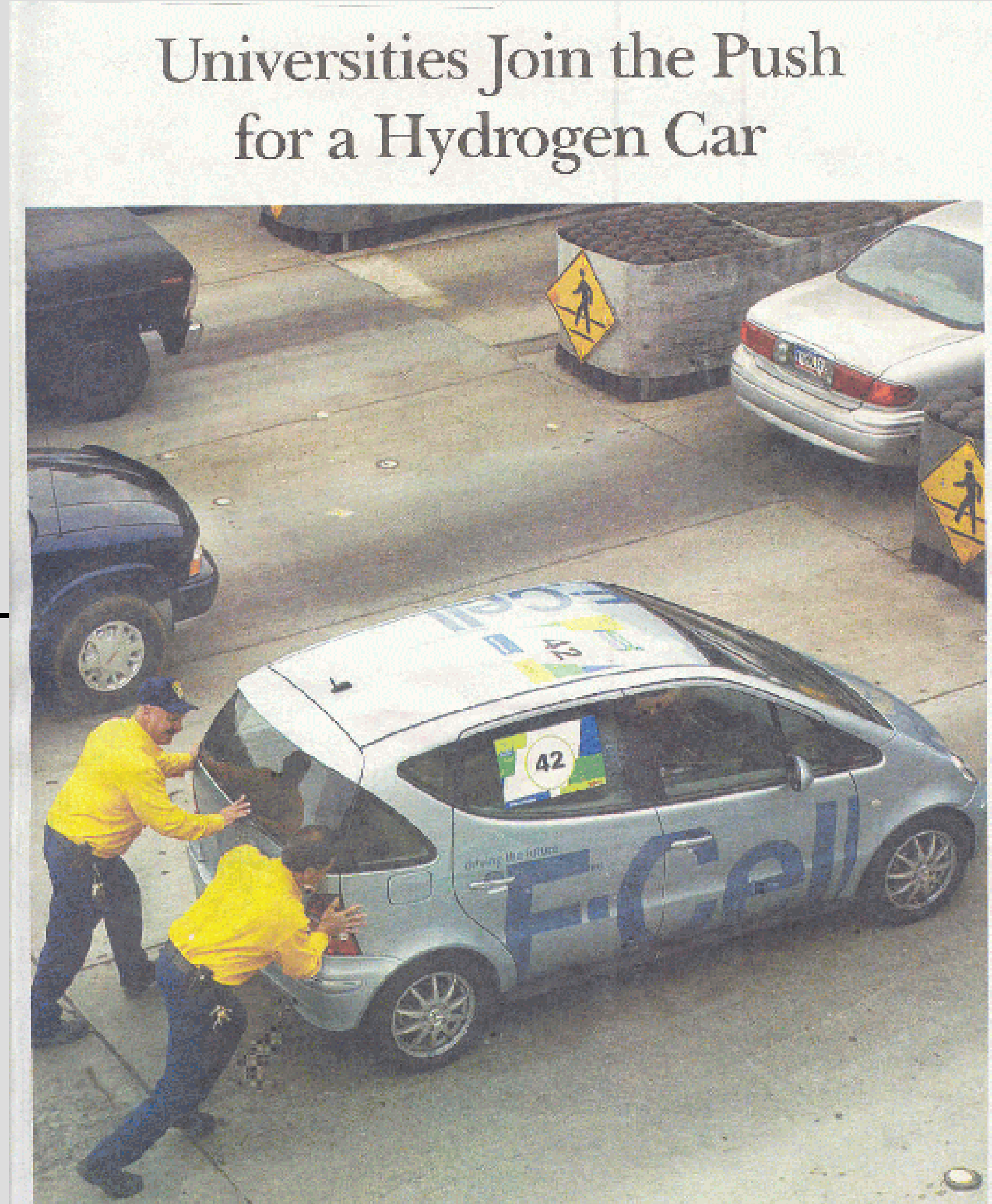
H:C 0.5:1 $_{coal}$ 2:1 $_{oil}$ 4:1 $_{NG}$:1 $_{NH3,H}$



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

The promise of a hydrogen economy

Fuel	ΔH^o_{comb}, *kJ/g*
Gasoline	48
Methane	56
Lithium	42
Hydrogen	143

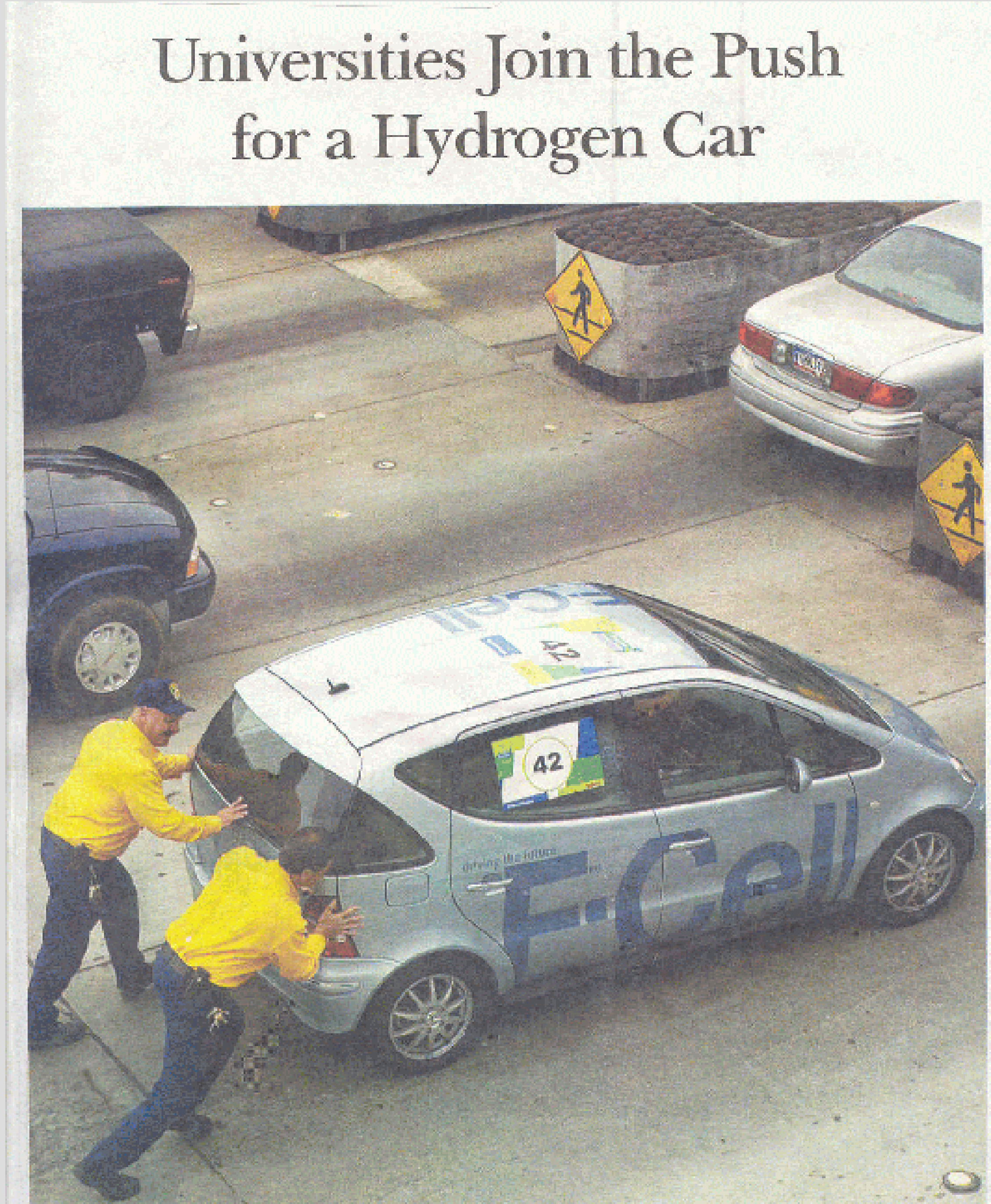


The Chronicle of Higher Education Oct 10, 2003.

The challenge of a hydrogen economy

storage

- amides $M(NH_2)_n$
- boranes BH_3NH_3
- ammines $M(NH_3)_nX_m$

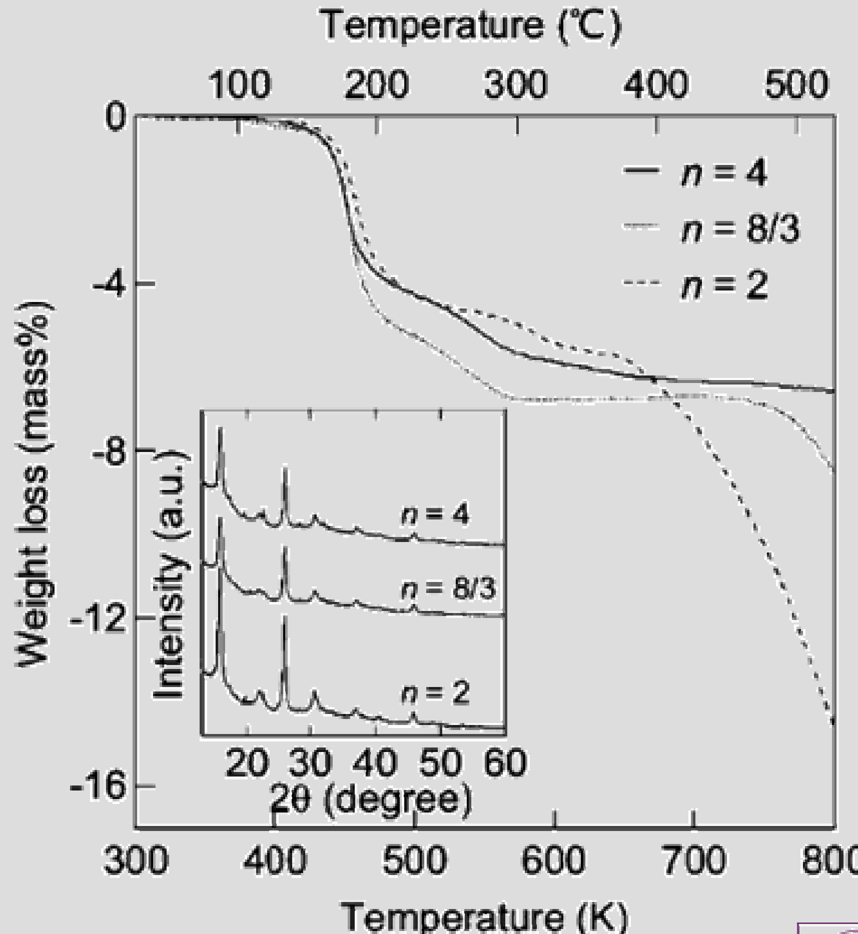


The Chronicle of Higher Education Oct 10, 2003.

Amides

$$Mg(NH_2)_2 + nLiH \longrightarrow Mg_3N_2 + Li_xNH_y + nH_2$$

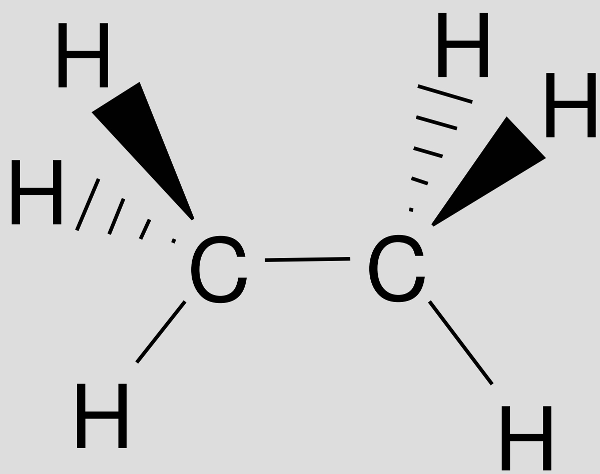
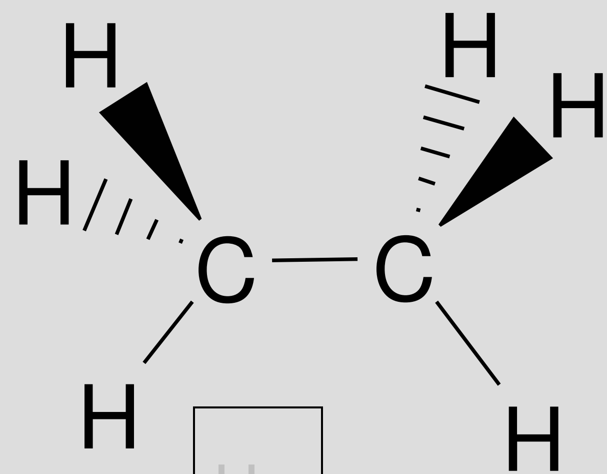
- Mixed amide/hydride improved desorption T
- Variable compositions provide tunable control
- $T(H_2)$ formation < $T(NH_3)$



Orimo, S.; Nakamori, Y.; Eliseo, J. R.; Z♒ttel, A.;Jensen, C. M. *Chem. Rev.* **2007**, *107*, 4111.

Ammine-borane

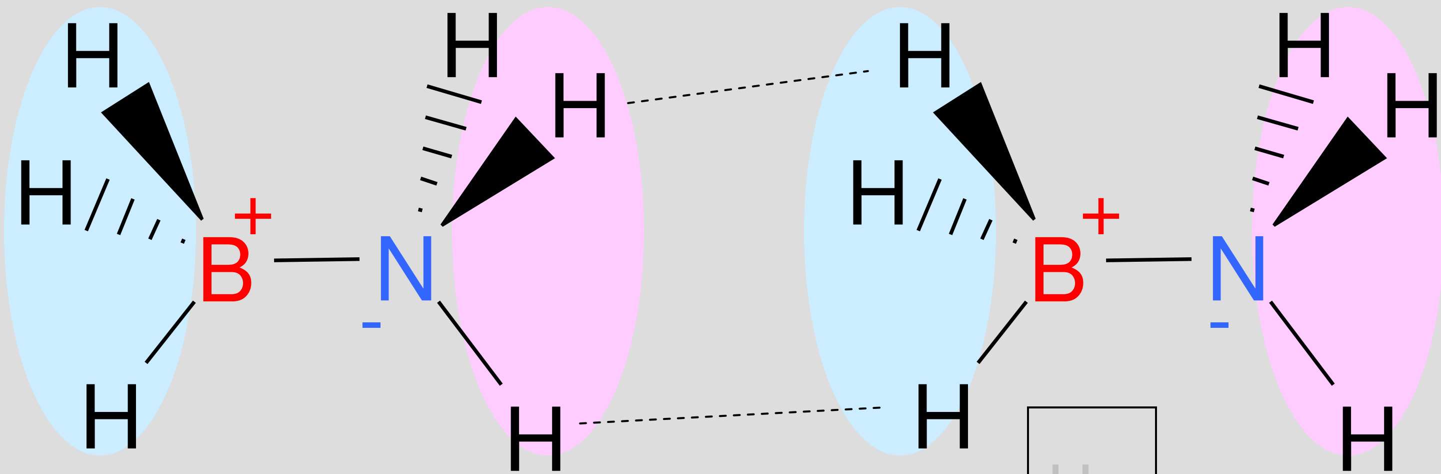
ethane(g)

					He
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar

Ammine-borane

ammine-borane(s)

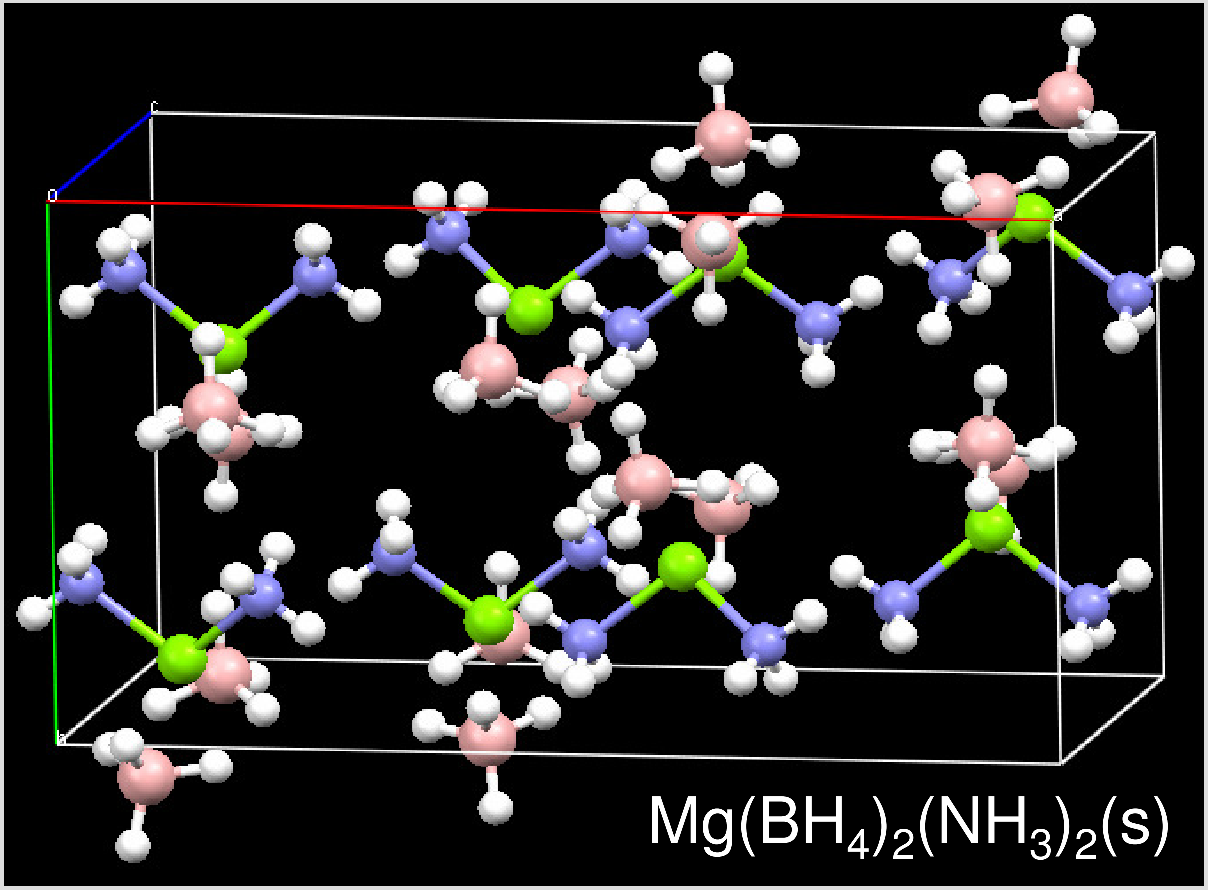


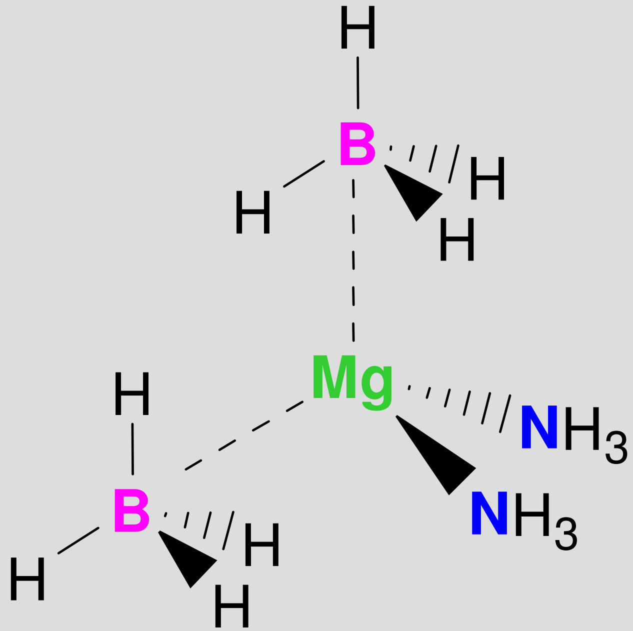
					He
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar

$$NaBH_4 + NH_4Cl \xrightarrow{THF} H_2 + BH_3NH_3 + NaCl$$

Ramachandran, P. V.; Gagare, P. D. *Inorg. Chem.* **2007**, *46*, 7810-7817.

Ammine-borane hybrids





m.p. 94 °C

- N-H···H and B-H···H parameters comparable to BH_3NH_3(s)
- *endothermic* H_2/NH_3 release *vs* BH_3NH_3(s)

Soloveichik, G.; Her, J. –H.; Stephens, P. W.; Gao, Y.; Rijssenbeek, J.; Andrus, M.; Zhao, J. -C. *Inorg. Chem.* **2008**, *47*, 4290-4298.

original report: Konoplev, V. N.; Silina, T. A. *Zh. Neorg. Khim.* **1985**, *30* (5), 1125.

Ammine-borane hybrids

$M(NH_2BH_3)_n$ (M = Ca, Mg, Ti, Sc; n = 1-6)

- variable thermal properties
- H_2 without foaming
- thermal stability improvement
- controlled H_2 release

American Chemical Society

Fuel Division

Inorganic Division

“Metal Derivatives of Ammonia-borane: Potential hydrogen storage materials”

Diyabalanage, H. V. K.; Shrestha, R. L.; Semelsberger, T. A.; Scott, B. L.; Burrell, A. K. 236th ACS Natl. Mtg, Philadelphia, August 2008: FUEL 56.

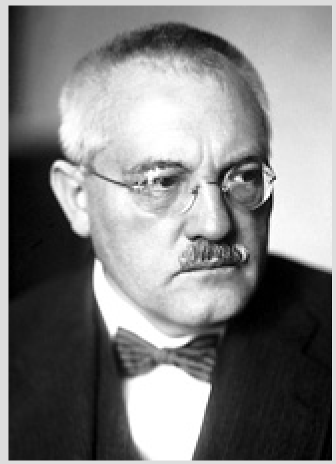
UCA

Haber-Bosch: Nobel worthy chemistry

motivated by *national security* interests

Fritz Haber

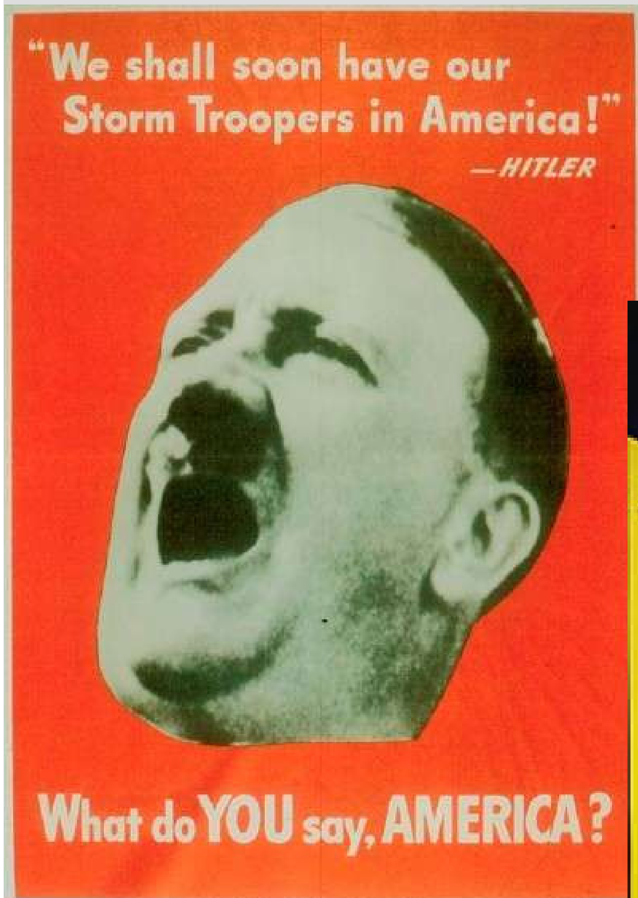
1918



Carl Bosch 1931

(shared with Friedrich Bergius)

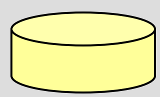
motivated by *national security* interests

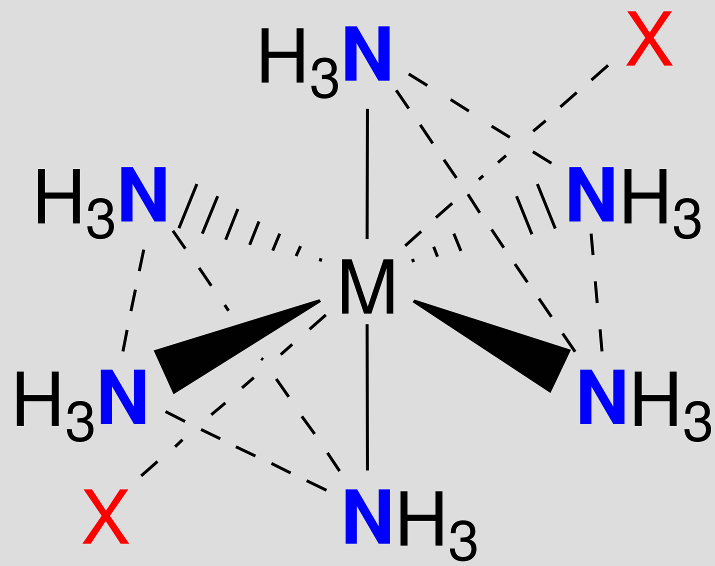


Ammines

AMMINEX

		mass % H	kg H/L
$Ca(NH_3)_8Cl_2$	increasing T_{des} ↓	9.8	0.116
$Mn(NH_3)_6Cl_2$		8.0	0.112
$Mg(NH_3)_6Cl_2$		9.2	0.115
$Ni(NH_3)_6Cl_2$		7.8	0.119



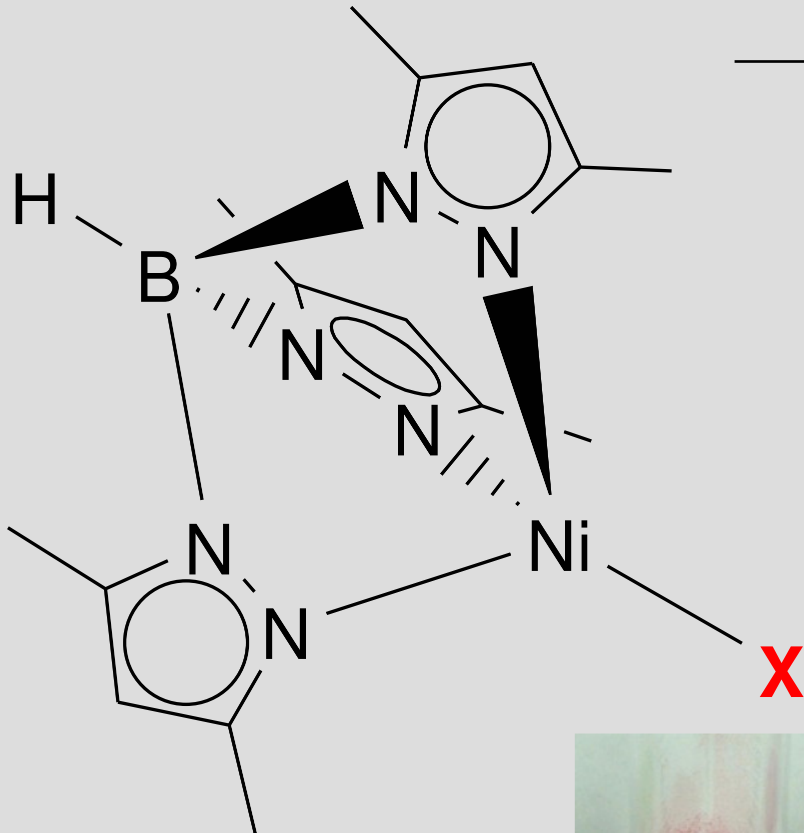


- ρ_{pellet} 95 – 99% of crystalline
- nanopores facilitate NH_3 transport
- heat transport controls NH_3 loss

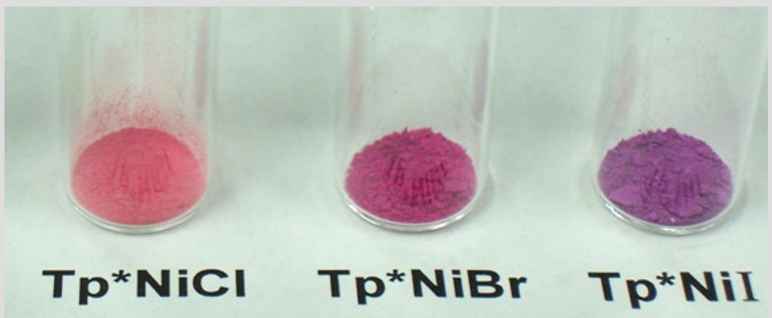
Sørensen, R. Z.; Hummelshøj, J. S.; Klerke, A.; Reves, J. B.; Vegge, T.; Nørskov, J. K.
Christensen, C. H. *J. Am. Chem. Soc.* **2008**, *130*, 8660–8668.
Christensen, C. H.; Sørensen, R. Z.; Johannessen, T. ; Quaade, U. J.; Honkala, K.; Elmøe, T. D.;
Køhler, R.; Nørskov, J. K. *J. Mater. Chem.*, **2005**, *15*, 4106 – 4108.

- Global energy gases—ammonia in context
- Tp*NiX(s) binding of ammonia
- Advantages of the organic anchorage
- Tp*NiBH_4: ammine-borane hybrid

Tp*NiX and ammonia

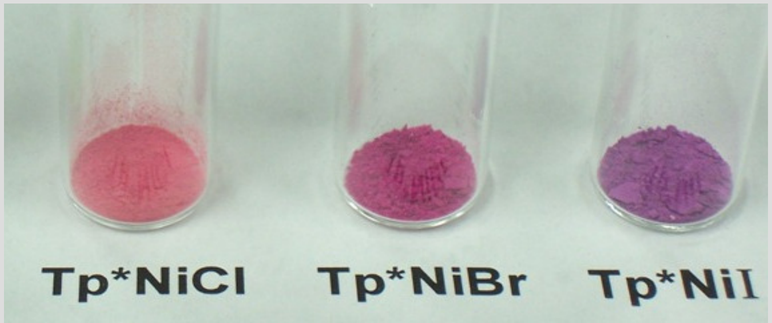


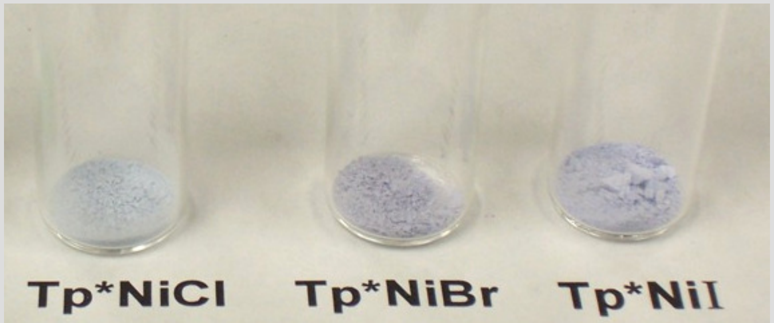
X	λ_{max} (nm)
Cl^-	490
Br^-	500
I^-	520

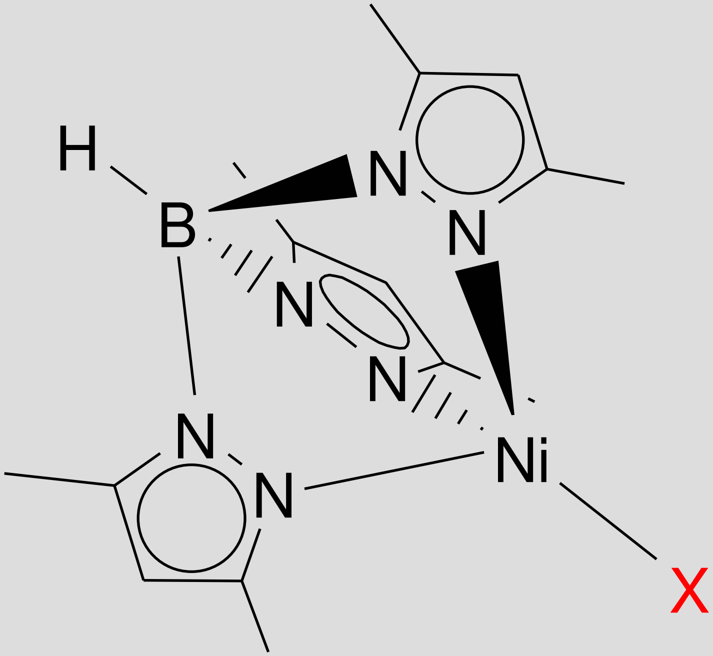


Desrochers, P. J.; Telser, J.; Zvyagin, S. A.;Ozarowski, A.; Krzystek, J.; Vicic, D. A. *Inorg. Chem.* **2006**, *45*, 8930-8941.

Form of bound ammonia independent of X



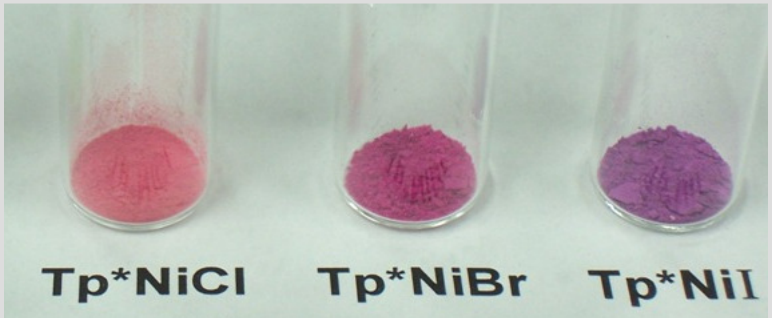


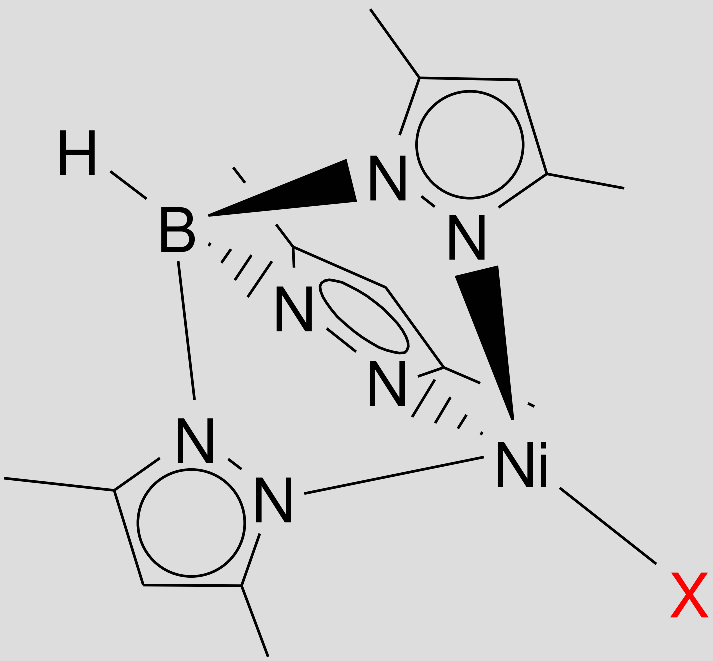


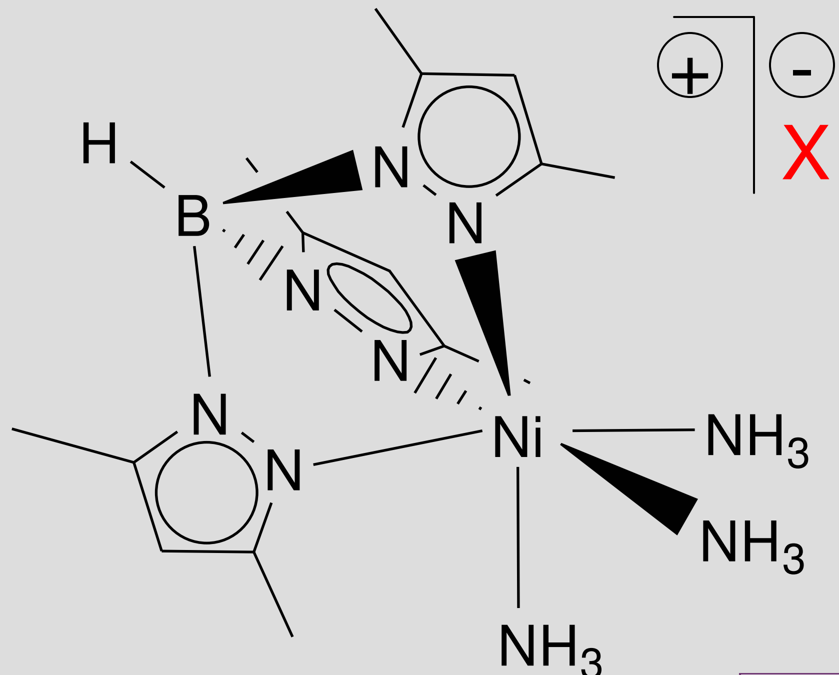
light absorption maxima
380 nm
570

similar to $Ni(NH_3)_6X_2$

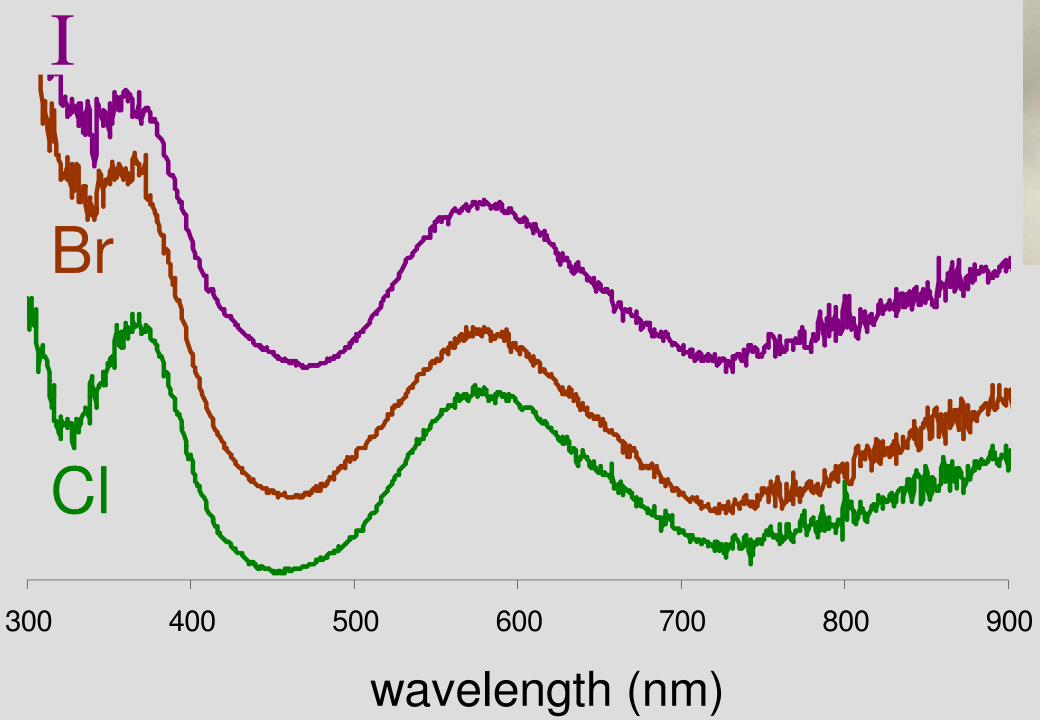
Form of bound ammonia independent of X

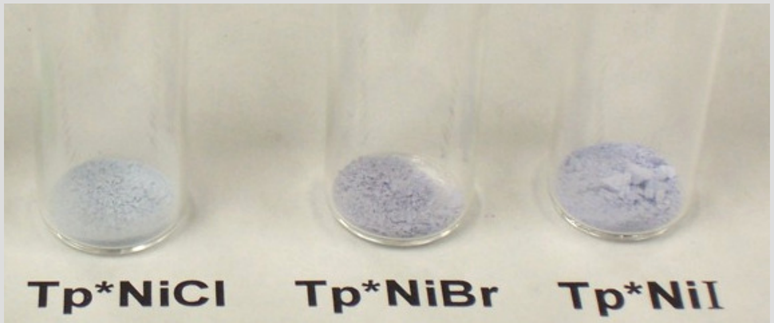


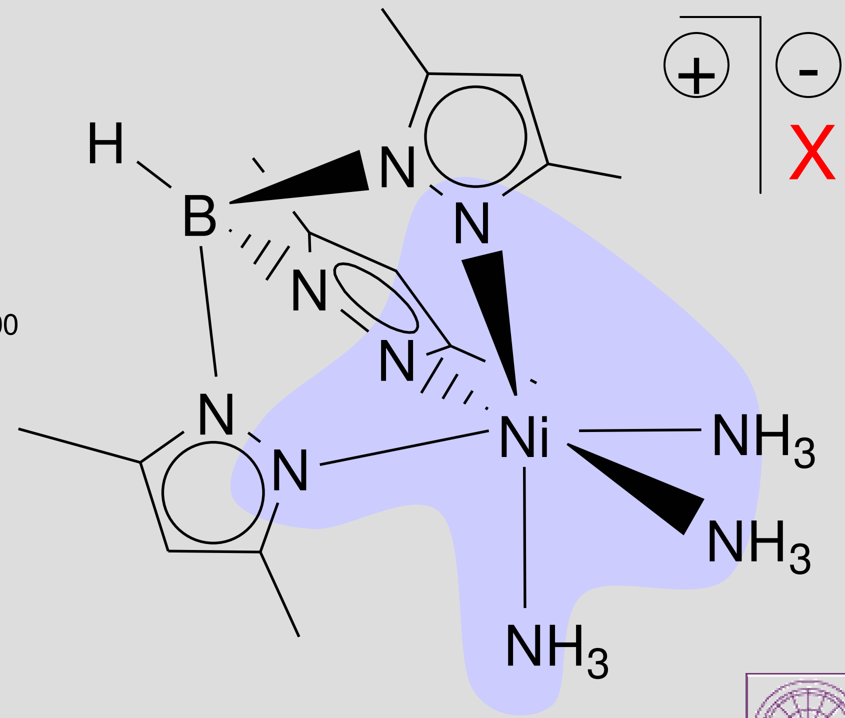




Form of bound ammonia independent of X

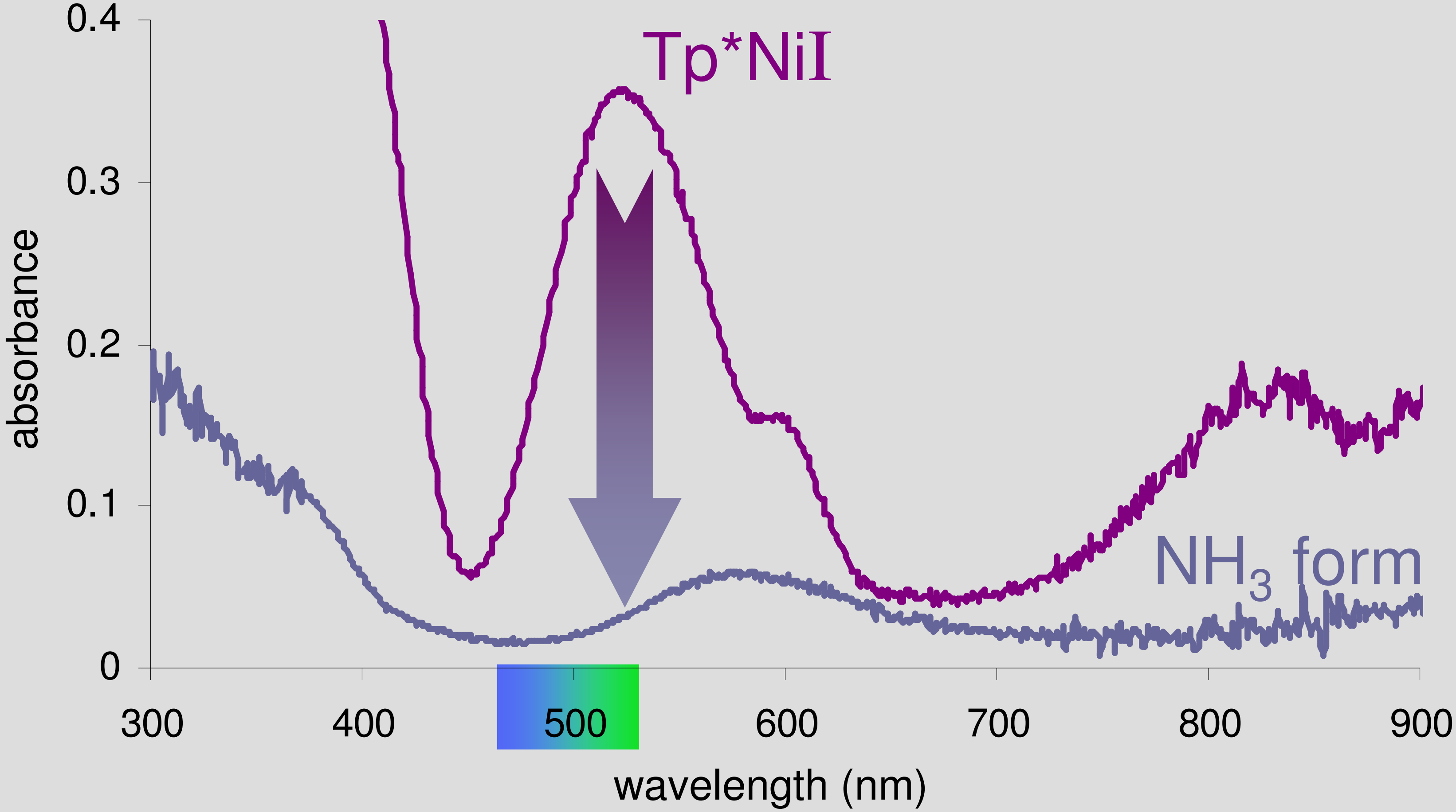






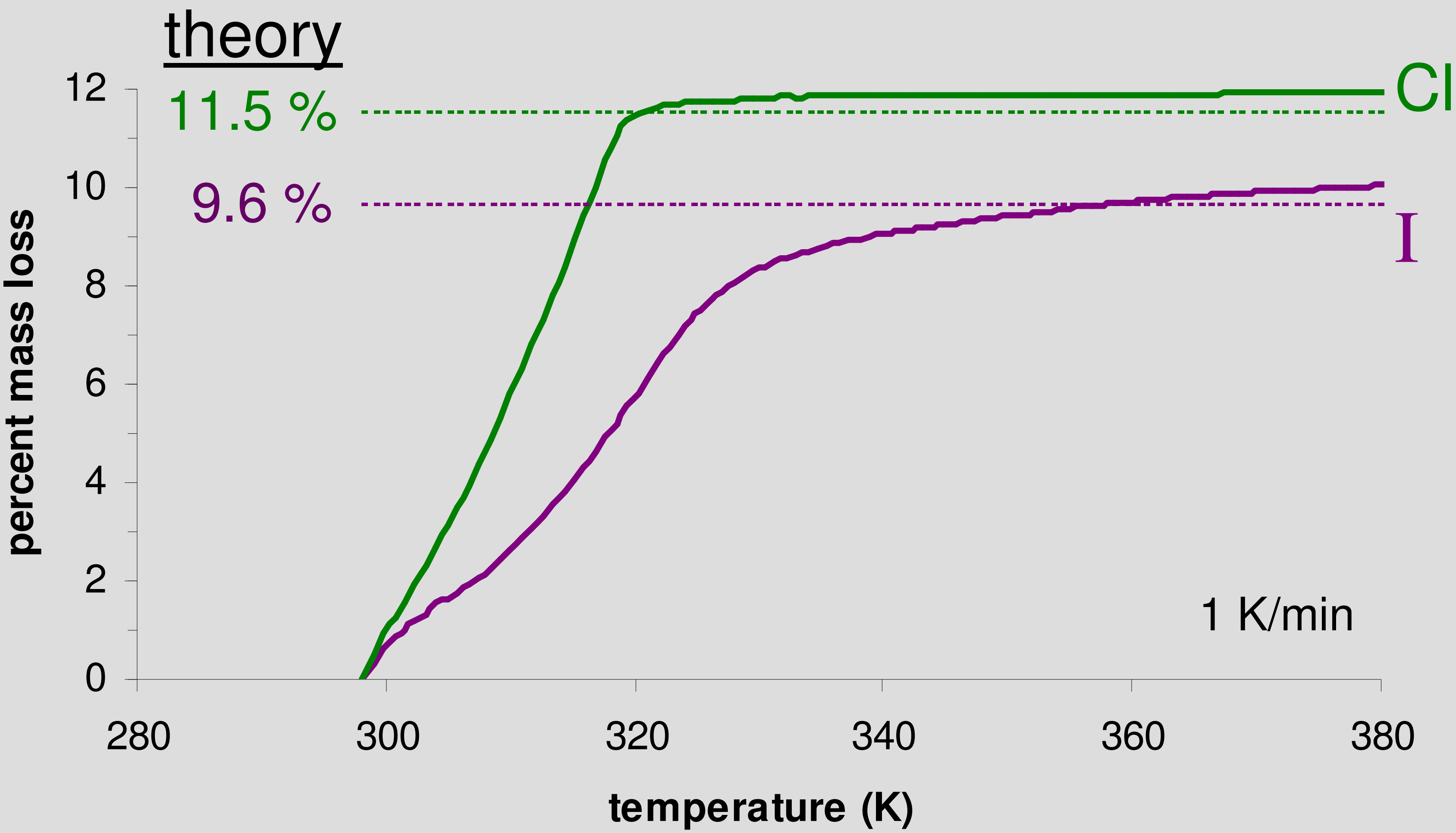
Largest optical absorption change with iodide

$Tp^*Ni(NH_3)_3\mathrm{I}(s) \longrightarrow Tp^*Ni\mathrm{I}(s) + 3NH_3(g)$

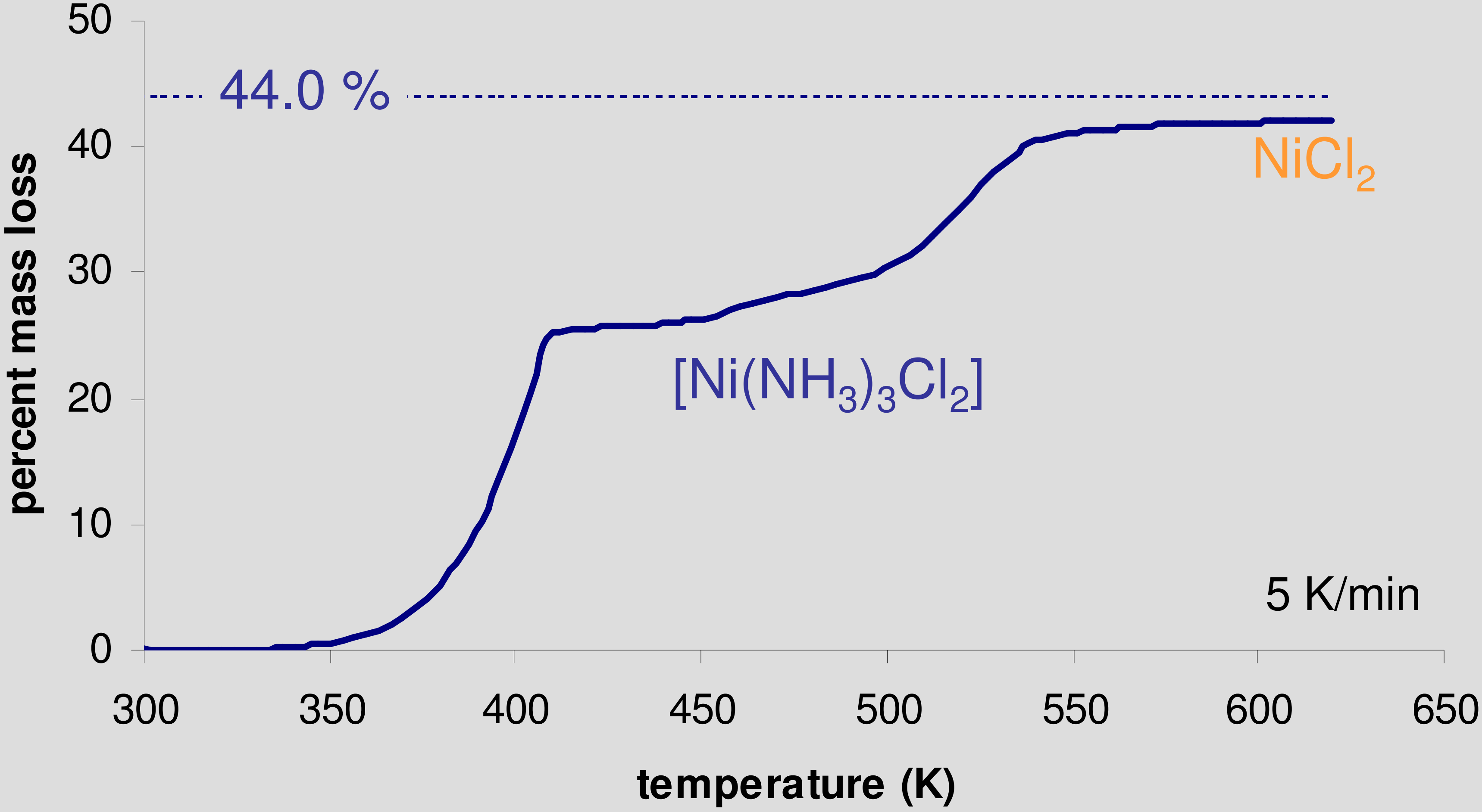


Quantitative ammonia uptake/release by Tp*NiX

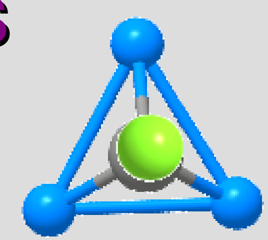
$$Tp^*Ni(NH_3)_3X(s) \longrightarrow Tp^*NiX(s) + 3NH_3(g)$$



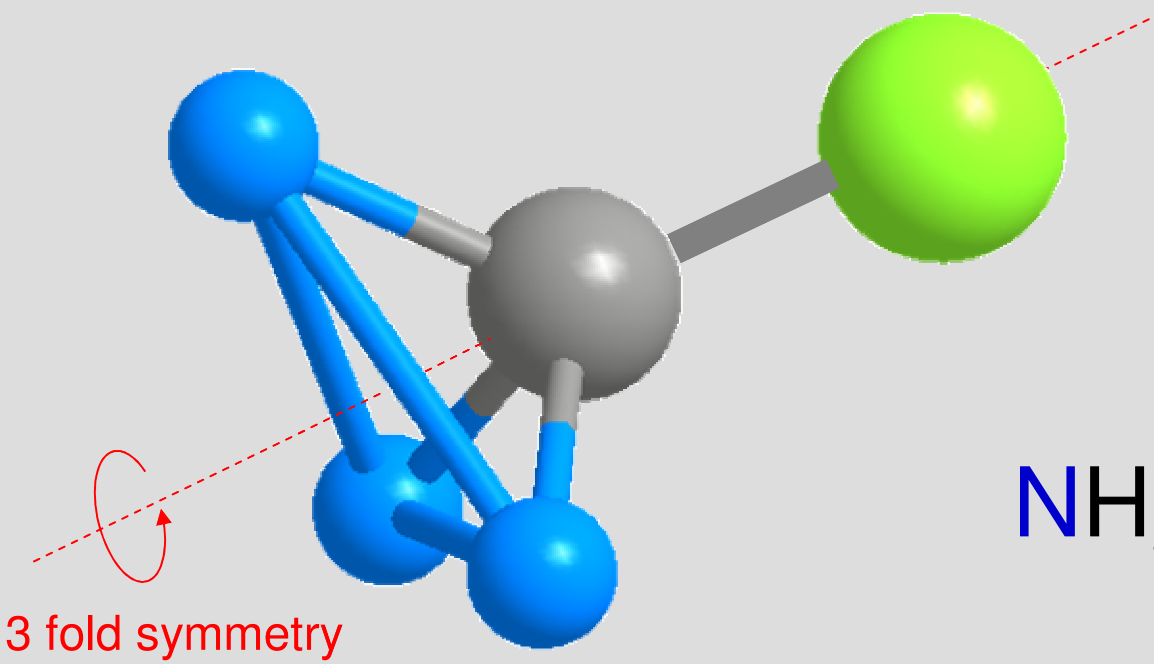
Compare to $[Ni(NH_3)_6]Cl_2$



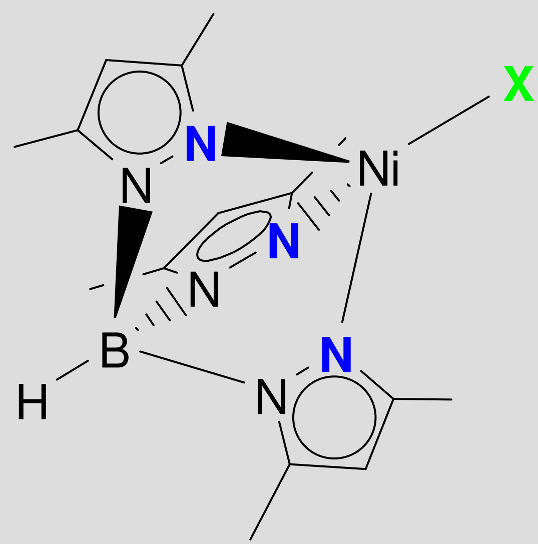
Halogen control may follow three fold axis



NH_3 NH_3

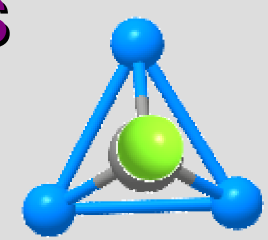


NH_3

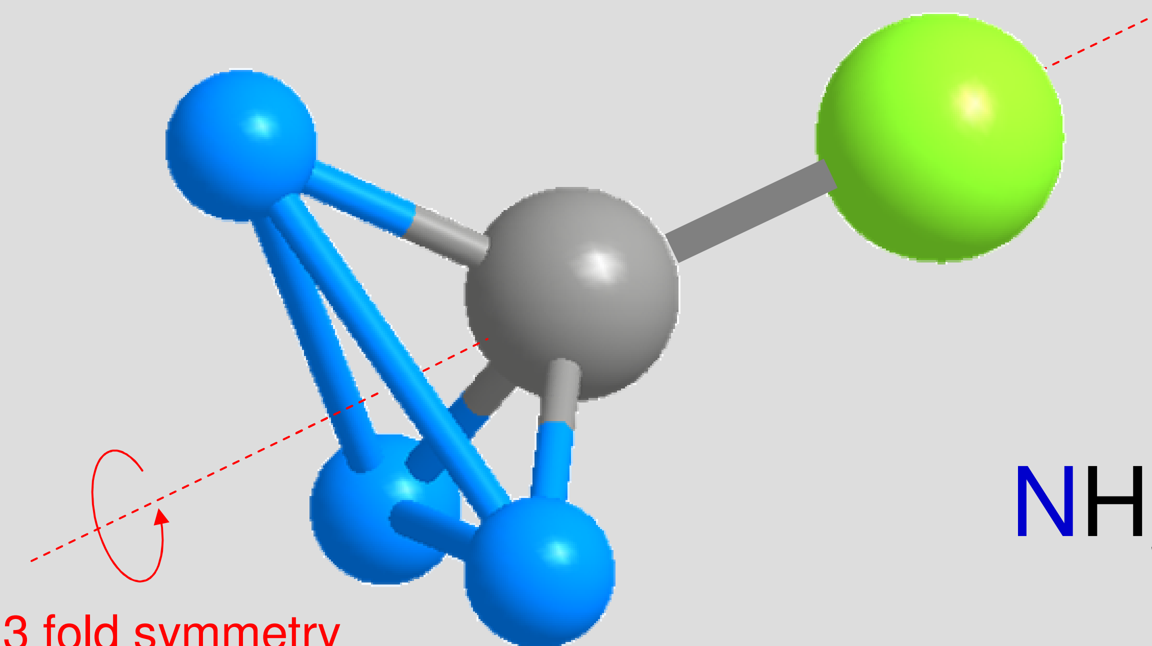


Halide typically along 3-fold axis of metal-ammines.
Hwang, I. –C.; Drews, T.; Seppelt, K. *J. Am. Chem. Soc.* **2000**, *122*, 8486.
Scheibel, P.; Prandl, W.; Papoular, R.; Paulus, W. *Acta Cryst* **1996** *A52*, 189.

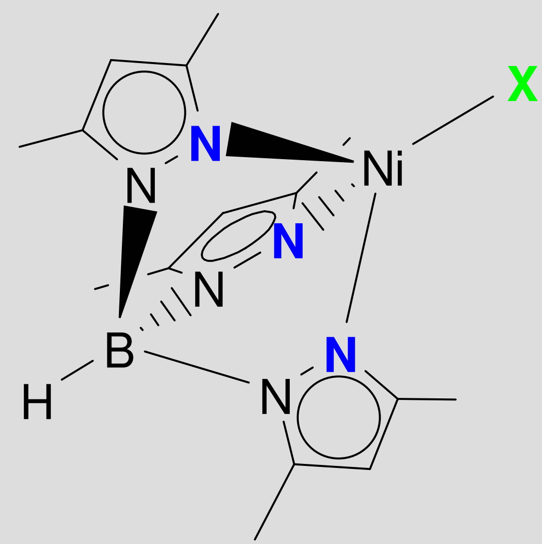
Halogen control may follow three fold axis



NH_3 NH_3

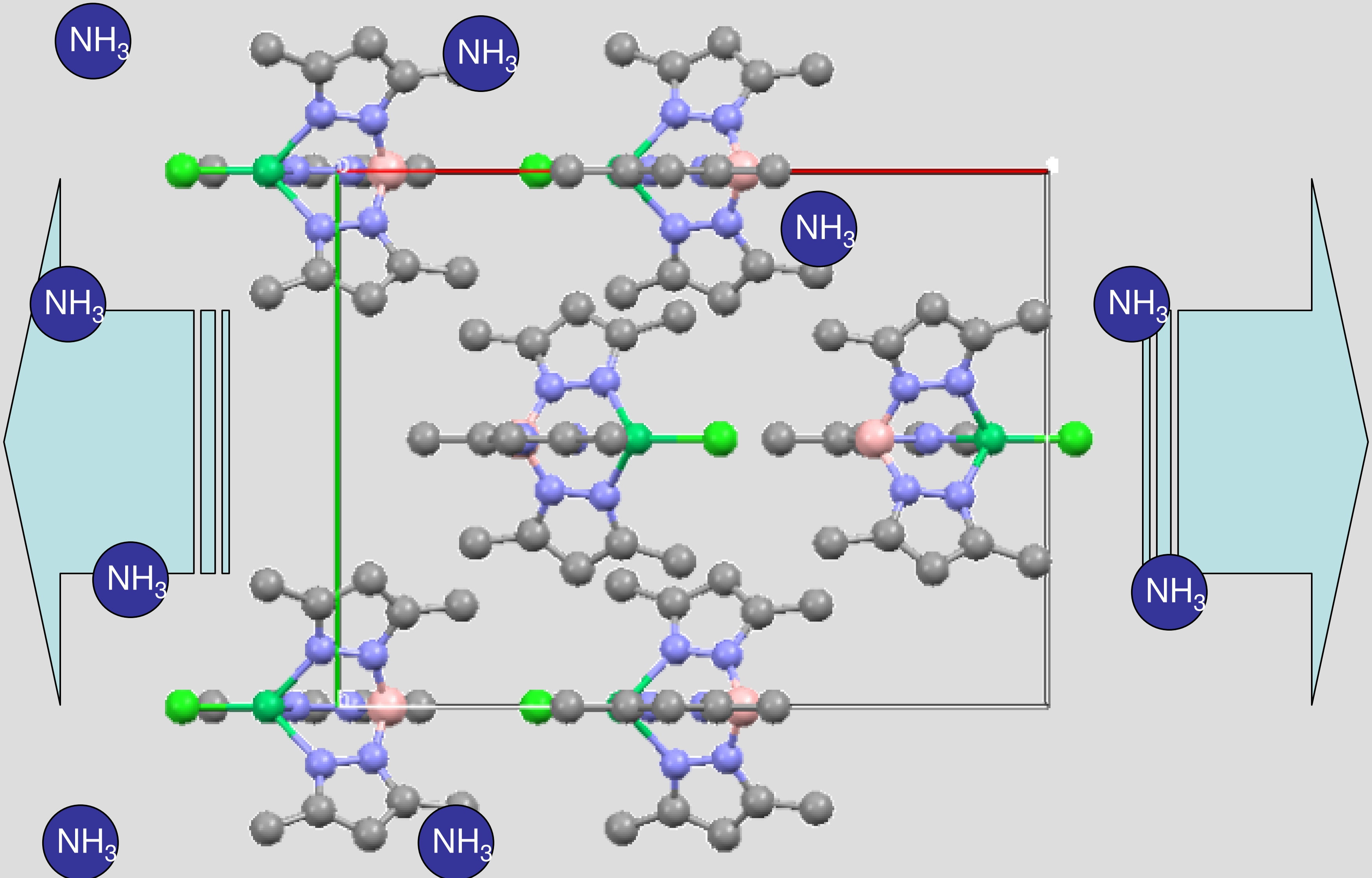


3 fold symmetry



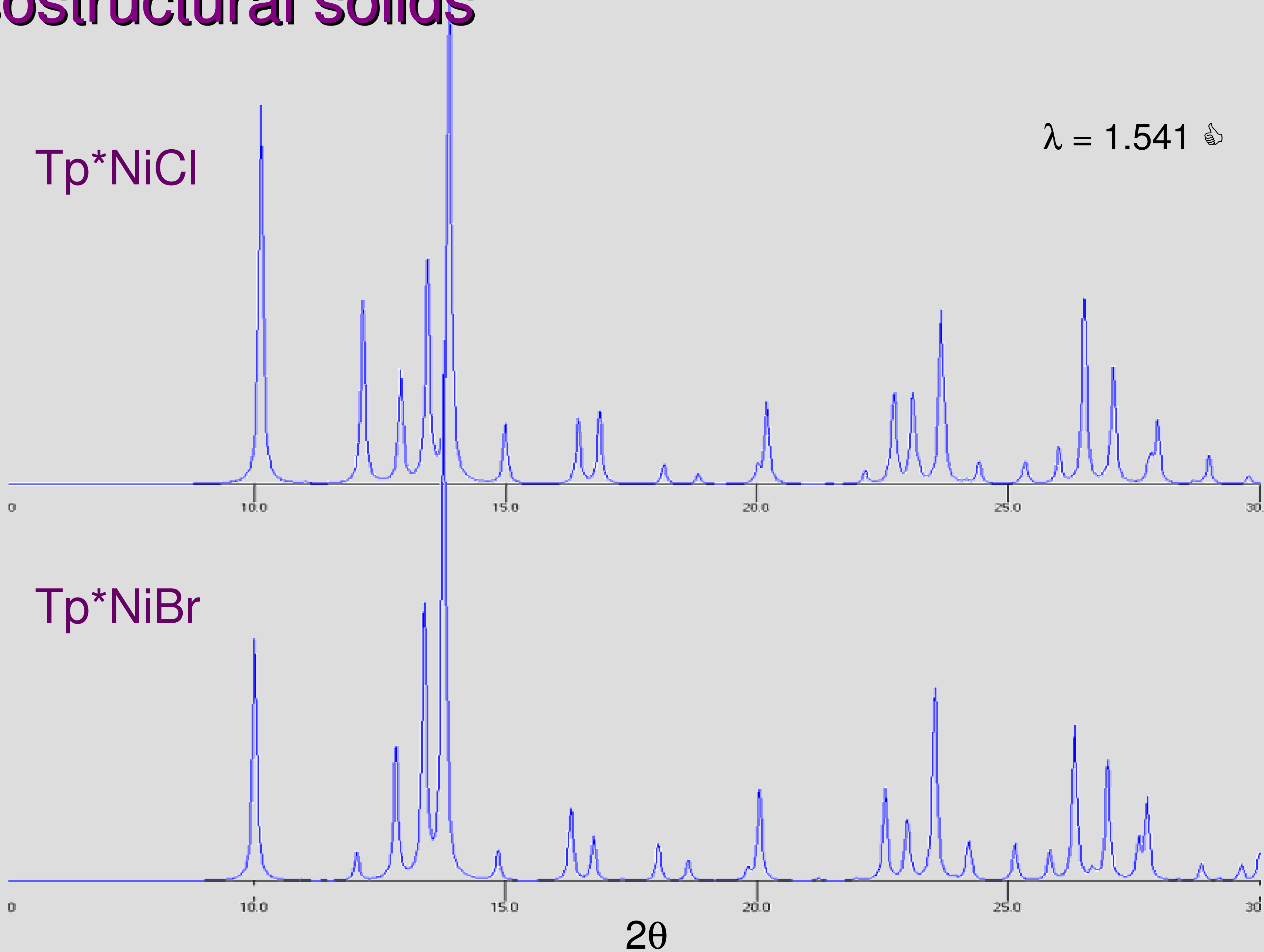
NH_3

Directional expansion with ammonia uptake



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

Isostructural solids



powder patterns simulated using Mercury v1.4.1 CCDC

Energetics of ammonia loss

$$Tp^*Ni(NH_3)_3X(s) \rightleftharpoons Tp^*NiX(s) + 3NH_3(g)$$

$$\Delta H - T\Delta S = -RT\ln K$$

enthalpy (ΔH): for Cl form $\Delta H = 190$ kJ/mol

$P_{NH3} \sim 0.1$ bar @ 300 K

entropy (ΔS): $\Delta S \sim 576$ J/K

Affinity for nitrogen substrates

$$Tp^RCo(NCMe)_3{}^+I^- \rightleftharpoons Tp^RCoI + 3NCMe$$

K = 45 (-22 ^oC)
$4x10^4$ (27)

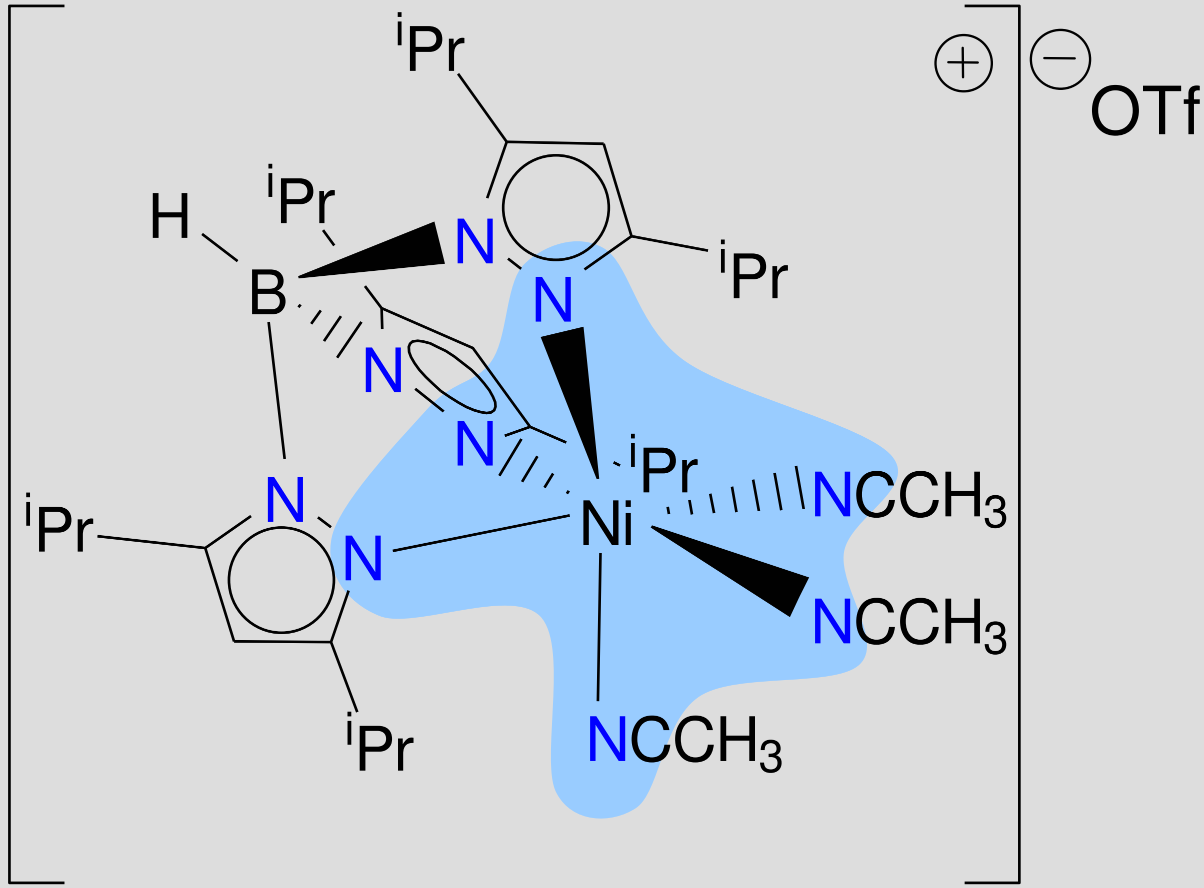
enthalpy (ΔH = 87 kJ): Co-NCMe bond strength
Co-I bond strength

entropy (ΔS = 377 J/K): mostly 3NCMe
3(151 J/K) = 453 J/K

Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *Inorg. Chem.* **1994**, *33*, 2306-2308.
$Tp^R = Tp^{iPrMe}$ (in chloroform solution)

Metals with 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.

Metals with high affinity for nitrogen substrates

Fe	Co cobalt	Ni nickel	Cu copper	Zn zinc
Ru	Rh	Pd	Ag	Cd
Os	Ir	Pt	Au	Hg

- numerous transition elements with NH_3 affinity
- could combine storage, decomp. catalyst
- variable magnetic and optical properties

- Global energy gases—ammonia in context
- Tp*NiX(s) binding of ammonia
- Advantages of the organic anchorage
- Tp*NiBH$_4$: ammine-borane hybrid

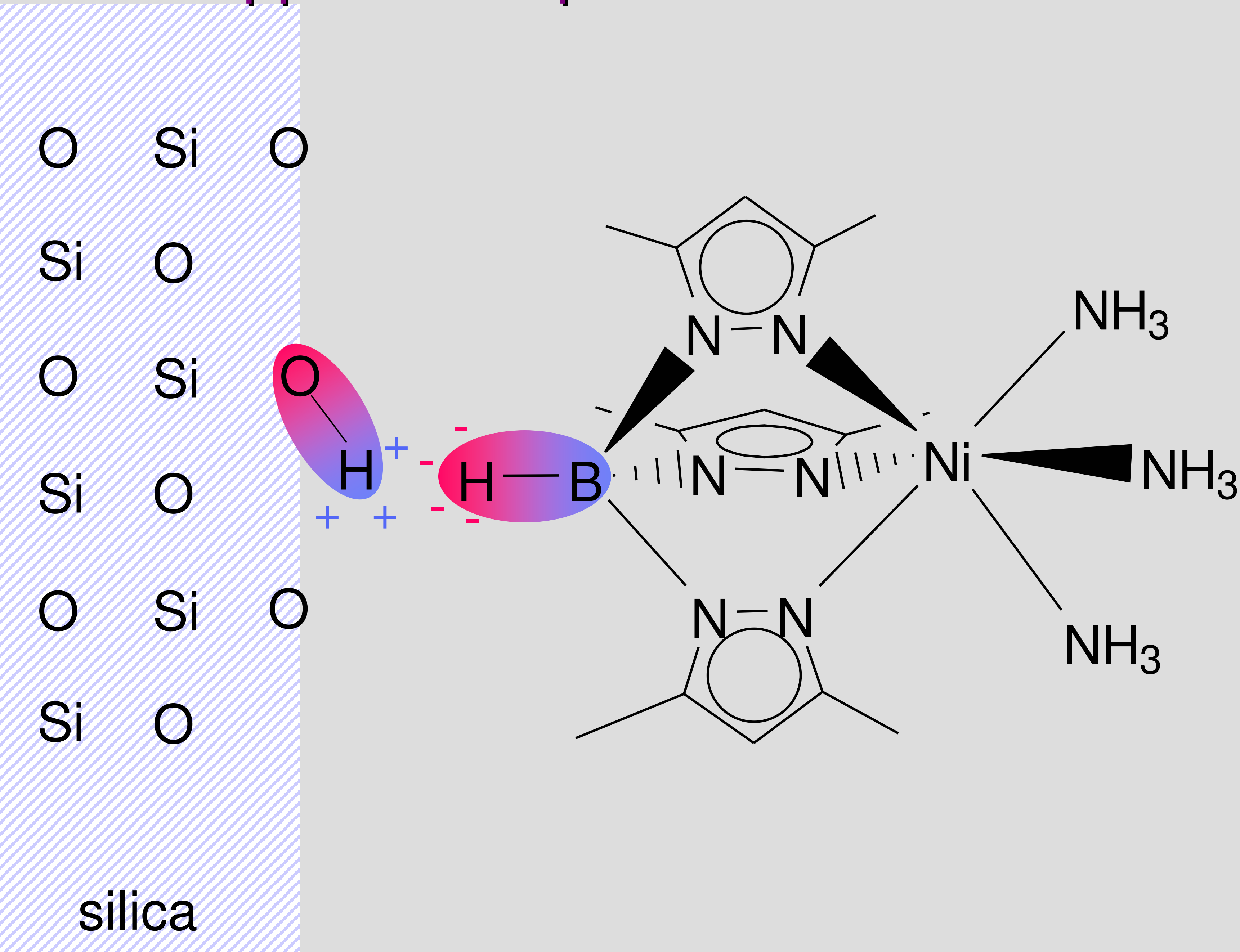
Solid supports for Tp*NiX

- bulk solid:
  distinct ammonia uptake

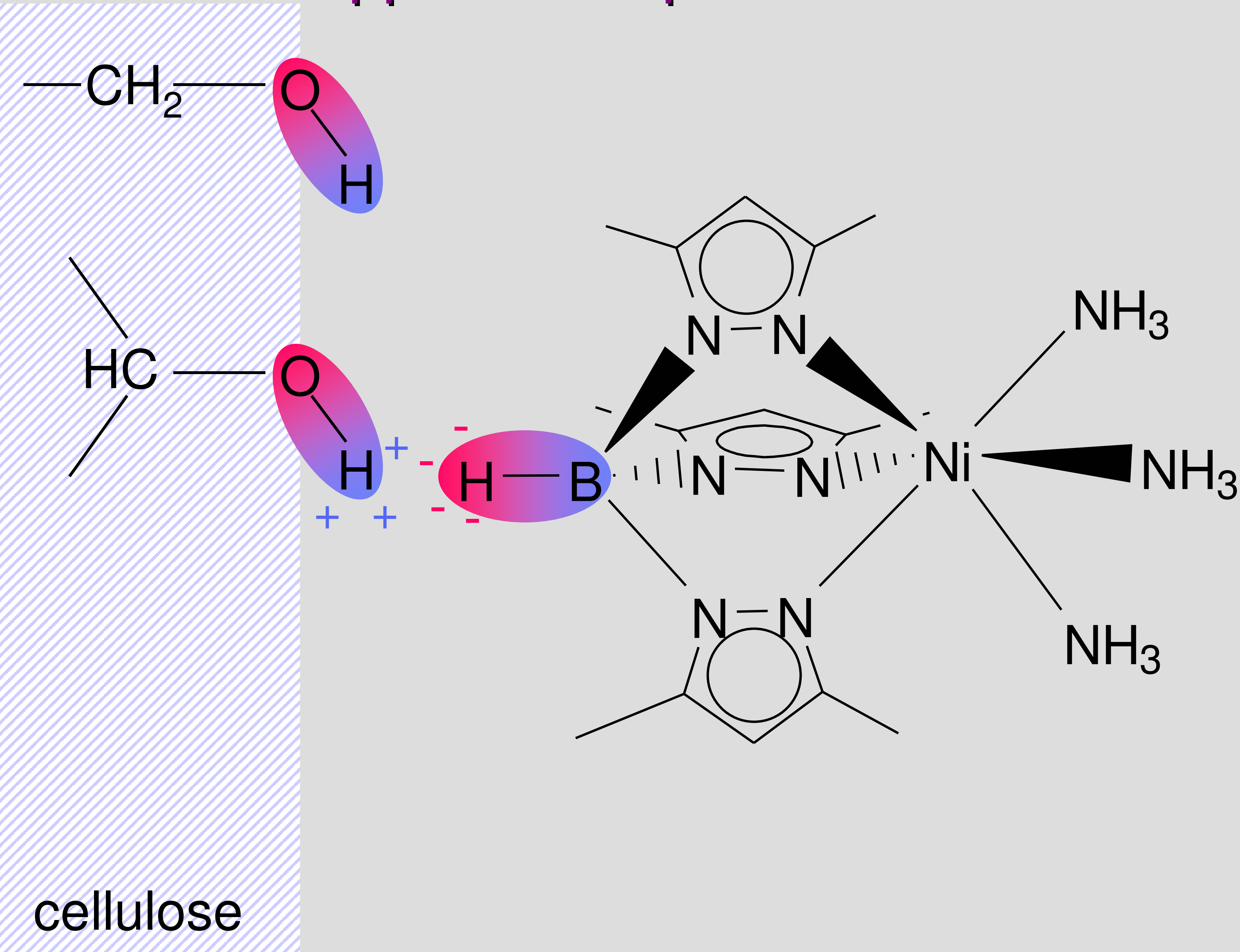
- phys-isorbed:
  1) silica thin-layer
  bulk powder
  2) cellulose fiber

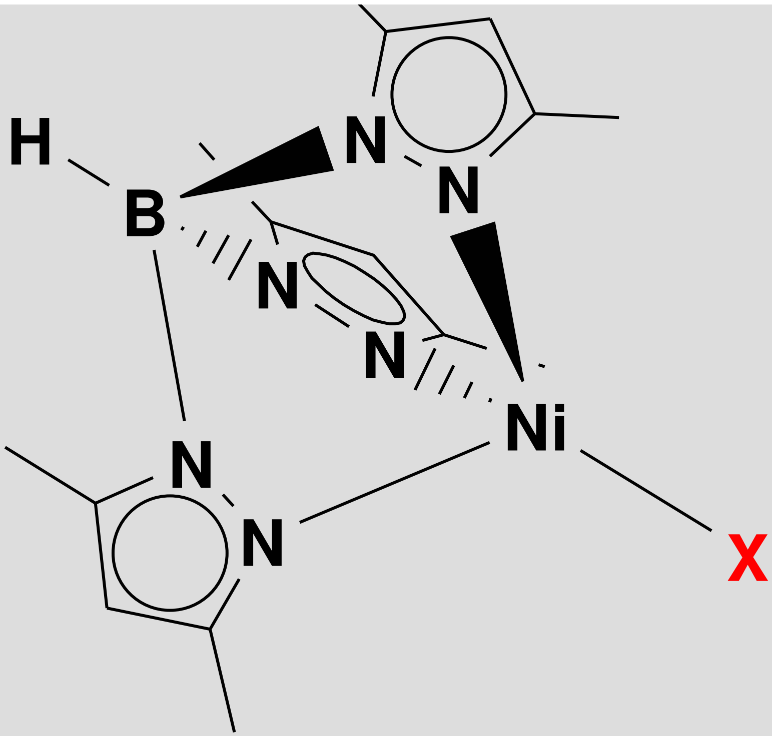
- chemically attached:
  tunable ancillary ligand
  reduce nickel leaching

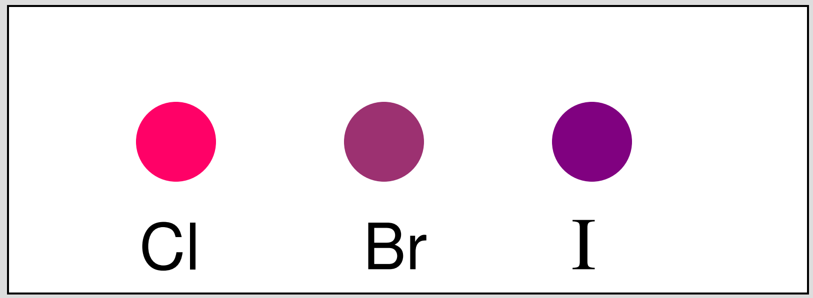
Silica supports for Tp*NiX

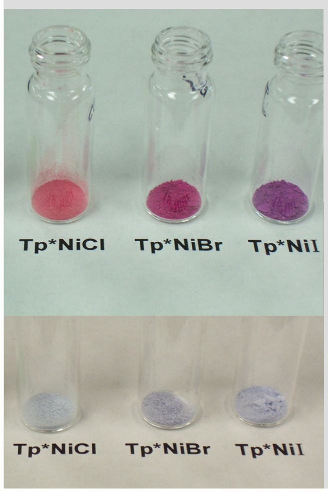


Cellulose supports for Tp*NiX

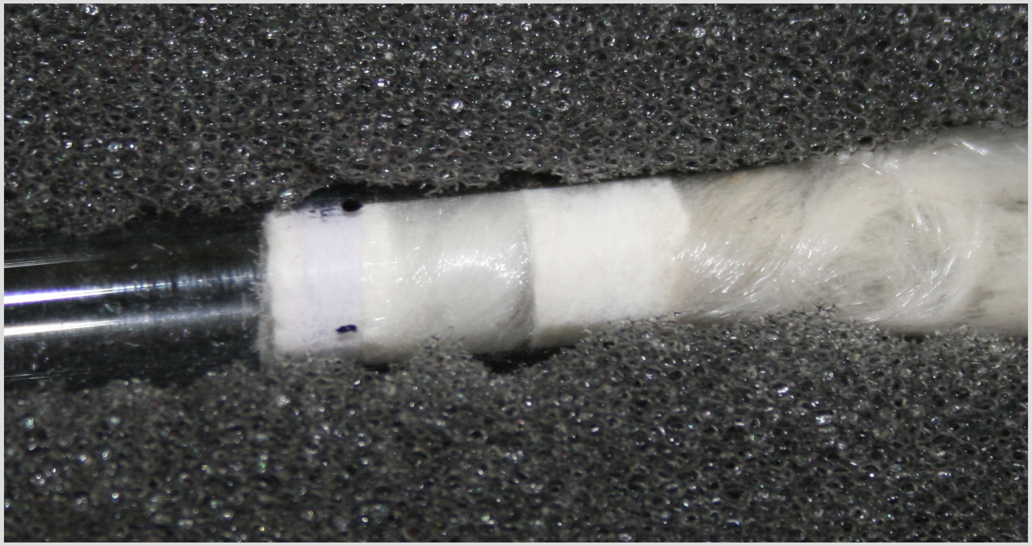



H
B
N
N
N
N
N
N
Ni
X


Cl
Br
I

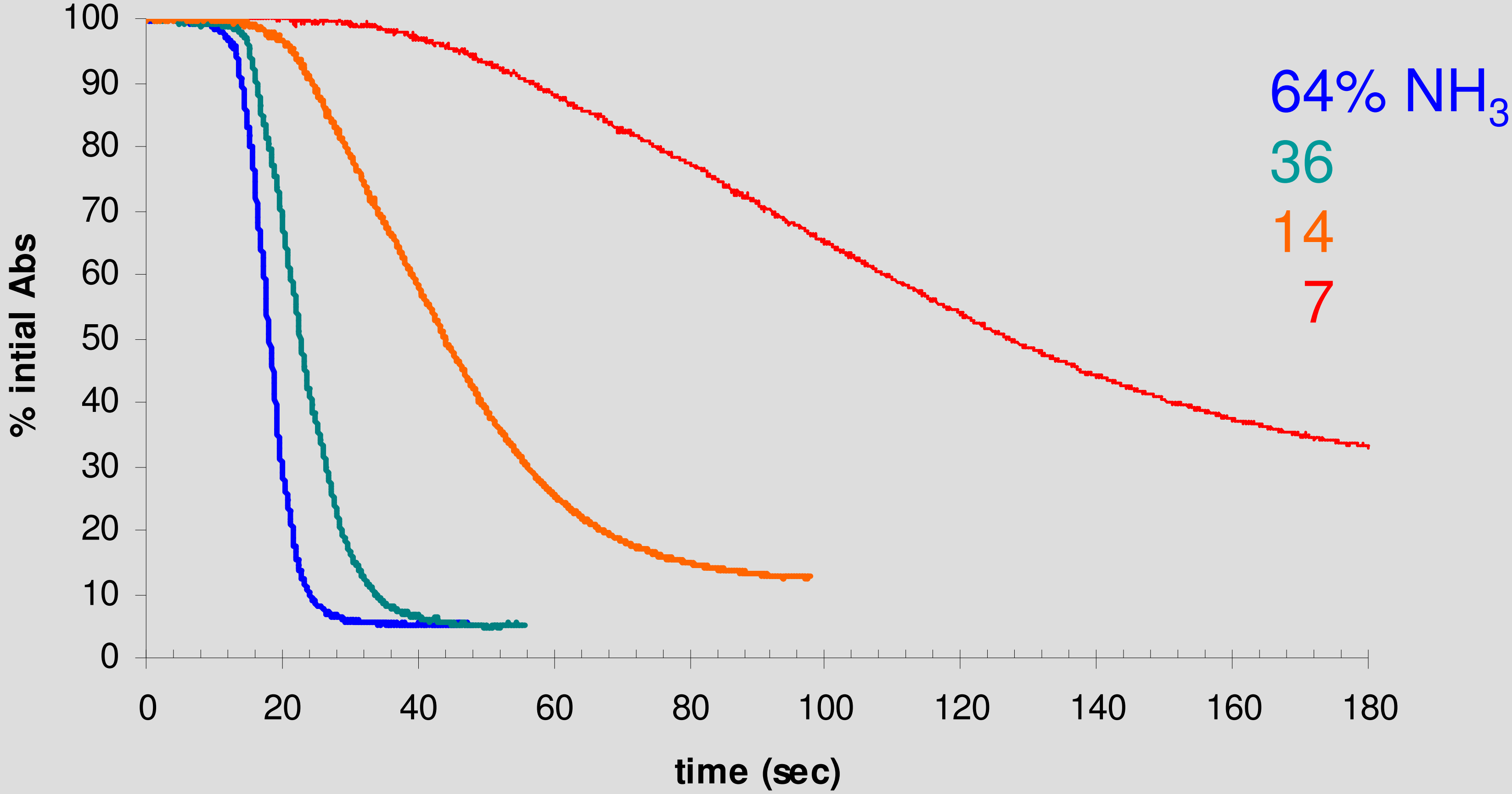

Tp*NiCl
Tp*NiBr
Tp*NiI
Tp*NiCl
Tp*NiBr
Tp*NiI

Optical Monitoring of Ammonia Uptake



Tp*NiBr on silica

Ammonia uptake by Tp*NiI

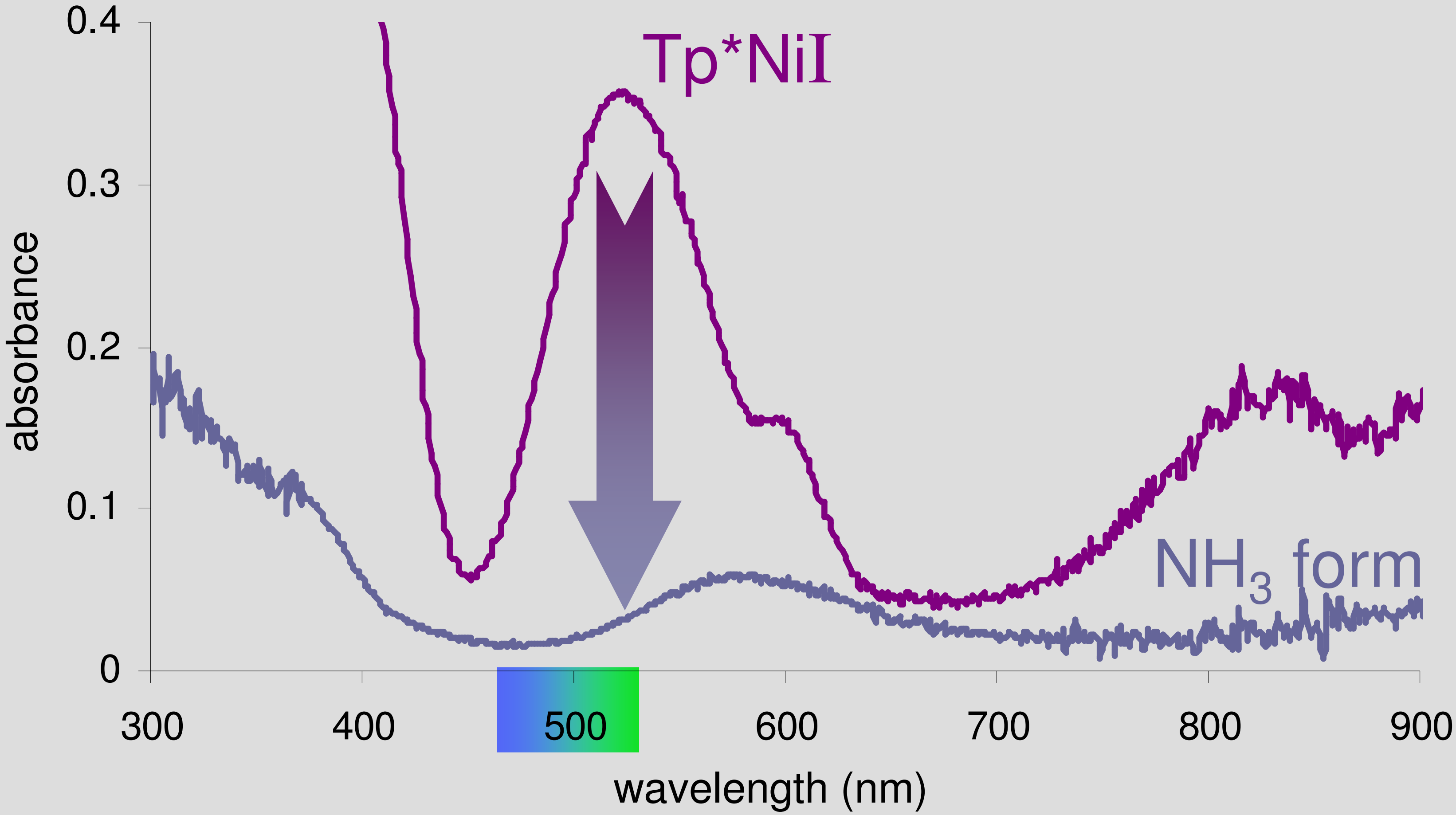


NH_3 at 12 mL/min, 25 ^oC

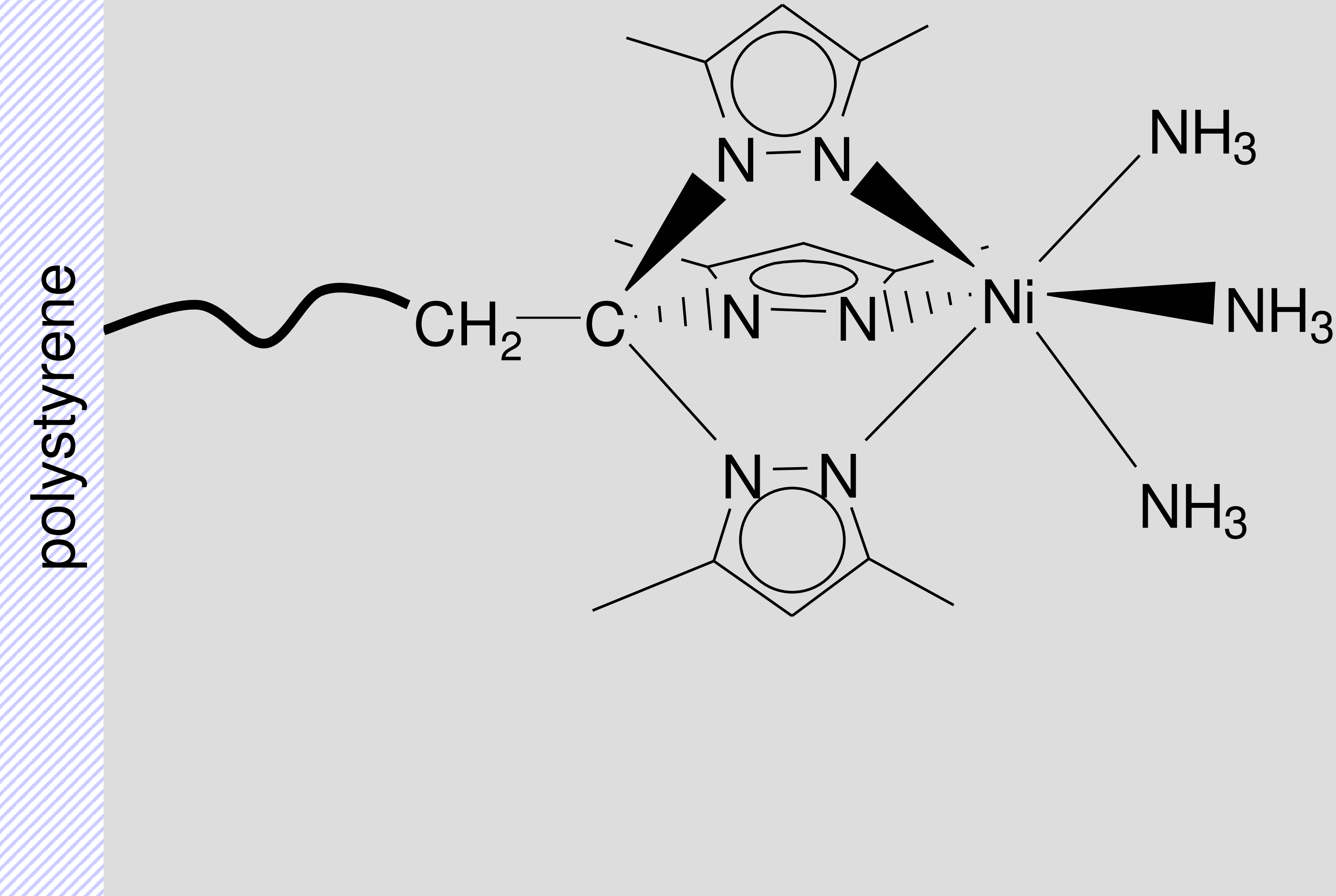
sensor reset: 80 ^oC, 3 min, pure N_2

Largest optical absorption change with iodide

$$Tp^*Ni(NH_3)_3\mathrm{I}(s) \longrightarrow Tp^*Ni\mathrm{I}(s) + 3NH_3(g)$$



Potential covalent supports for Tp*NiX

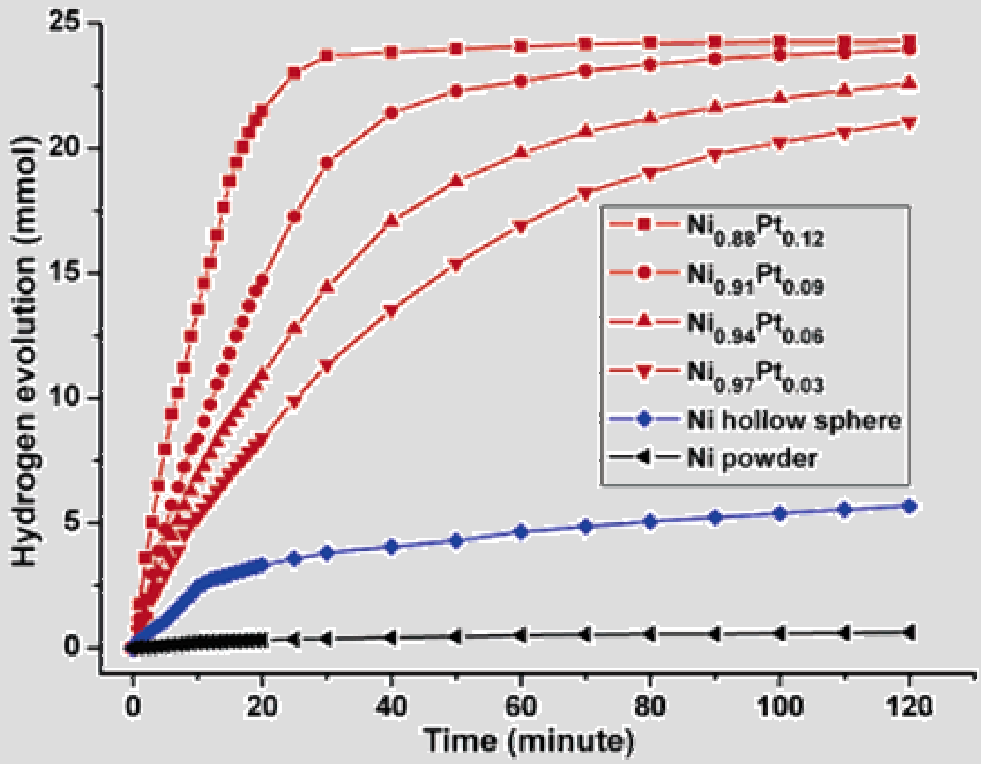


- Global energy gases—ammonia in context
- Tp*NiX(s) binding of ammonia
- Advantages of the organic anchorage
- Tp*$NiBH_4$: ammine-borane hybrid

Ammine-borane and Ni_{Pt}

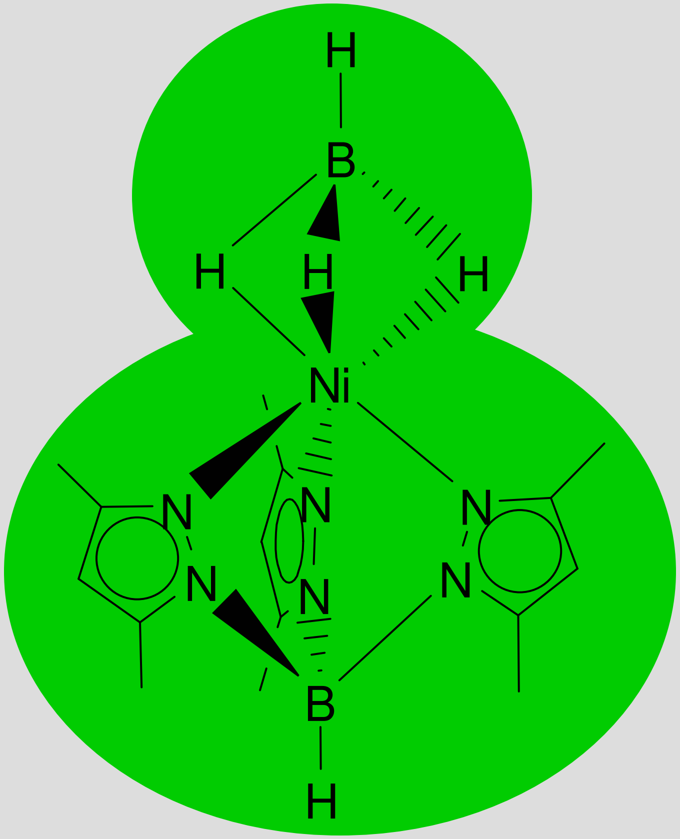
$$NH_3BH_3 + H_2O \xrightarrow{Ni_{Pt}} NH_4^+ + BO_2^- + 3H_2$$

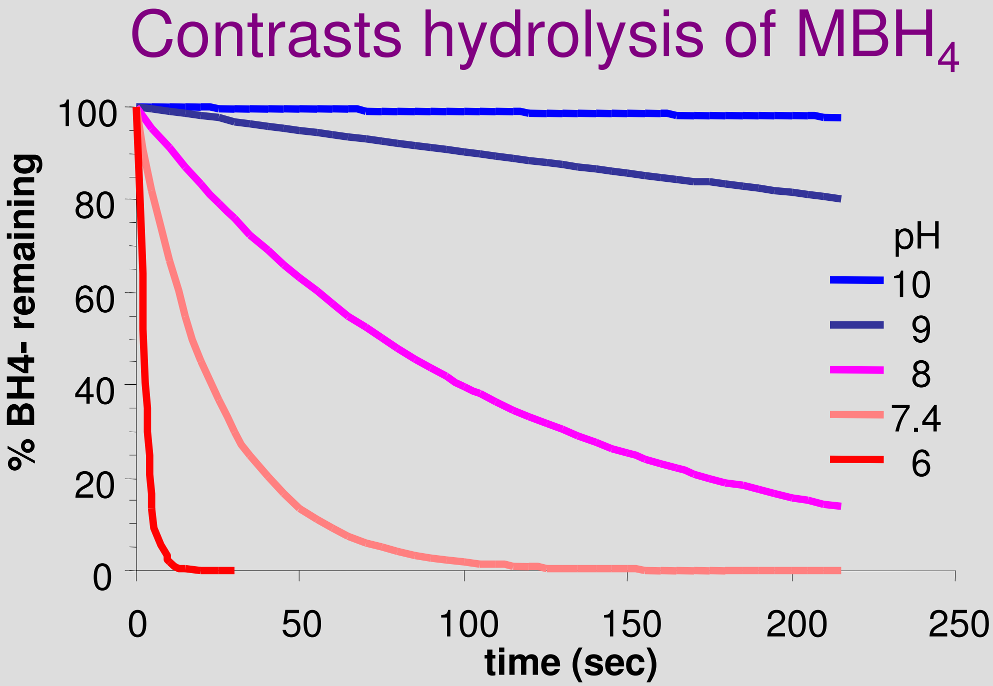
small % Pt in Ni catalyzes rapid hydrolysis



Cheng, F.; Ma, H.; Li, Y.; Chen, J. *Inorg. Chem.* **2007**, *46*, 788-794.

A stable borohydride



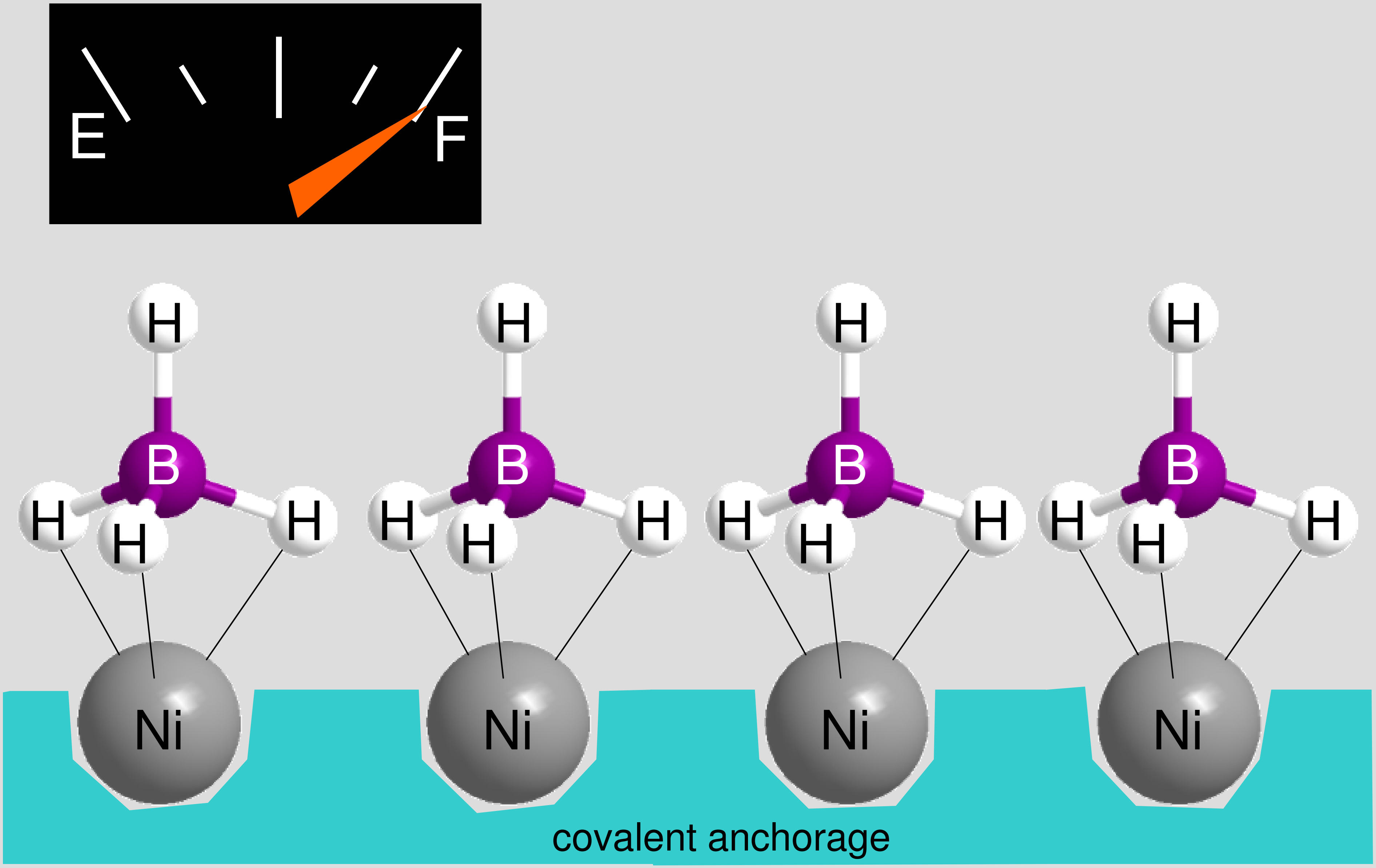


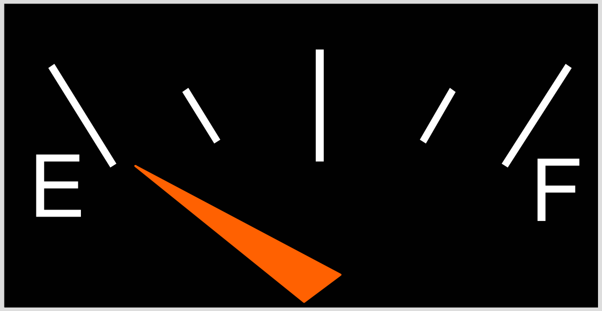
Davis, R. E.; Bromels, E.; Kibby, C. L. *J. Am. Chem. Soc.* **1962**, *84*, 885.

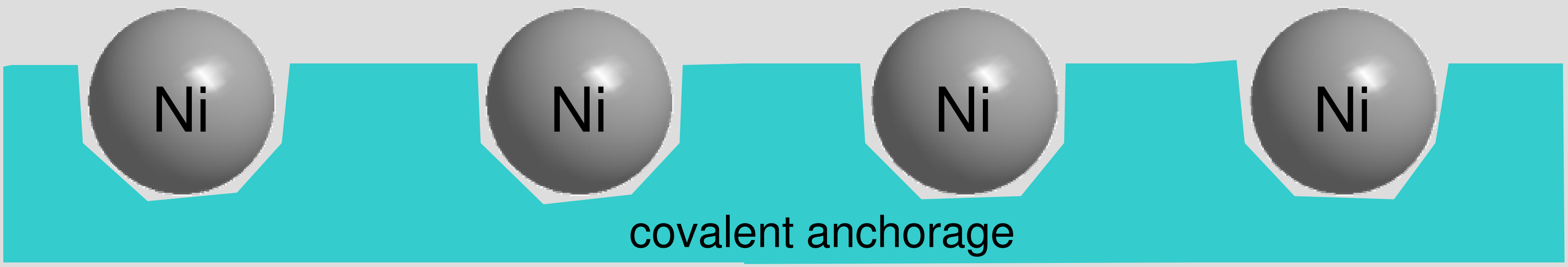
Tp* anchorage tempers reducing power of H-rich substrates

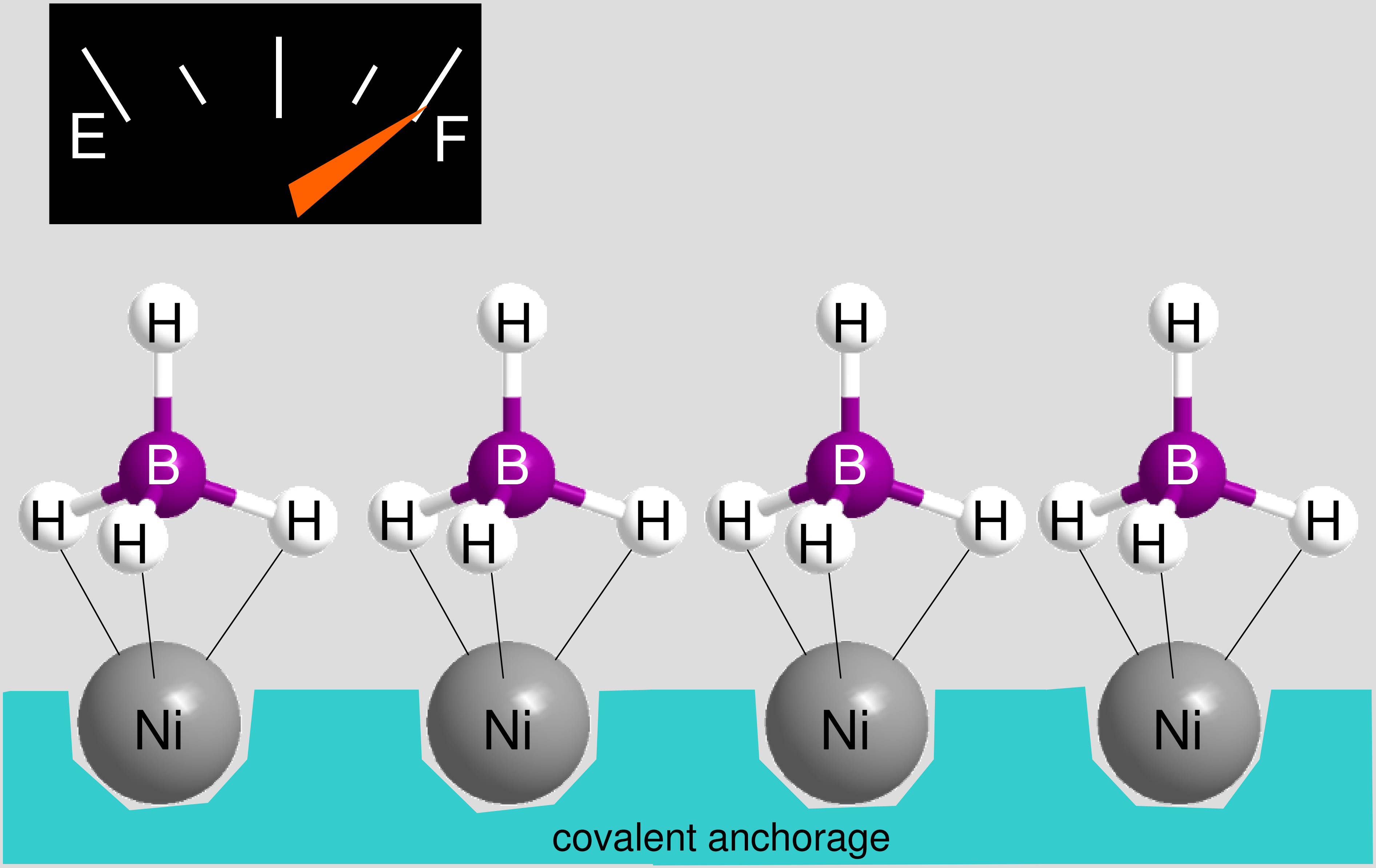
- inert to hot water
- stable in air

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.

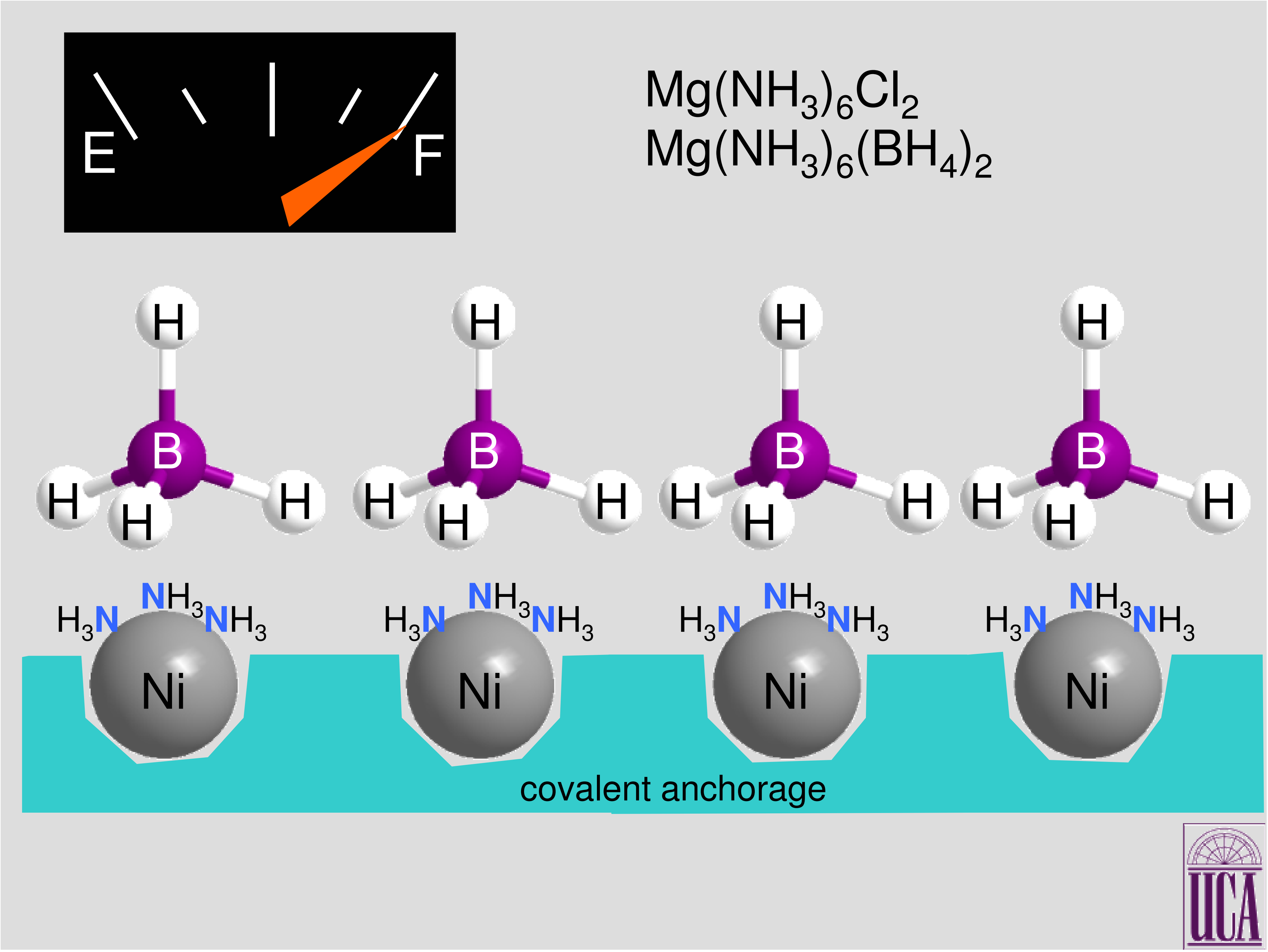

E
F
H
B
H
H
H
Ni
covalent anchorage


E
F


Ni
Ni
Ni
Ni
covalent anchorage



E
F
H
B
Ni
covalent anchorage



E
F
$Mg(NH_3)_6Cl_2$
$Mg(NH_3)_6(BH_4)_2$
H
B
H_3N
NH_3
Ni
covalent anchorage
UCA

- **Tp*NiX(s) binds ammonia**
  - reversible, quantitative $3NH_3$:1Ni
  - X-dependent uptake, release; 3-fold axis control
  - colorimetric, magnetic signals, sensor potential
- **Organic anchorage advantages**
  - lowers ammonia release T
  - synthetically modifiable for specialized applications
- **Tp*NiBH$_4$ stable H-rich substrate**
  - implications for ammonia-only reactions
  - potential NH_3BH_3 interactions

Acknowledgements:

Kristin Thorvilson, Chris Sutton, Josh Brown

Prof. R. Tarkka (UCA)

Prof. A. Biris (UA, Little Rock)
Ms. E. Dervishi (UA, Little Rock)

$$ Petroleum Research Fund (Am. Chem. Soc.),
Natl. Sci. Foundation, UCA Research Council