REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
July 2014	Briefing Charts	July 2014- August 2014

4. TITLE AND SUBTITLE

Novel Coordination Chemistry of Aluminum Borohydride

5a. CONTRACT NUMBER
In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Stefan Schneider, Steve Deplazes, Yonis Ahmed, Christina Franquera, Andrew Beauchamp

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
Q0RA

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQRP
10 E. Saturn Blvd
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RQR
5 Pollux Drive.
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RQ-ED-VG-2014-206

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
Briefing Charts presented at ACS Fall National Meeting, San Francisco, CA, 10-14 Aug 2014. PA#14361

14. ABSTRACT

Due to its high hydrogen content, aluminum borohydride(Al(BH4)3) (ABH) makes an attractive scaffold to build upon for ionic liquids used in rocket propulsion. Due to its highly pyrophoric nature ABH poses extreme handling hazards. This reactivity can be significantly tamed through the coordination of various ligands. Previously we investigated an IL based upon the $[Al(BH_4)_4]^-$ anion. This material showed a much improved air and moisture stability compared to ABH. Here we present research on the coordination of the cyanoborohydride anion (NCBH3-) with ABH. The coordination chemistry of this anion is by far more complex than that of the simple BH4- anion and led to the discovery of, new di- and tri-anions of aluminum.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Stefan Schneider
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	26	**19b. TELEPHONE NO** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**			661-275-5759

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

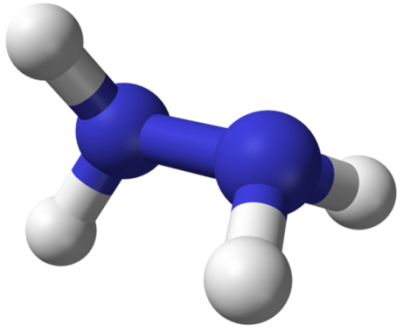
Novel Coordination Chemistry of Aluminum Borohydride

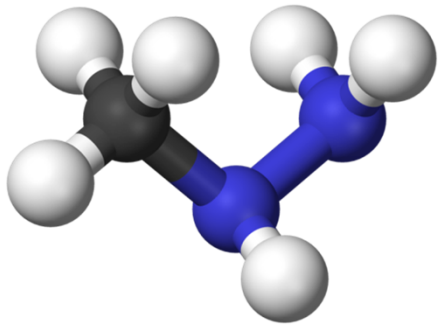
ACS Fall National Meeting
Aug 10 -14th 2014

S. Deplazes
Edwards AFB, CA

Hydrazine – A state of the art rocket fuel

Hydrazine **Monomethylhydrazine**





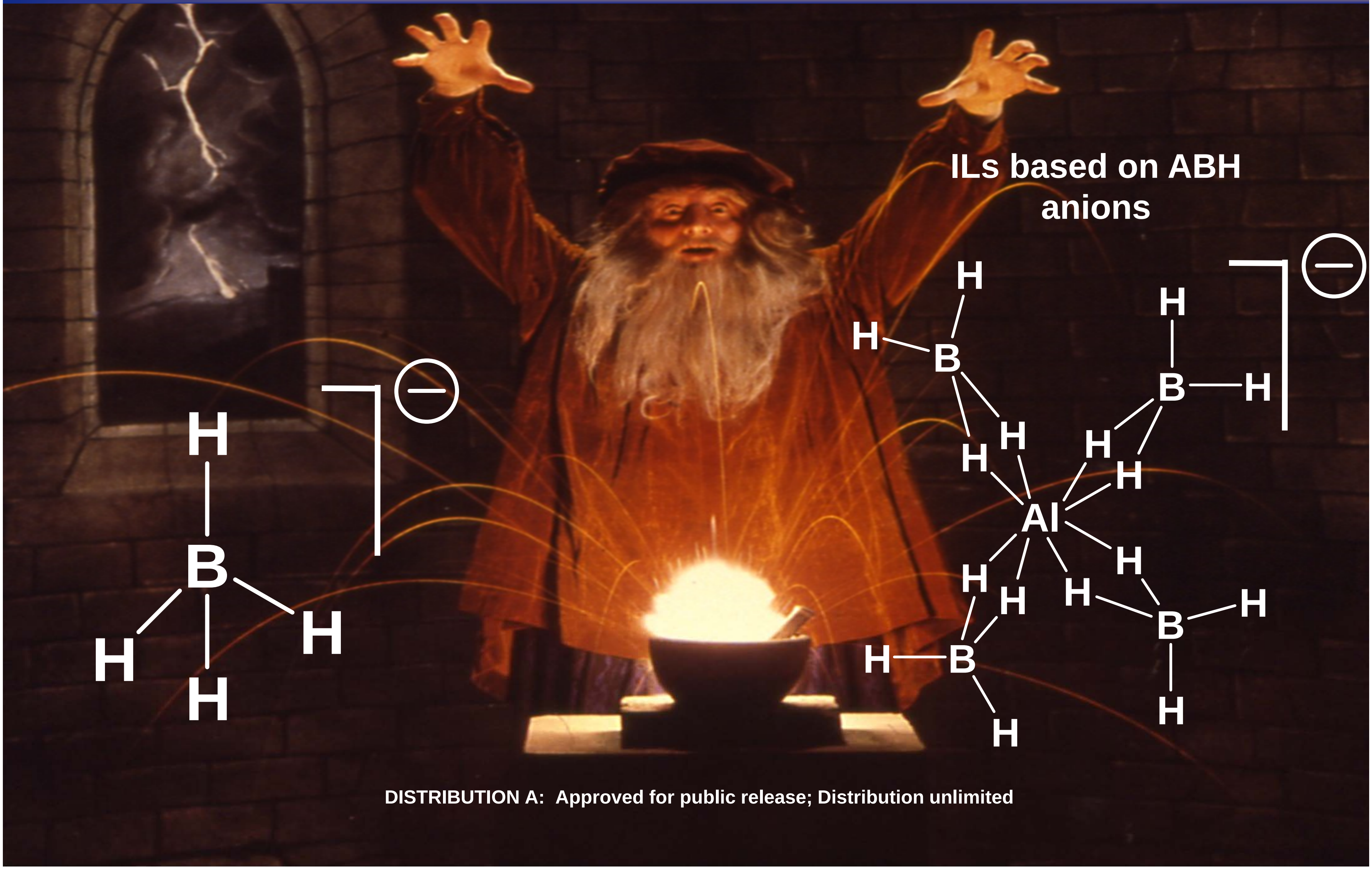
- **Hydrazine fuel vapor toxicity can increase testing/operations costs:**
  - **System Handling/Fueling by certified crews in high level PPE**
  - **Monitoring system in field**
- **Vapor toxicity can limit transportation options**

Ionic Liquid fuels can eliminate vapor toxicity and possess acceptable safety properties

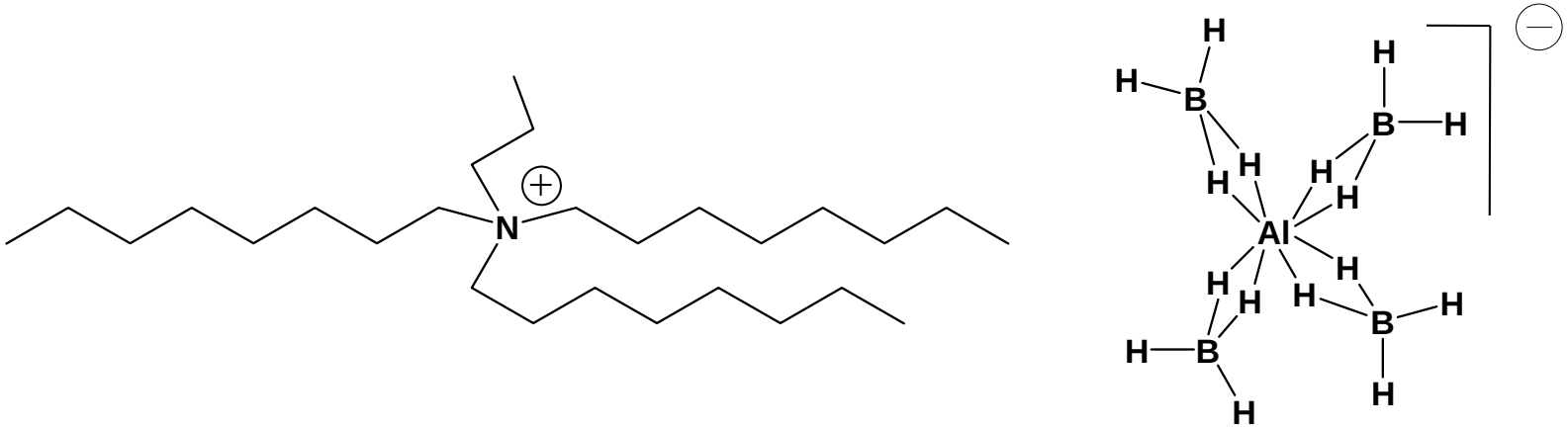
Use of hydrazine is getting more stringent

- As of today, most of our in-space propulsion systems are powered by the MMH and NTO bi-propellant system, known to be hypergolic and severely toxic.
- In the frame of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), the European Union is enforcing the utilization of hazardous chemicals.
- In the mid- to long-term, the commercial use of MMH/NTO or its derivatives such as hydrazine may thus be strongly limited or even prohibited.
- As of June 2011 hydrazine has been added to the list of SVHC (Substance of Very High Concerns)
- The listing controls its use for corrosion inhibition, plating on plastics, and as a rocket fuel.

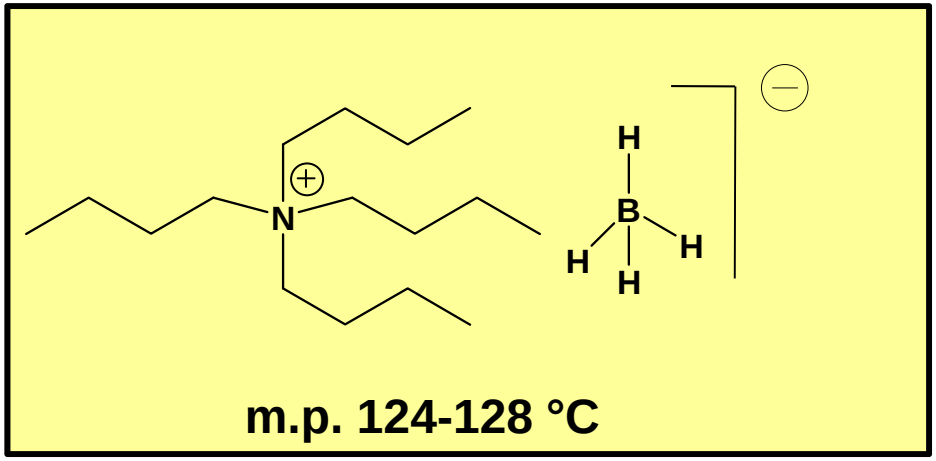
Use of Borohydride Based Salts

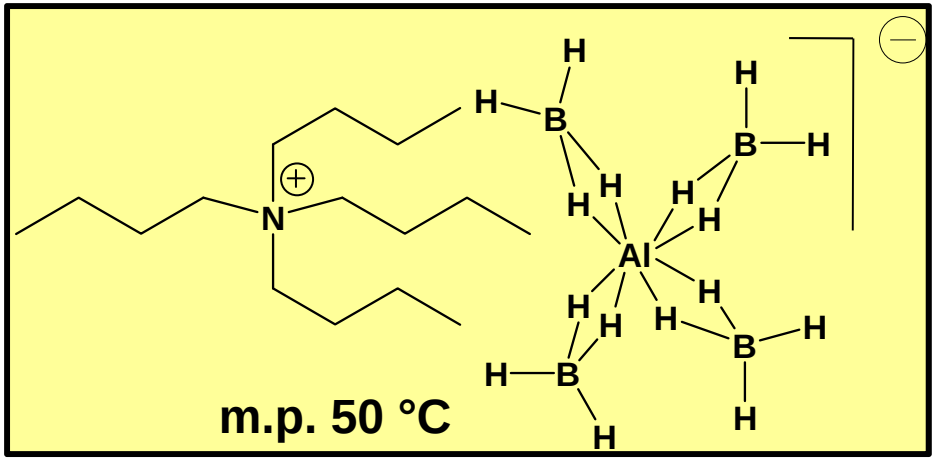


$Al(BH_4)_4^-$ - PROMOTES LIQUIDUS



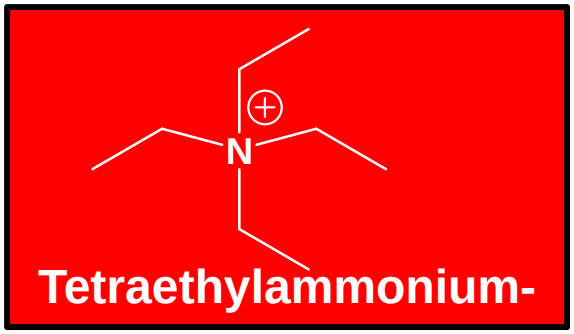
A viscous oil crystallizing very slowly, from which neither H_2, B_2H_6, nor $Al(BH_4)_3$ could be removed even by pumping at 60°C.

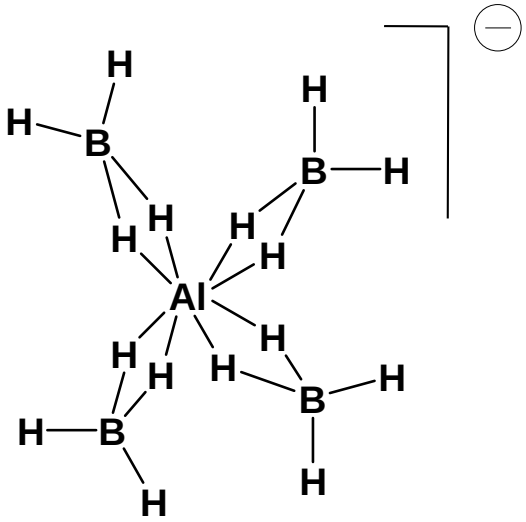


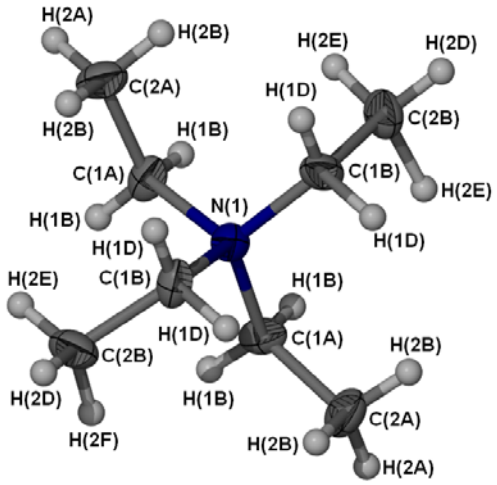


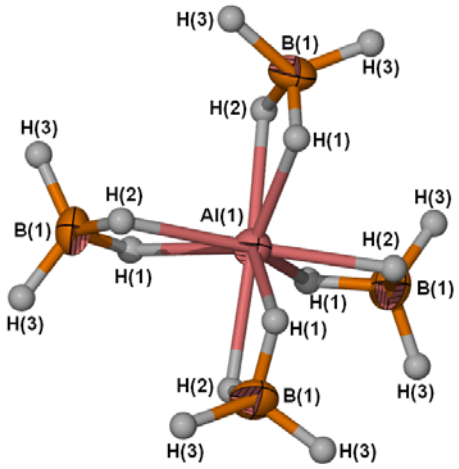
Melting point depression of 75 °C.

Tetraethylammonium tetrakis(tetrahydroborato)aluminate









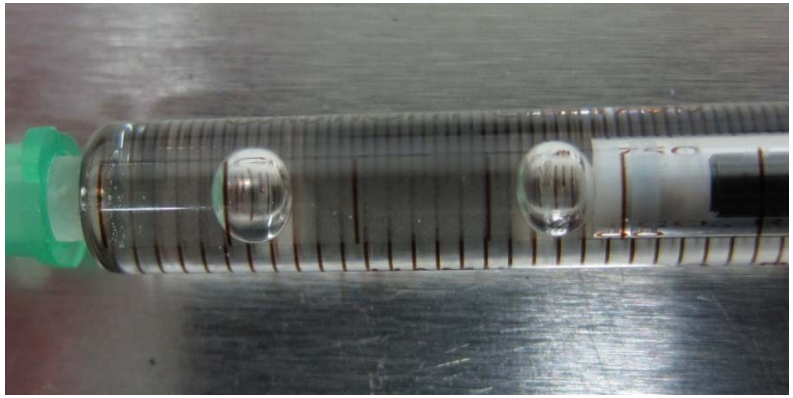
$C_8N_1H_{36}Al_1B_4$, 216.60 g/mol, ρ = 0.81 g/cm^3

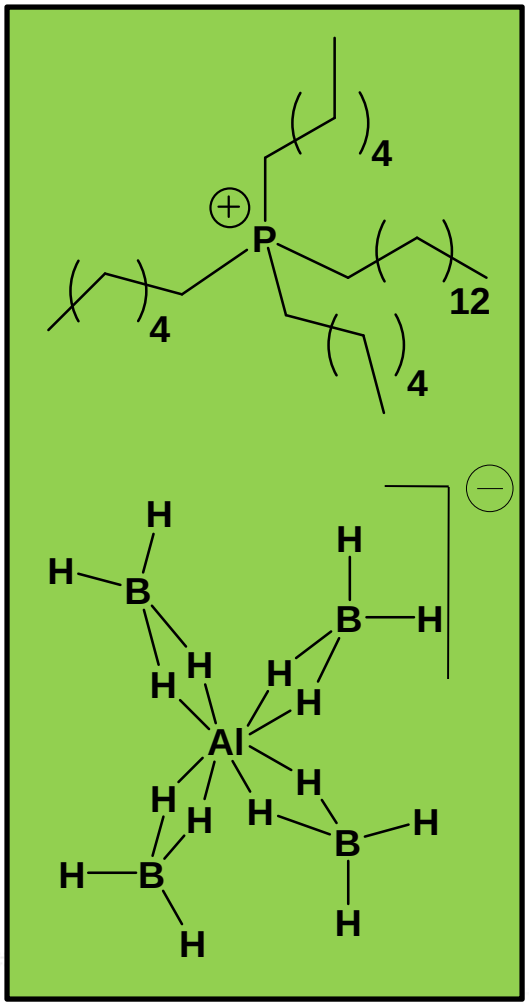
decomposition onset ~ 150°C

36.28 g/mol H in ILABH = 16.7% or 0.135 g/cm3

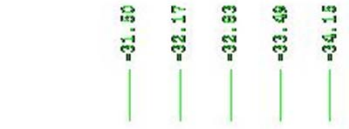
~ 99% more H than LH_2/mL

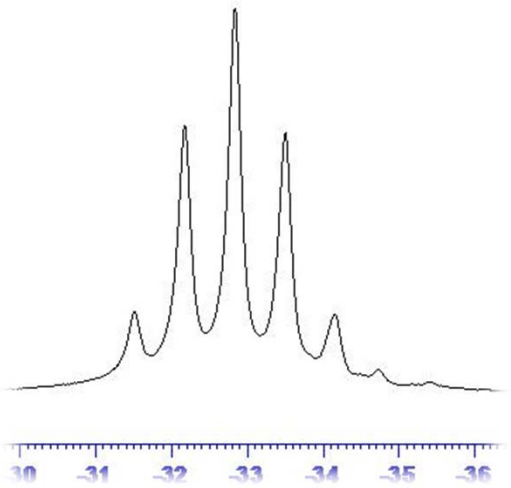
Trihexyltetradecylphosphonium tetrakis(tetrahydroborato)aluminate

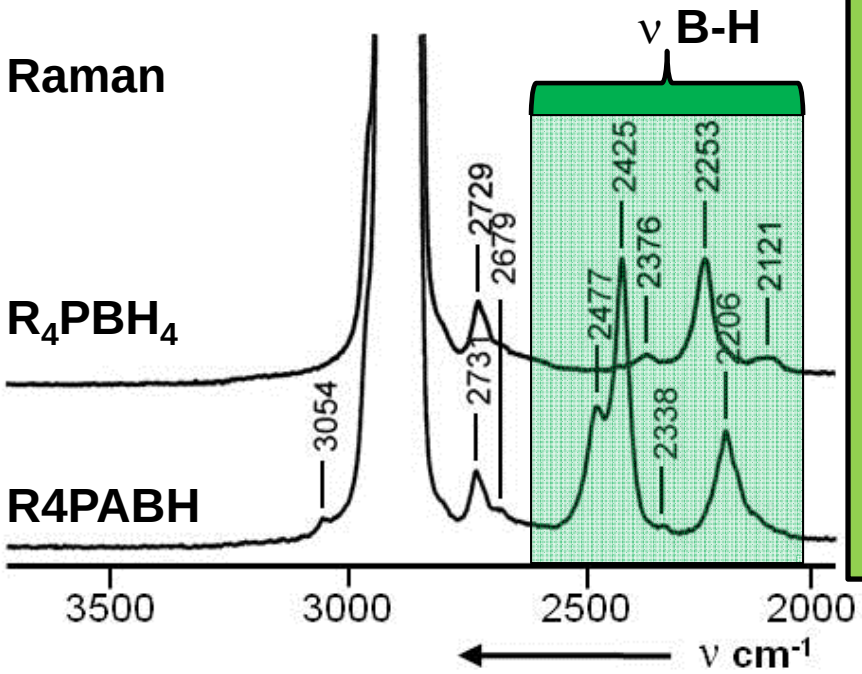




^{11}B NMR of R_4PABH







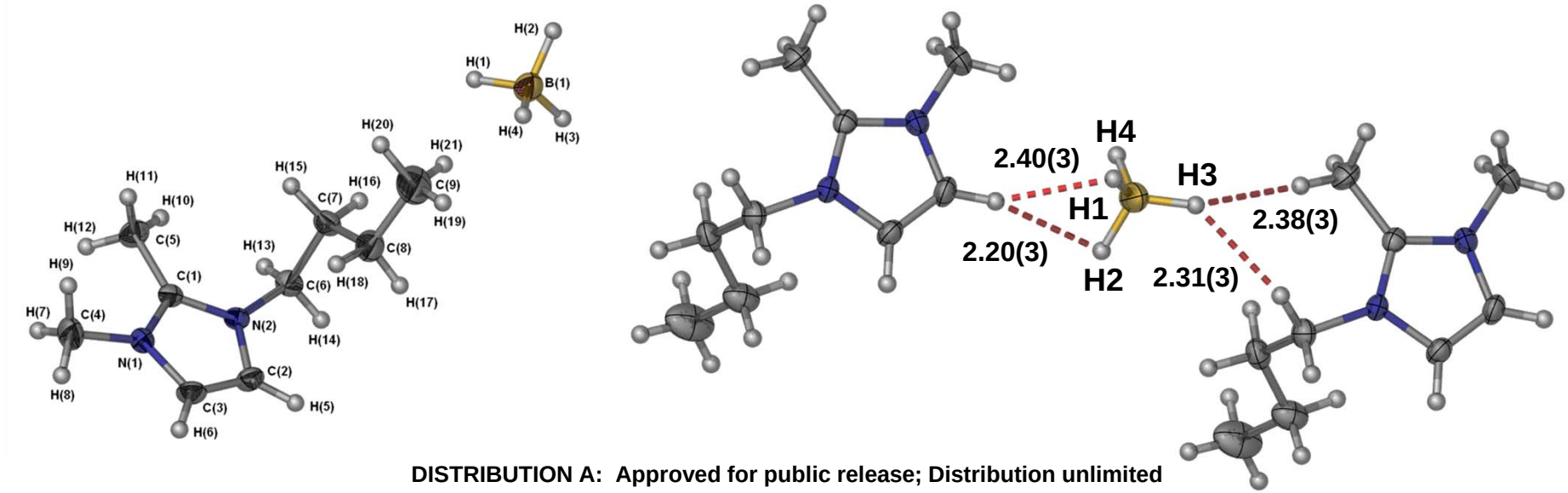
Lack of heterocyclic BH_4 salts

- **Published routes to BMIM BH_4 used IL halide in acetonitrile or CH_2Cl_2**
- **This work could not be reproduced and only yielded material with substantial halide content**

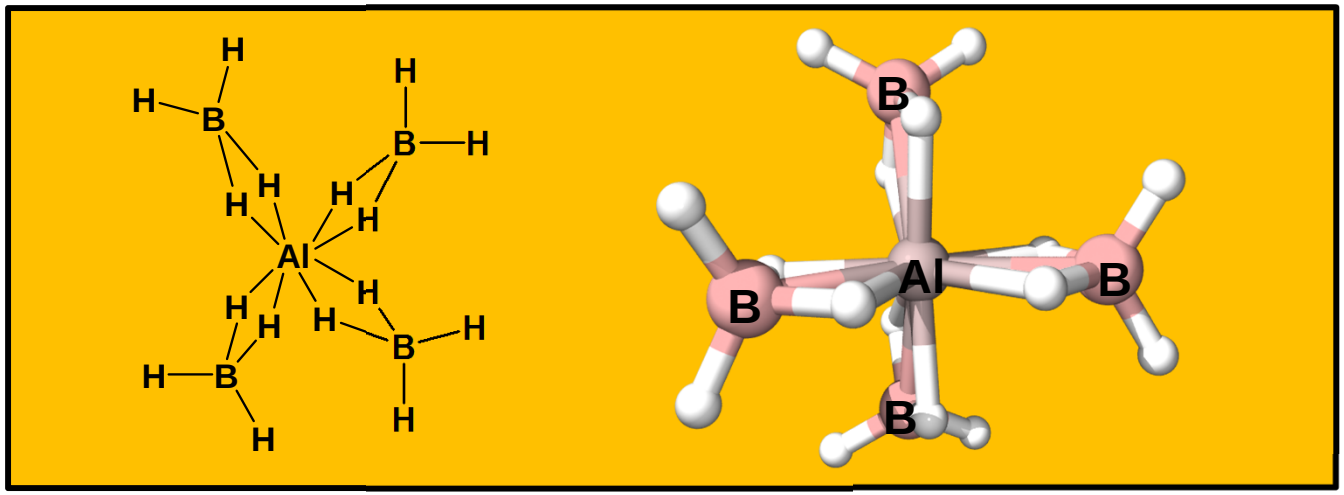
  Best results 77.5% $[BH_4]^-$ halide content 22.5%

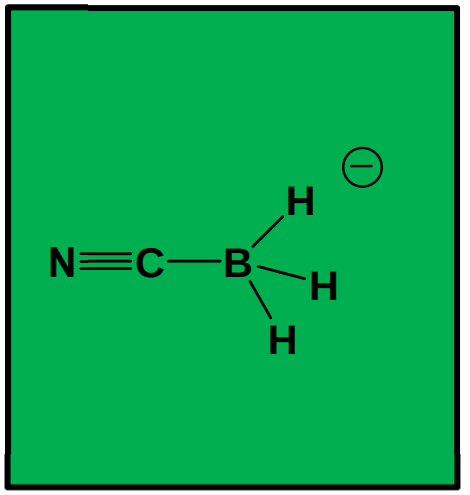
  M. Bürchner, A.M.T. Erle, H. Scherer, I. Krossing *Chem. Eur. J.* **2012**, *18*, 2254.

- **Developed new room temperature process which yields pure materials**

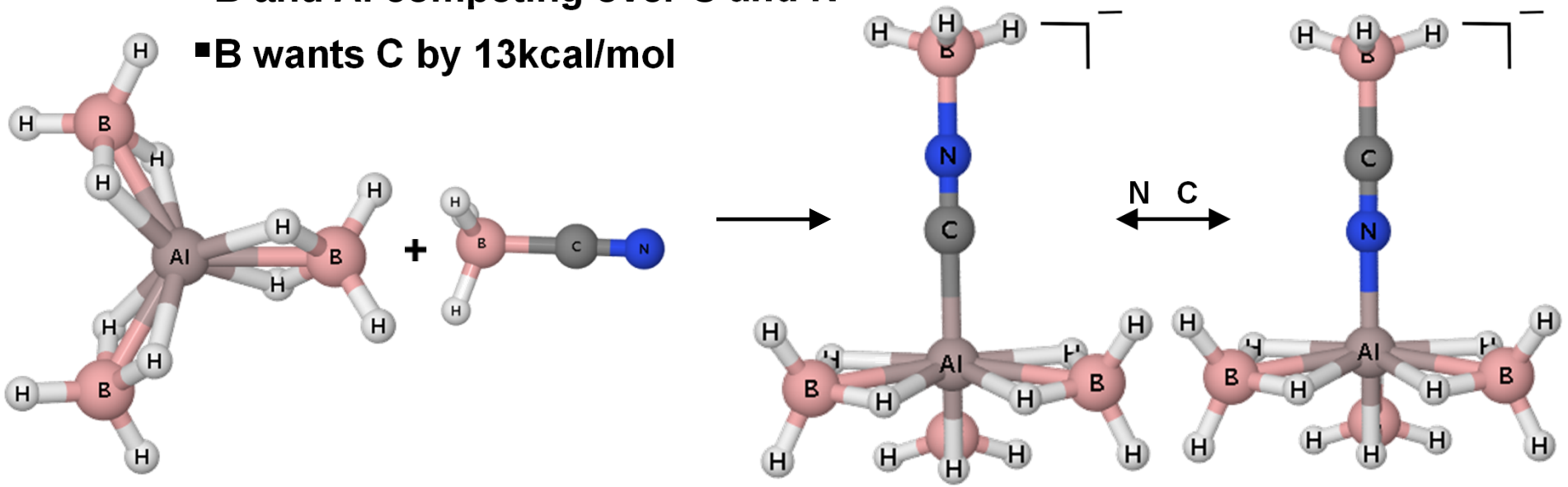


Anion Alteration

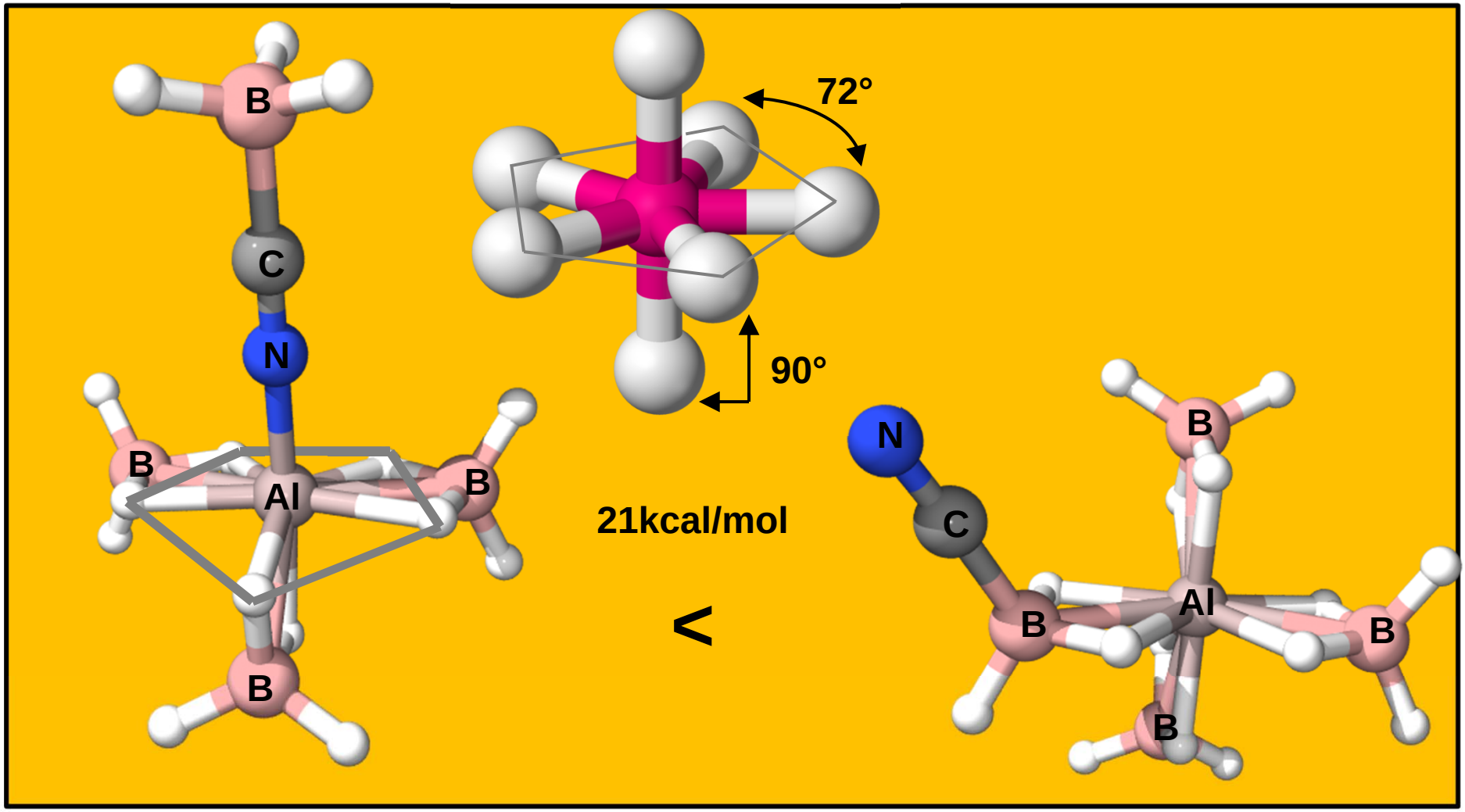




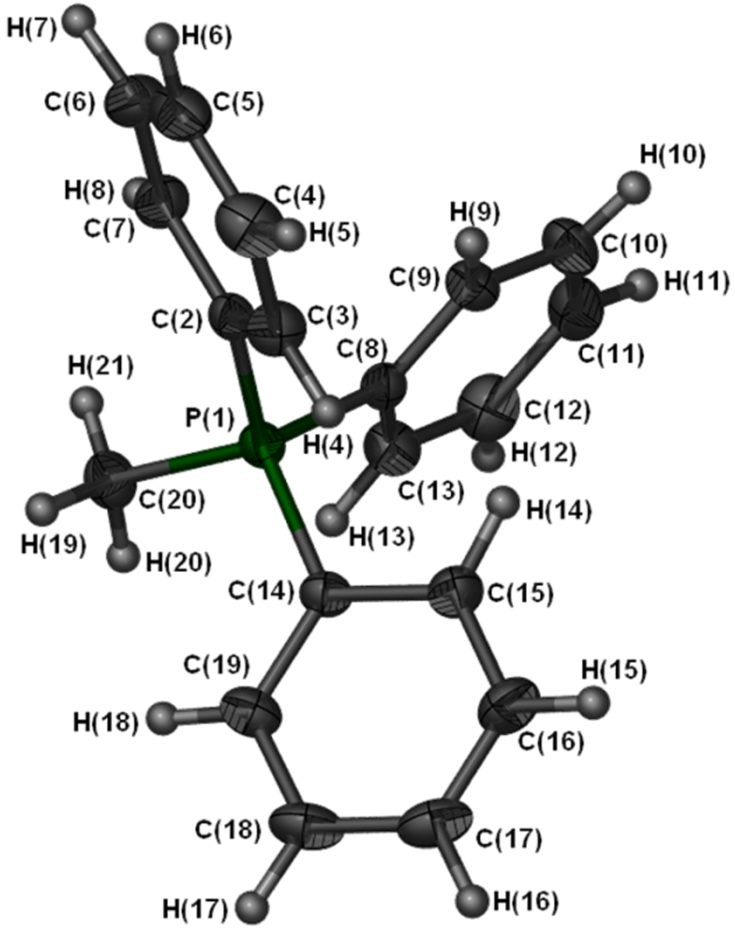
- B and Al competing over C and N
- B wants C by 13kcal/mol

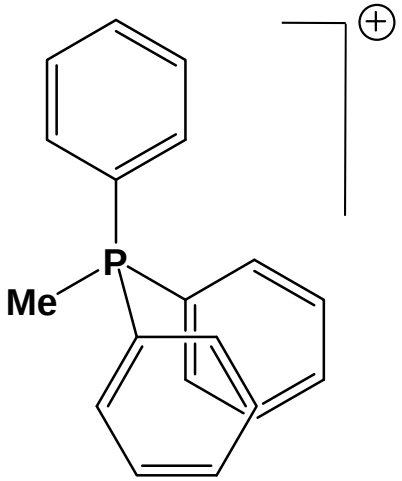


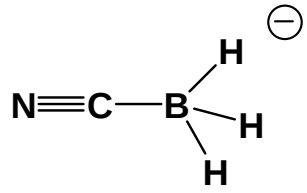
Cyanoborohydride coordination

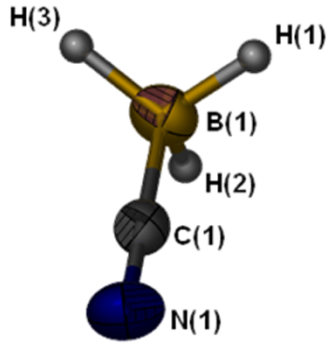


X-ray crystal structure analyses as tool of characterization

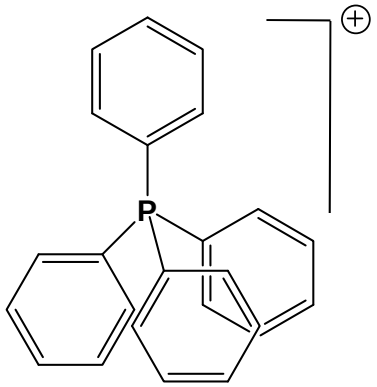


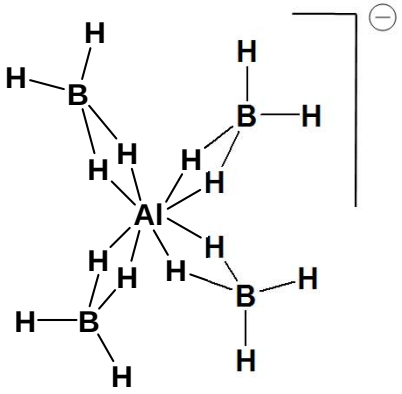


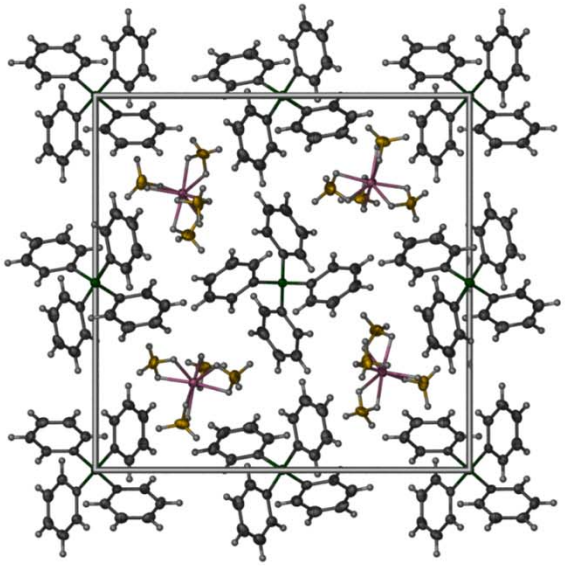


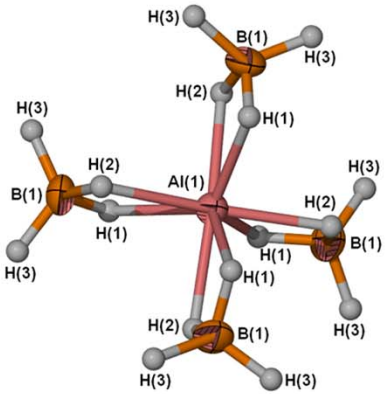


Surprise! tetrakis(tetrahydroborato)aluminates





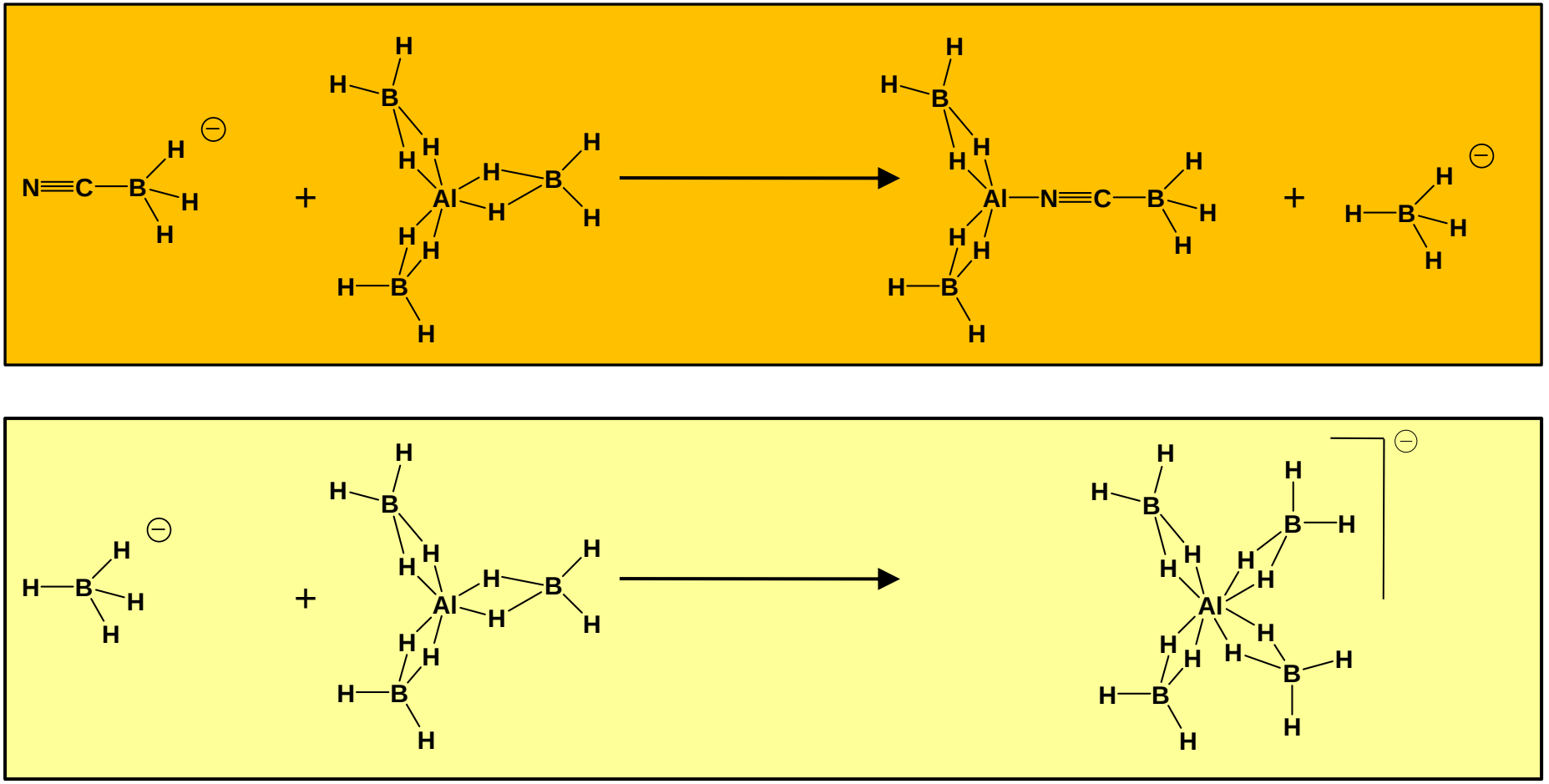




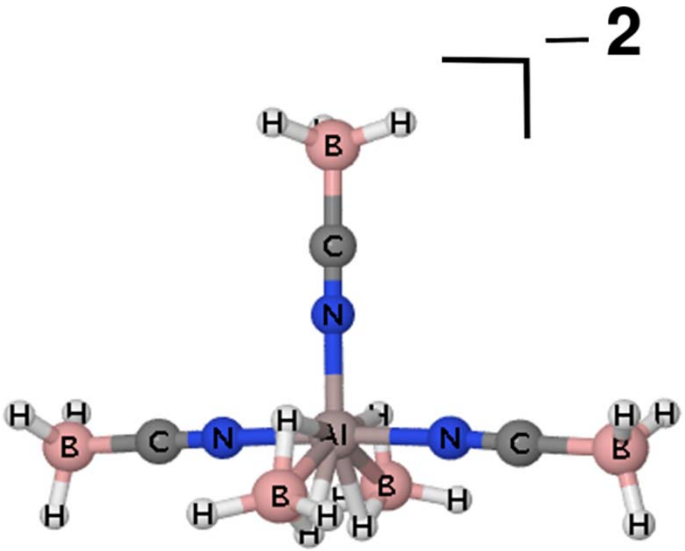
$BH_3CN^- + Al(BH_4)_3 \longrightarrow BH_4^- + Al(BH_4)_2BH_3CN$

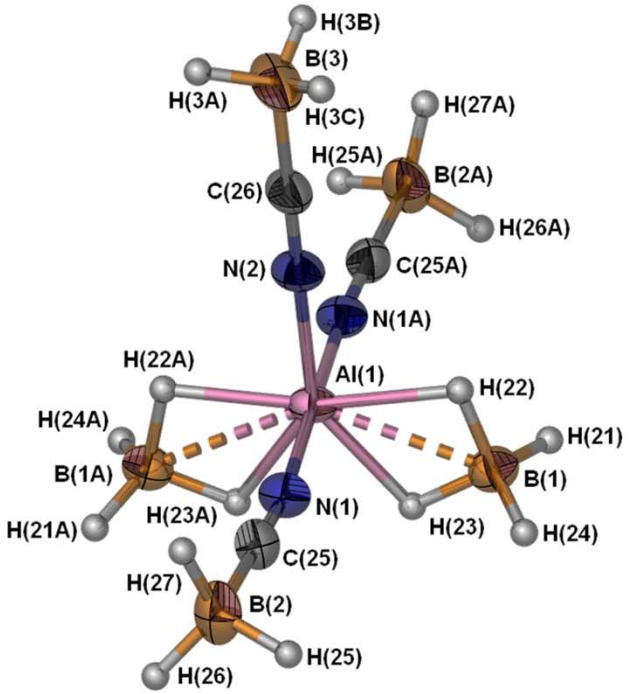
$BH_4^- + Al(BH_4)_3 \longrightarrow Al(BH_4)_4^-$

A general path to tetrakis(tetrahydroborato)aluminates?



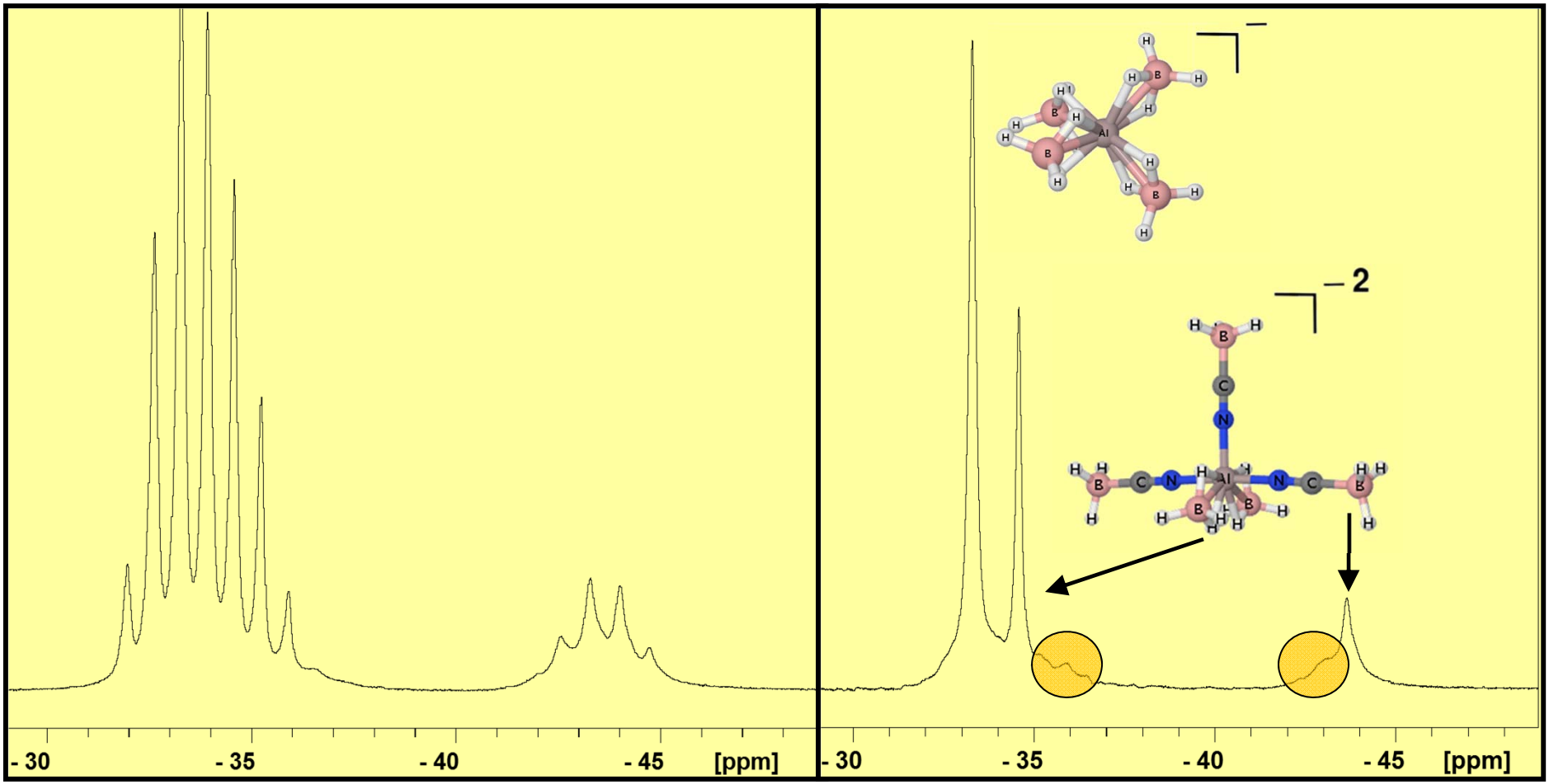
What happened to $Al(BH_4)_2BH_3CN$?



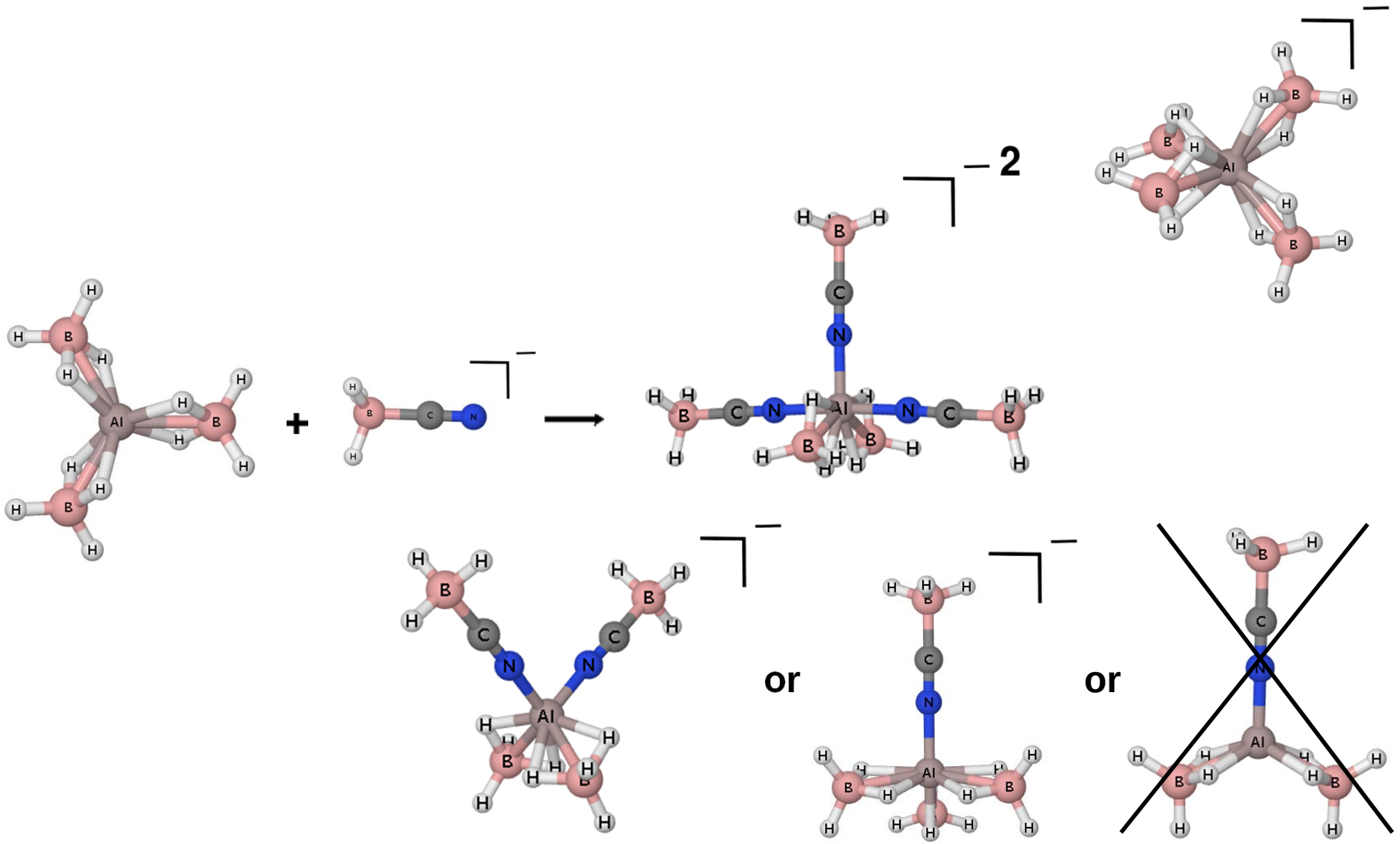


$BH_3CN^- + Al(BH_4)_3$	⟶	$BH_4^- + Al(BH_4)_2BH_3CN$
$BH_4^- + Al(BH_4)_3$	⟶	$Al(BH_4)_4^-$
$Al(BH_4)_2BH_3CN + 2\ BH_3CN^-$	⟶	$Al(BH_4)_2(BH_3CN)_3^{2-}$
$3\ BH_3CN^- + 2\ Al(BH_4)_3$	⟶	$Al(BH_4)_4^- + Al(BH_4)_2(BH_3CN)_3^{2-}$

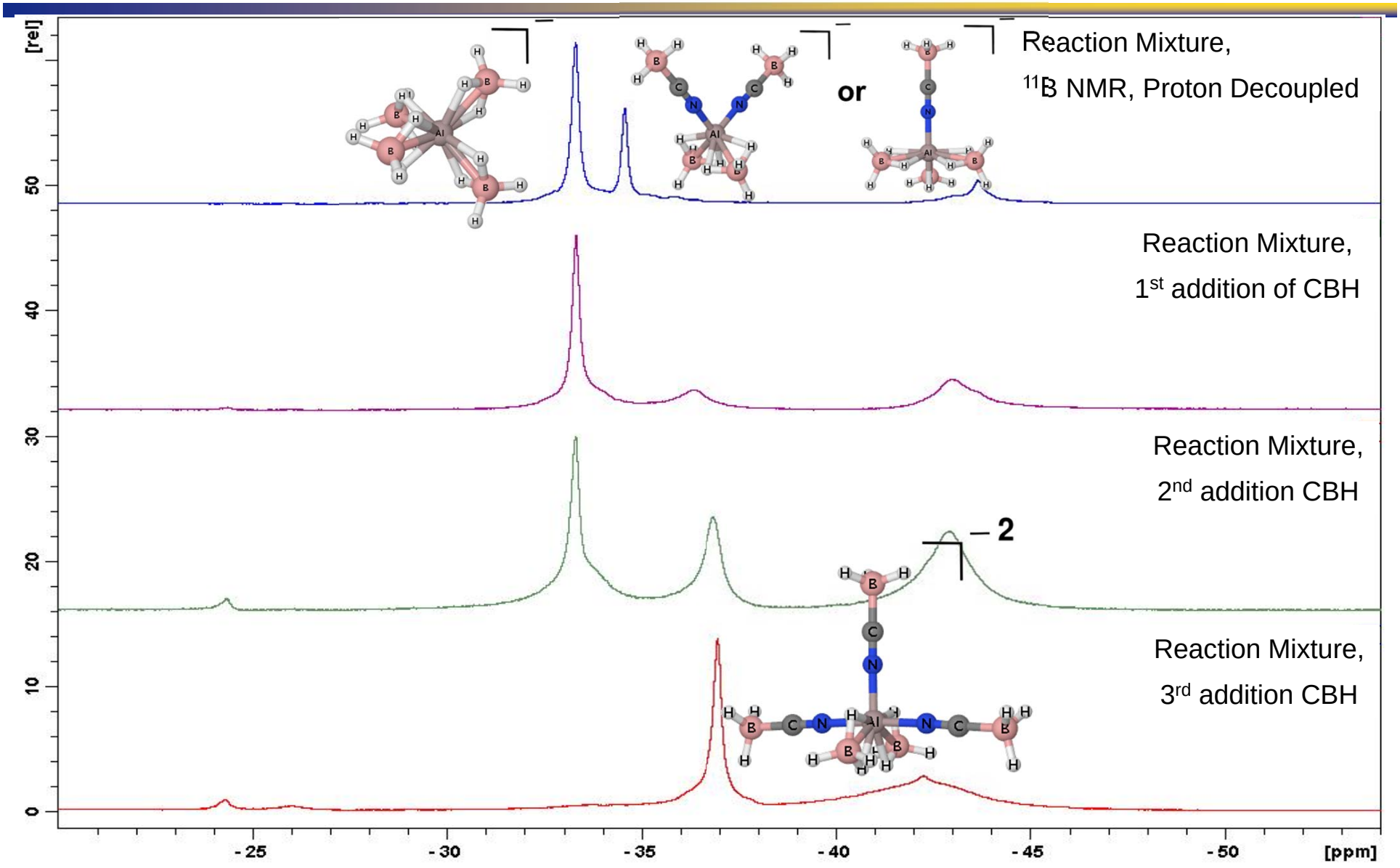
11B NMR of reaction mixture



Maybe Chemistry is more complicated

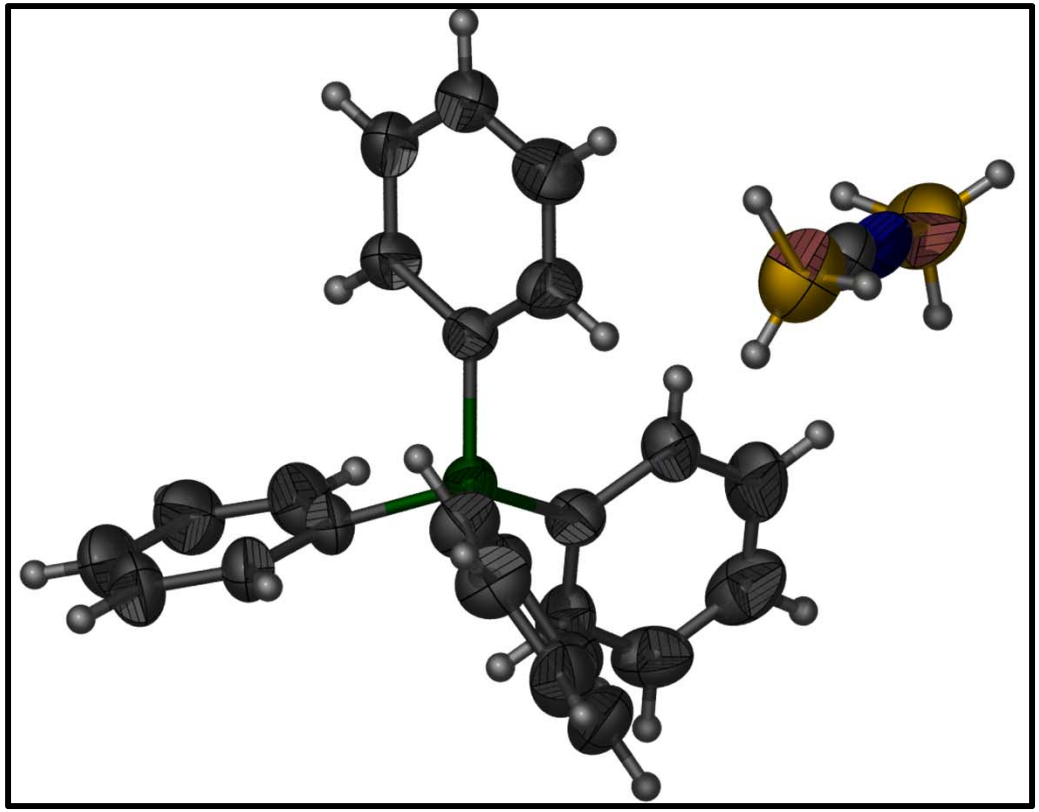


Spiking reaction mixture with CBH

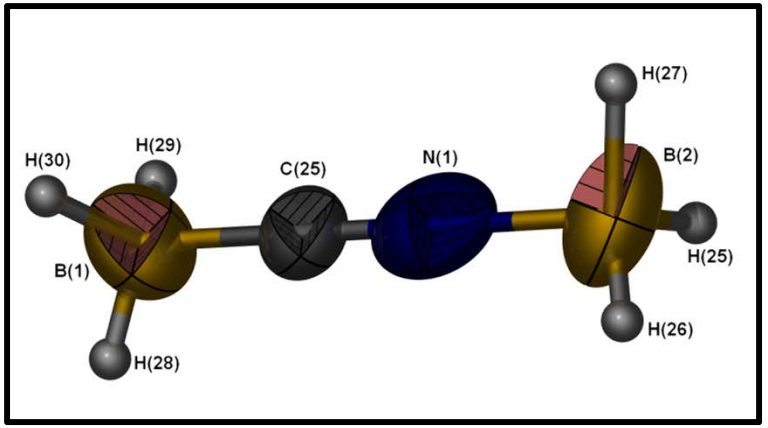


Single crystal X-ray structure analysis provided the answer

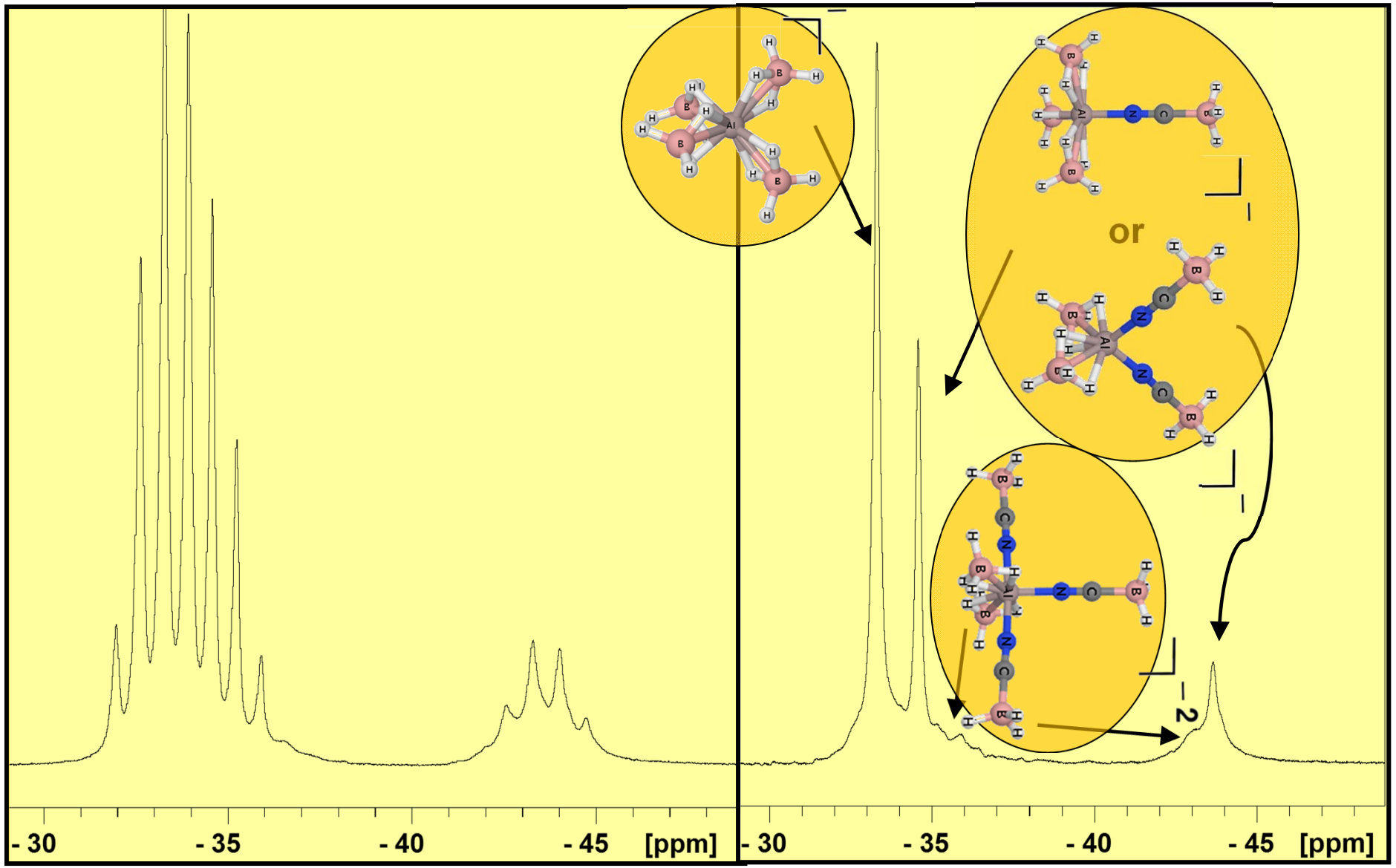
- **A total of four different crystal shapes were identified under a microscope.**
- **Super thin plates are not a preferred crystal shape for X-ray analysis.**



Anion enlarged and rotated



The real picture of the crude reaction mixture

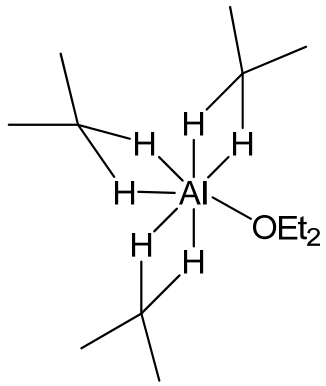


Heat of reaction calculations

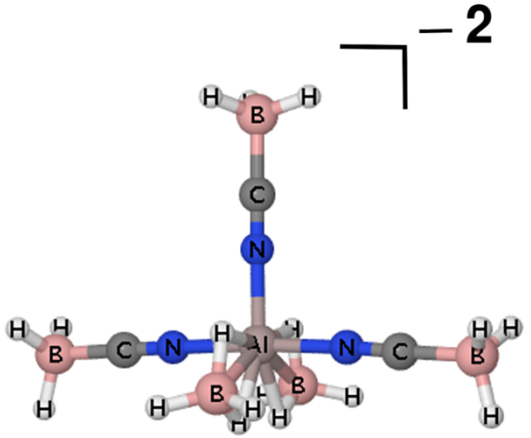
$4\ Al(BH_4)_3 + 4\ [NCBH_3]^-$	$\xrightarrow{-103}$	$2\ [Al(BH_4)_4]^- + [Al(NCBH_3)_3(BH_4)_2]^{2-} + Al(NCBH_3)(BH_4)_2$
$[NCBH_3]^- + Al(BH_4)_3$	$\xrightarrow{+17}$	$Al(NCBH_3)(BH_4)_2 + [BH_4]^-$
$Al(BH_4)_3 + [NCBH_3]^-$	$\xrightarrow{-49}$	$[Al(NCBH_3)(BH_4)_3]^-$
$[Al(NCBH_3)(BH_4)_3]^- + [NCBH_3]^-$	$\xrightarrow{+3}$	$[BH_4]^- + [Al(NCBH_3)_2(BH_4)_2]^-$
$2\ Al(BH_4)_3 + 2\ [NCBH_3]^-$	$\xrightarrow{-96}$	$[Al(BH_4)_4]^- + [Al(NCBH_3)_2(BH_4)_2]^-$
$[Al(NCBH_3)_2(BH_4)_2]^- + [CNBH_3]^-$	$\xrightarrow{+18}$	$[Al(NCBH_3)_3(BH_4)_2]^{2-}$

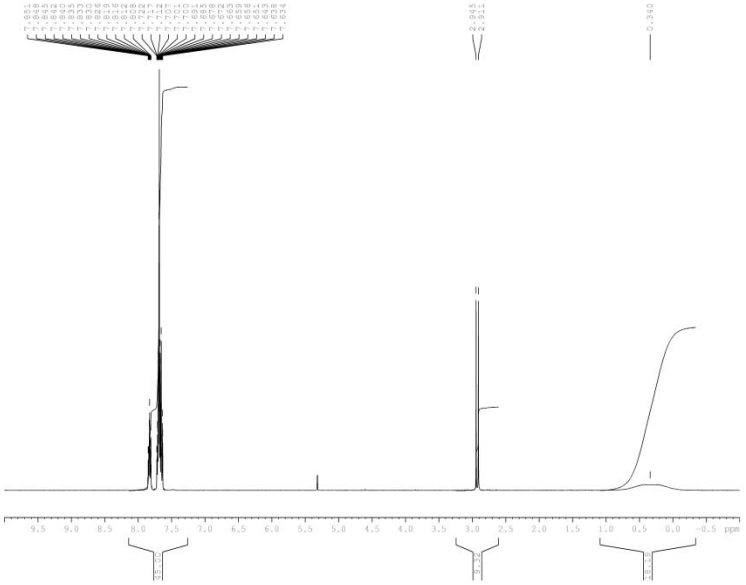
*** Gas phase; all values are kcal/mol**

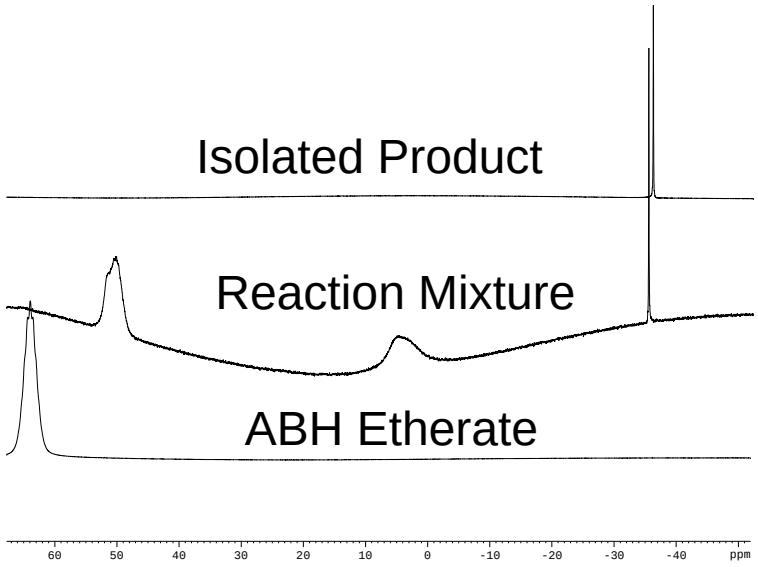
What Happens with a Large Excess of CBH?



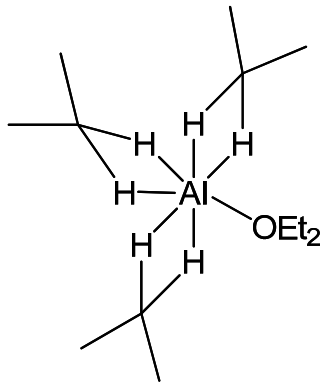
+ $CNBH_3$ (Excess) ⟶



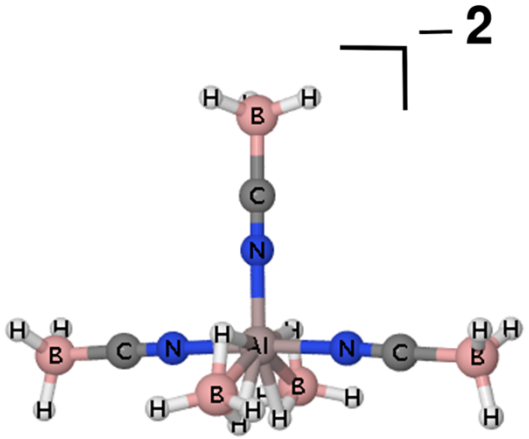


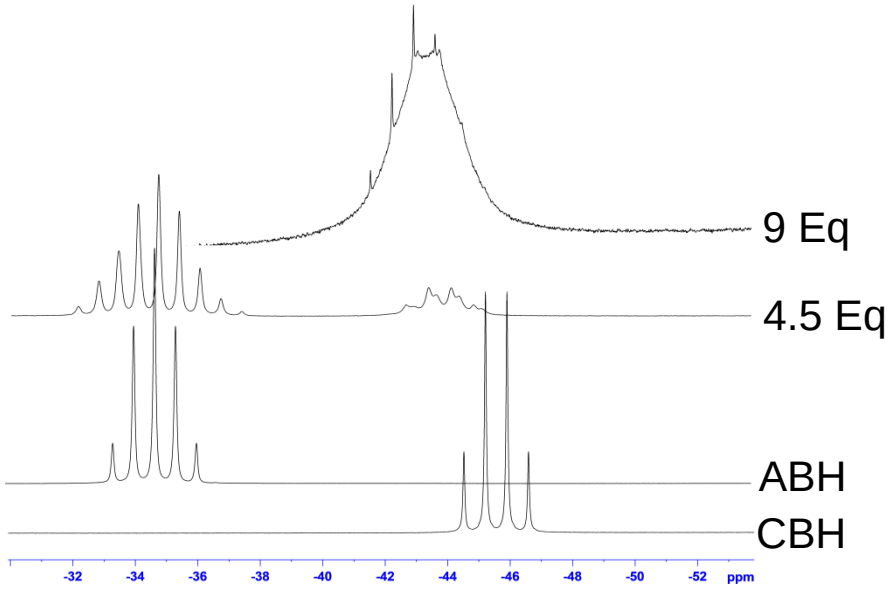


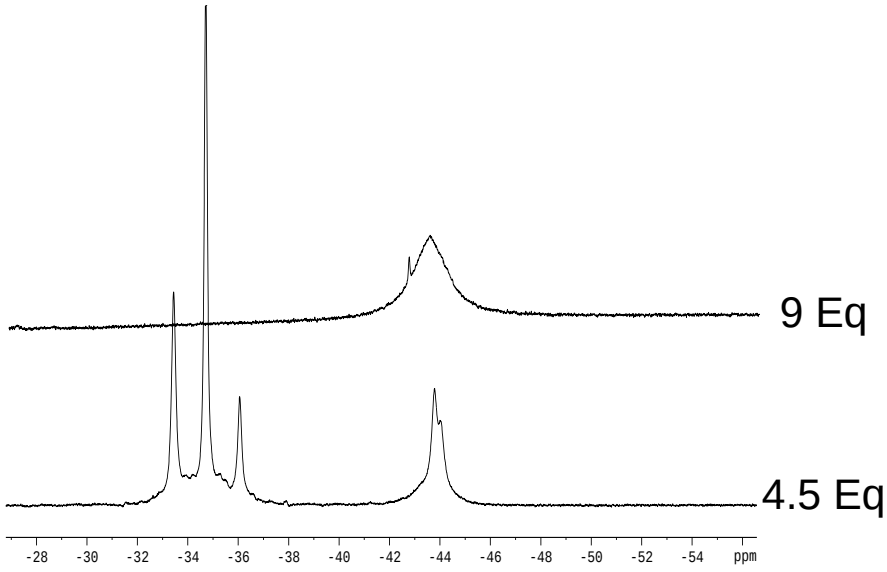
What Happens with a Large Excess of CBH?



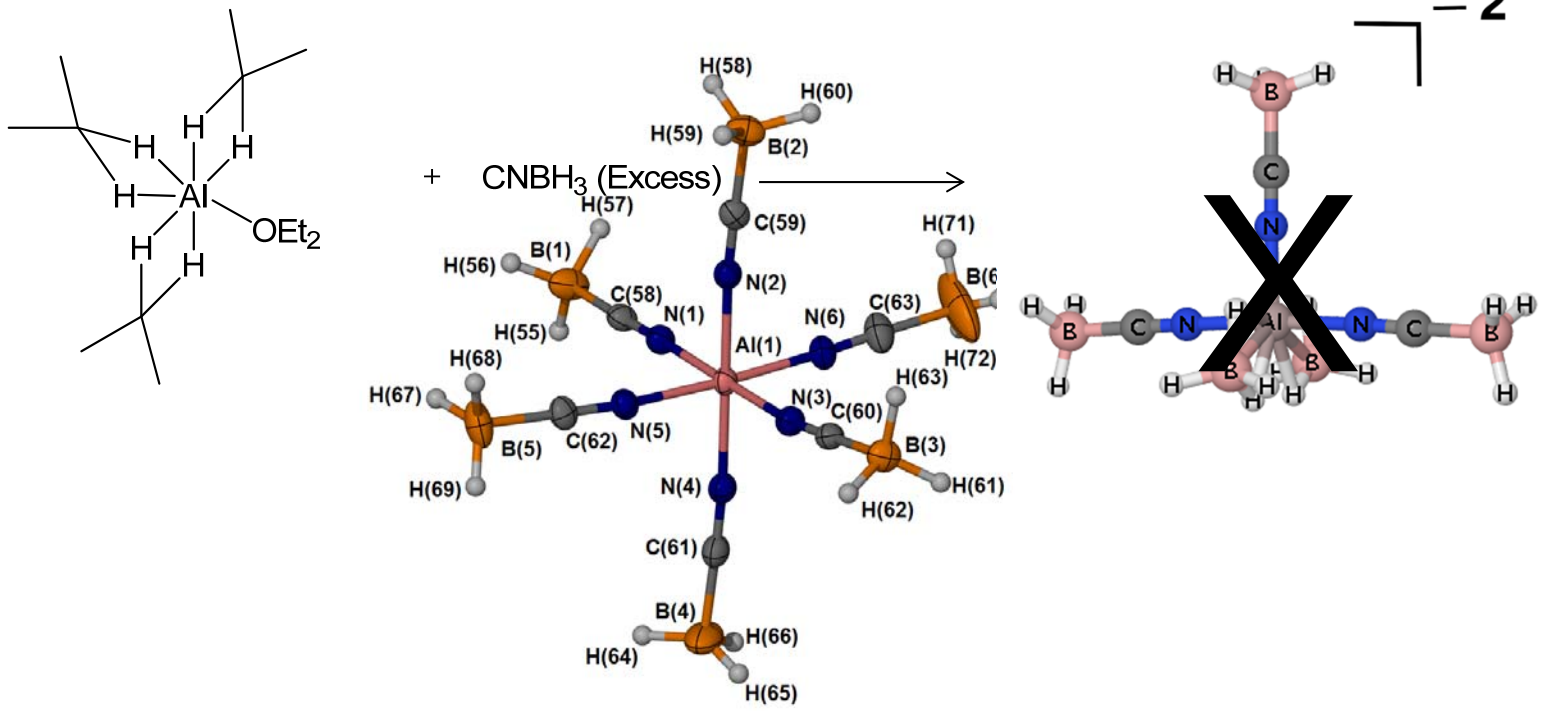
+ $CNBH_3$ (Excess) ⟶







Crystal Structure Shows Product



Bond	Angle (°)	Bond	Angle (°)	Bond	Length (Å)
Al1-N1-C58	178.17(16)	N1-C58-B1	178.1(2)	Al1-N2	1.9734(16)
Al1-N2-C59	174.11(15)	N2-C59-B2	178.06(18)	Al1-N3	1.9577(16)
Al1-N3-C60	172.72(15)	N3-C60-B3	179.1(2)	Al1-N6	1.9512(17)
Al1-N4-C61	175.67(16)	N4-C61-B4	178.5(2)	Al1-N4	1.9623(16)
Al1-N5-C62	174.92(16)	N5-C62-B5	179.4(2)	Al1-N5	1.9563(17)
Al1-N6-C63	177.09(17)	N6-C63-B6	177.8(3)	Al1-N1	1.9697(16)

The current reaction sequence

$$3[NCBH_3]^- + Al(BH_4)_3 \longrightarrow [Al(BH_4)_4]^- + [Al(BH_4)_2(NCBH_3)_3]^{2-}$$

$$[Al(BH_4)_3] \xrightarrow{\text{exc } NCBH_3^-} [Al(NCBH_3)_6]^{3-}$$

$$2\,[NCBH_3]^- \rightleftharpoons [BH_3CNBH_3]^{-*} + [CN]^-$$

* Emri, J *et. al.*, *Polyhedron*, **1994**, *13*, 2353

Summary and Conclusion

- The reactivity of aluminum borohydride is not always predictable
- Demonstrated dependence on the reaction partner and concentration
- It is challenging to characterize compound mixtures
- New species need to be isolated and incorporated into IL's to evaluate their reactivity and physical properties
- New synthetic routes to heterocyclic BH_4 salts open new possibilities

Acknowledgement

Tom Hawkins

Jeff Mills

Stefan Schneider

Capt. Andrew Beauchamp

Yonis Ahmed

Daniel Ditzhazy

Christina Franquera

ERC

Air Force Office of Scientific Research (AFOSR)

Michael Berman