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S.F. Deplazes; S. Schneider; T.W. Hawkins; and J.D. Mills

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**14. ABSTRACT**

This presentation covered an overview of AFRL's rocket propulsion laboratory and discussed hydrazine as a state-of-the-art rocket fuel, objectives for ionic liquids as bipropellant fuels, anion control of hypergolic activity, work on shorter ID times with a "green(er)" mindset, the reliability of ignition delay times, how test procedures affect ignition delay, "the green flame," first approaches to "green(er)" hypergols, requirements for a "green(er)" oxidizer, what else is out there, and the challenge of borohydride anions in ionic liquids.

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| | | | | | Dr. Tom W. Hawkins |
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**Standard Form 298 (Rev. 8-98)**
**Prescribed by ANSI Std. 239.18**

THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER

# Green bipropellants: Ionic liquids that are hypergolic with hydrogen peroxide

243rd ACS National Meeting
San Diego California
March 25, 2012

S. Deplazes
Edwards AFB, CA

# *Where are we located?*

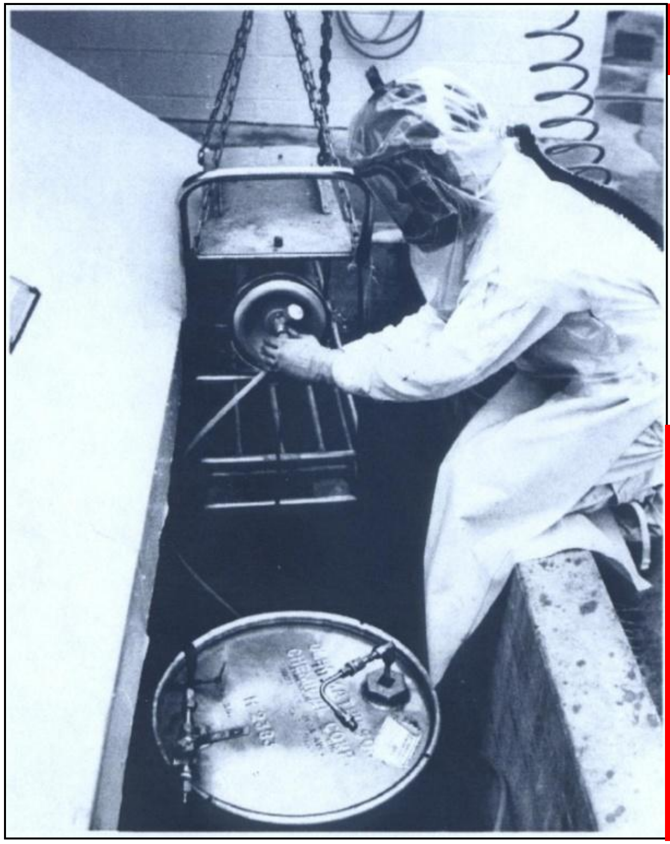
**California, I thought California and California and California.**

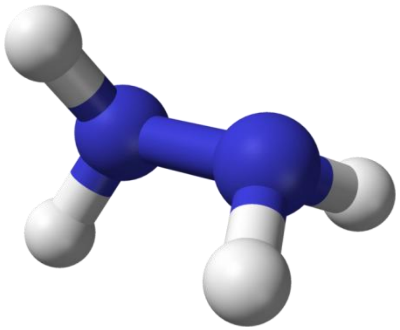
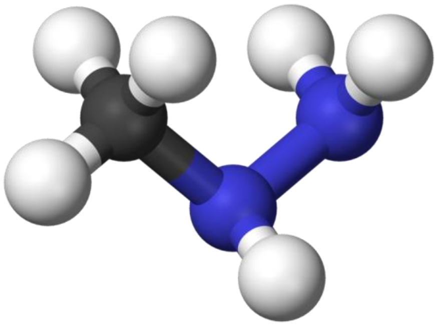
**Two-piece swimsuits and liquor and lawyers.**

- **100 miles North-East of Los Angeles**

•Images: NASA satellite photo of Edwards Air Force Base, taken from http://www.dreamlandresort.com/info/edwards. This file is in the public domain because it was created by NASA. NASA copyright policy states that “NASA material is not protected by copyright unless noted”; The Center for Land Use Interpretation

# 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*

# Objectives for Ionic Liquids as Bipropellant Fuels

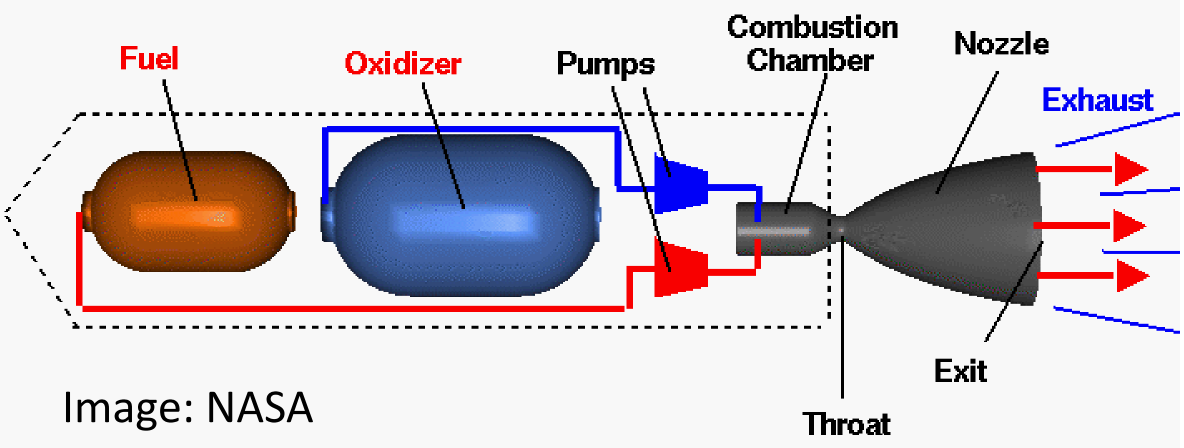



Image: NASA

- ❑ Ignites on contact (Hypergolic)
- ❑ Ignites Fast (<10ms)
- ❑ Ignites Fast & Green(er)

# Anion Control of Hypergolic Activity

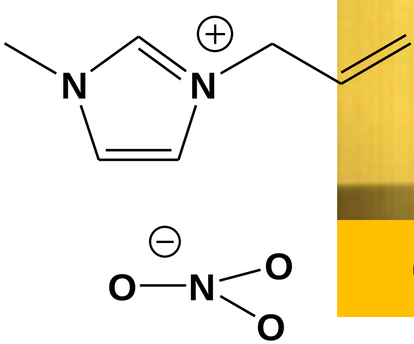
*Energy & Fuels* **2008**, *22*, 2871–2872

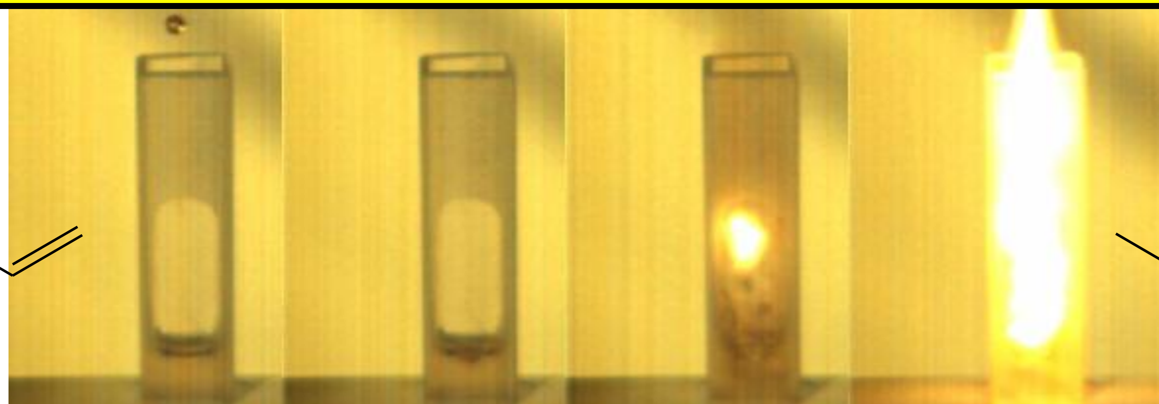
*Received April 24, 2008. Revised Manuscript Received June 2, 2008*

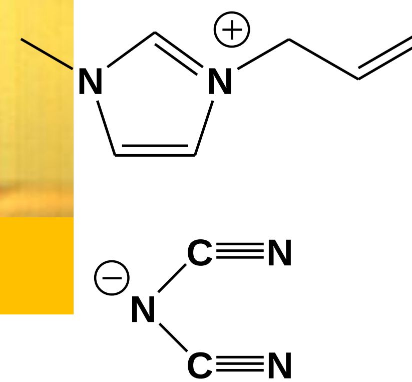
## Ionic Liquids as Hypergolic Fuels

Stefan Schneider,*,† Tommy Hawkins,† Michael Rosander,† Ghanshyam Vaghjiani,† Steven Chambreau,† and Gregory Drake‡

| Oxygenated | Fuel-Rich |
|---|---|
| <u>Not</u> Hypergolic! | Hypergolic! |



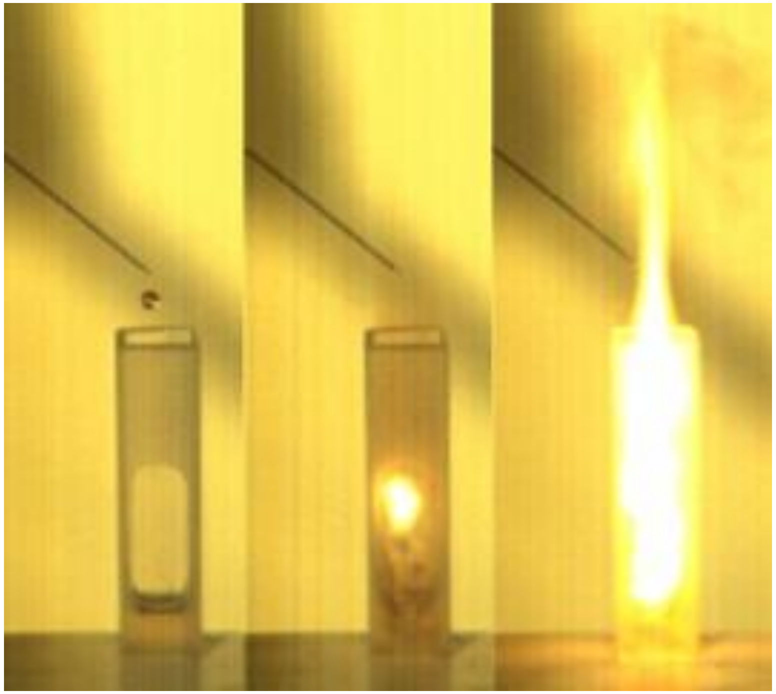
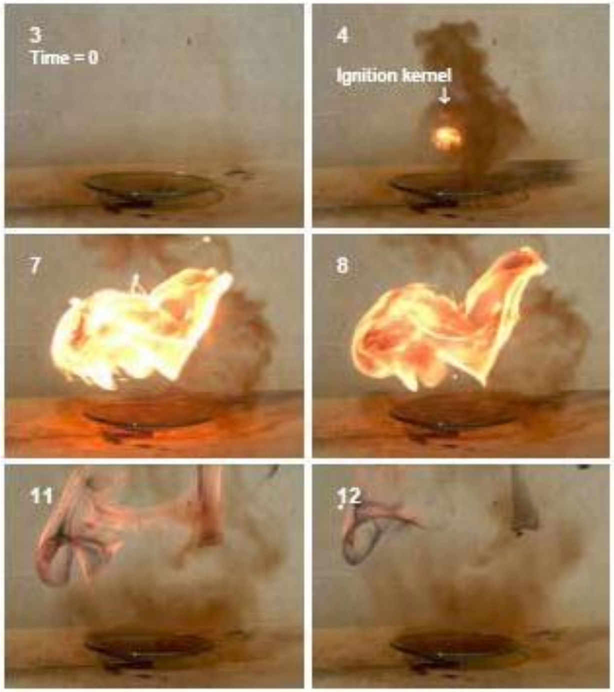


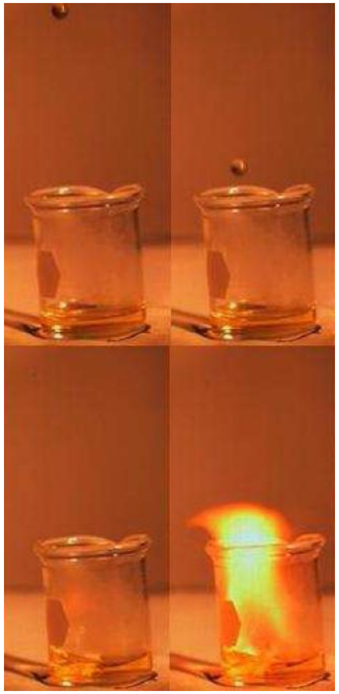

**Only hypergolic with nitric acid!!!**

# Work on shorter ID times with "green(er)" mindset

- Ignites hypergolic, <10ms

# *How reliable are ignition delay times?*

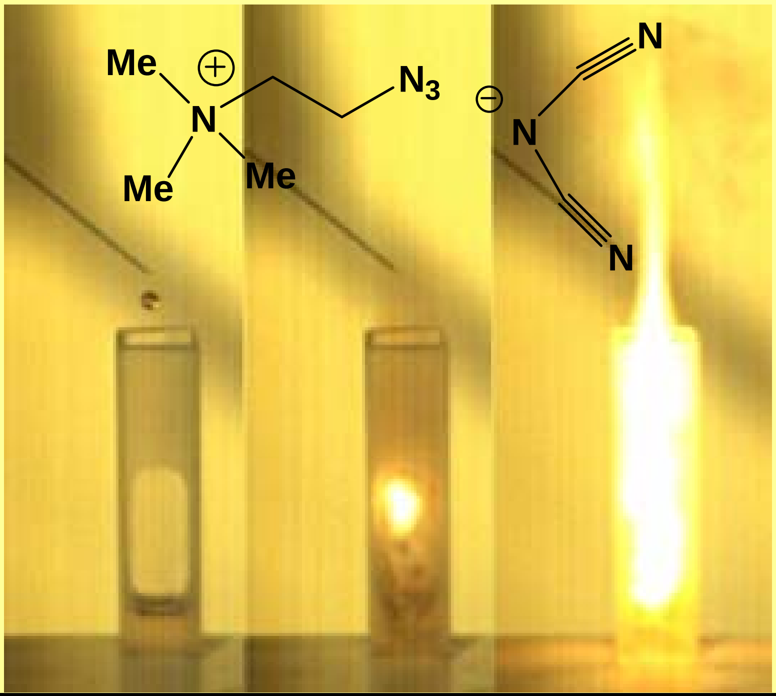





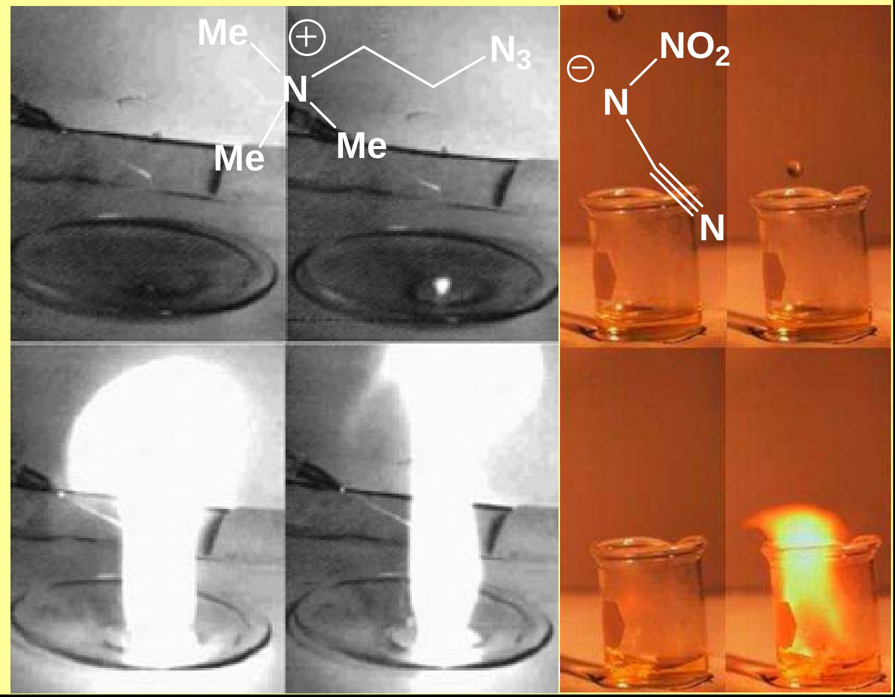
- No two laboratories will report the same ignition delay times (different test-setups result in e.g. different speed and efficiency of mixing)
- General agreement in ranking propellant combinations

# *Test procedures affect ignition delay*

**TMAZ DCA***




**TMAZ NCA***

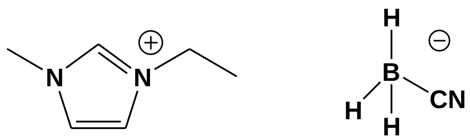
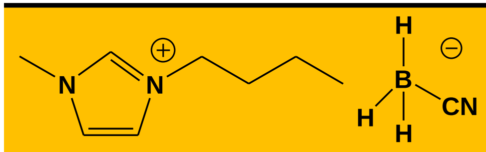
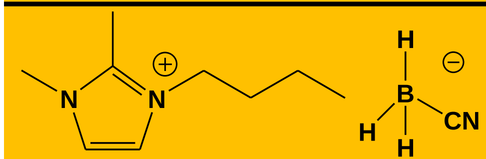
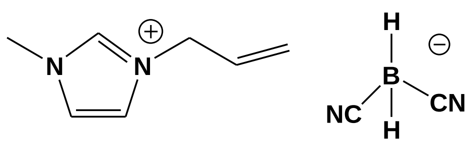
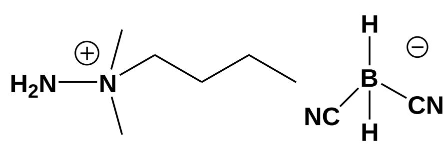



**The ignition delay were reported between 20 and 40 ms based on ~ 100 drop tests**

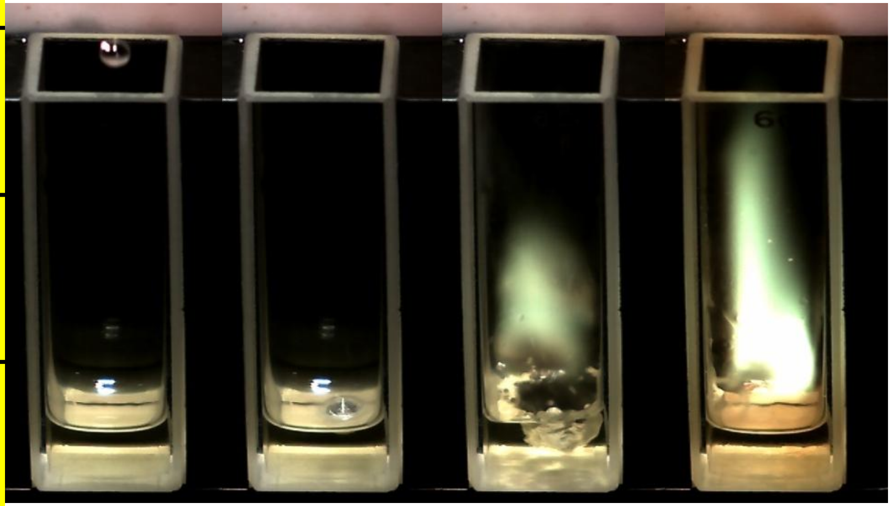
**Reactivity can be dependent on test procedures to the extremes of:**
**No ignition observed with 21 G needle**
**Ignition with 18 G needle**

*Shreeve, J.M. *et. al.* *Inorg Chem.* **2010**, *49*, 3282

# "The GREEN Flame"

| | Structure | Ignition delay [ms] | Decomp. onset [°C] |
|---|---|---|---|
| * |  | 5 | nd |
| * |  | 11 | 146 |
| * |  | 600 | 249 |
| ** |  | 28 | 307 |
| ** |  | 8 | 266 |
| ** |  | 6 | 222 |

**Again Only hypergolic with nitric acid!!!**



- **Remarkable impact of cation structure on reactivity**

* "Environmentally enhanced hypergolic ionic liquids" , T. Hawkins, S. Schneider, L. Hudgens, M. Rosander Invention Disclosure, Feb 4, 2010; Provisional Patent Application, June 17, 2010.

** Y. Zhang, J. M. Shreeve, *Angew. Chem.* 2011, *123*, 965-967; *Angew. Chem. Int. Ed.* **2011**, *50*, 935-937.

# First approaches to “green(er)” hypergols

- Ignites hypergolic, <10ms & green(er)

# Requirements for a "Green(er)" Oxidizer

- ❑ Storable! (non cryogenic)
- ❑ High performing!

Desirable –

- ❑ Can be served as a refreshing drink ☺

# What's Out There?

- **WATER!**
  - **Nitric Acid (extremely corrosive)**
  - **$N_2O_4$**

    **(less corrosive, high toxicity combined with high vapor pressure)**

- **$H_2O_2$**

  **(less toxic vapor and less corrosive, environmental benign decomposition products)**

# Anion Control of Hypergolic Activity

## Liquid Oxidizer


**Commercially available solutions of LiAl hydrides and $LiBH_4$ in ethers are hypergolic with $H_2O_2$.**

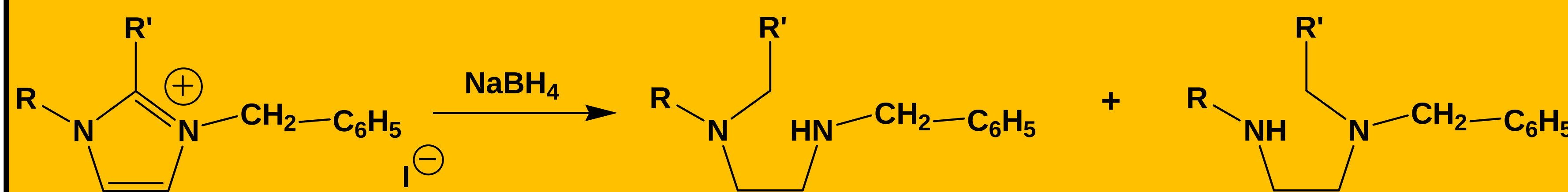

a) J.J. Rusek, *Proceedings of the 2nd International Conference on Green Propellants for Space Propulsion* (ESA SP-557), Sardinia, Italy June **2004**;

b) T.L. Pourpoint, J.J. Rusek, *5th International Hydrogen Peroxide Propulsion Conference*, Purdue University, West Lafayette, IN, September **2002**.

# Borohydride Anions in Ionic Liquids – A Challenge!

- Report on first borohydride RTIL (imidazolium based.) Tetrahedron Letters 49 (2008) 6518.*

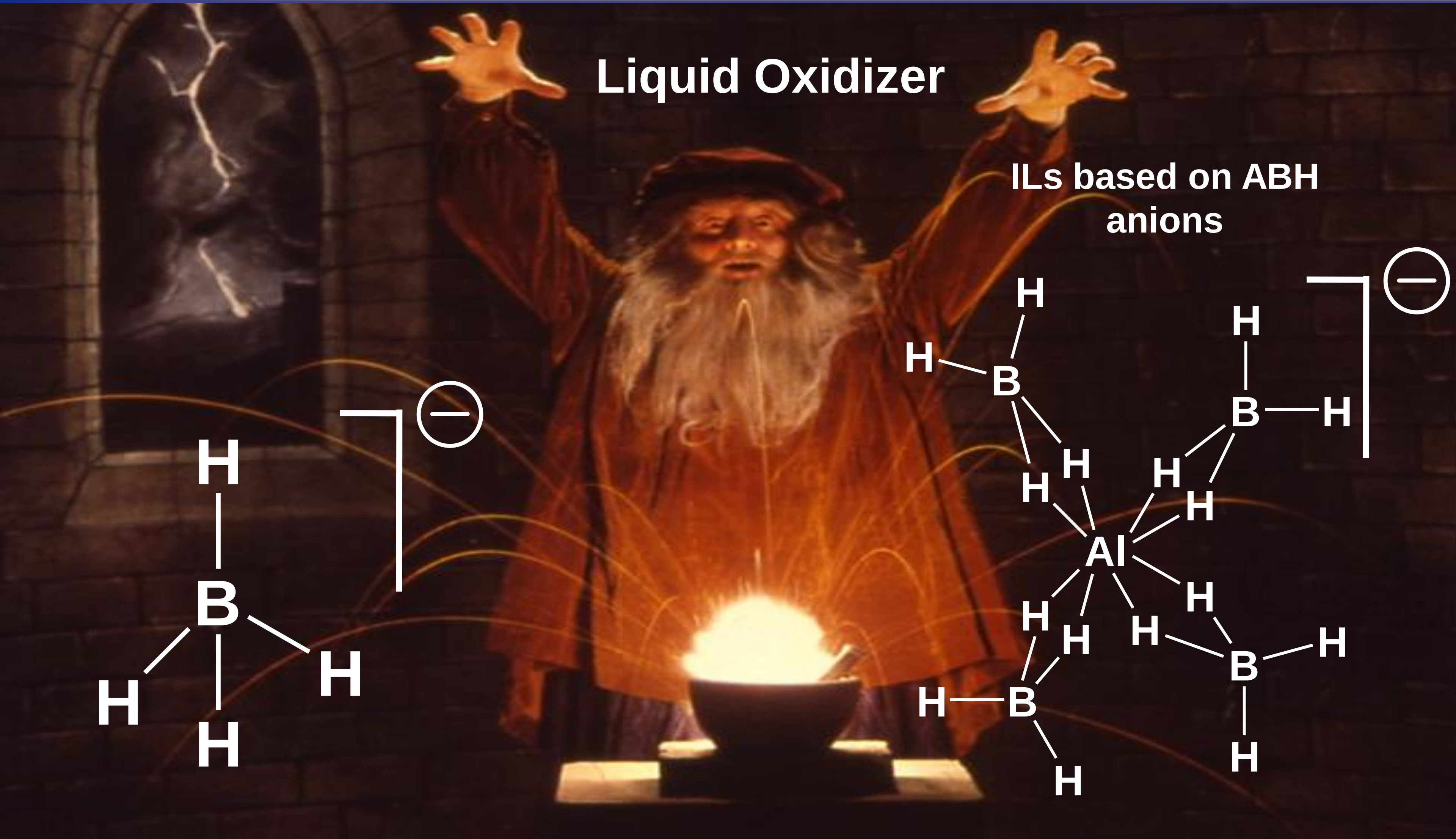

- IL product is highly viscous. When 100% pure it might be solid.
- Questionable stability.**



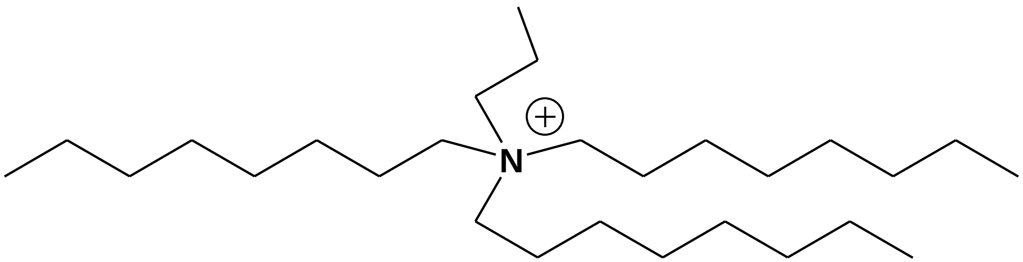

* Y. Zhang, J. M. Shreeve, *Angew. Chem.* 2011, *123*, 965-967; *Angew. Chem. Int. Ed.* **2011**, *50*, 935.

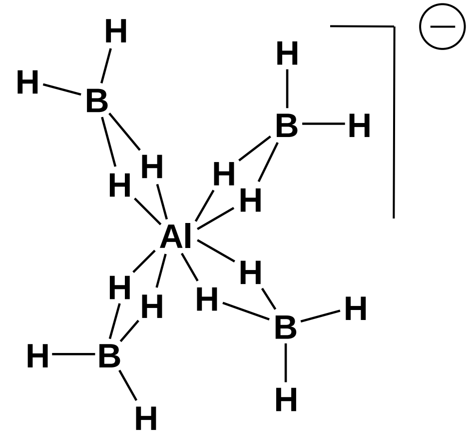
** E.F. Godefroi, *J. Org. Chem.* **1968**, *33*, 860.

# Anion Control
## Of Liquid Range

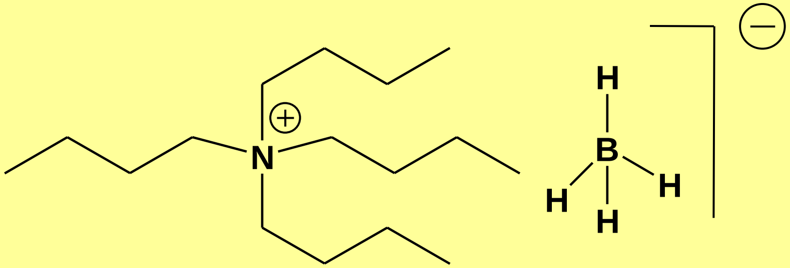


# $Al(BH_4)_4^-$ - PROMOTES LIQUIDUS

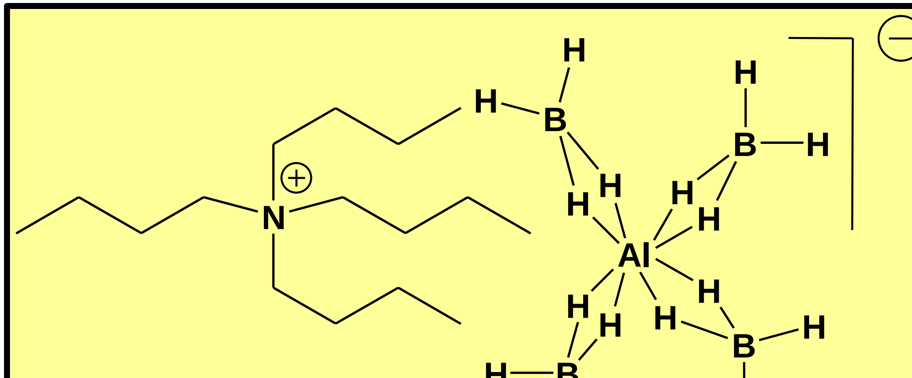




**A viscous oil crystallizing very slowly, from which neither $H_2$, $B_2H_6$, nor $Al(BH_4)_3$ could be removed even by pumping at 60°C.**



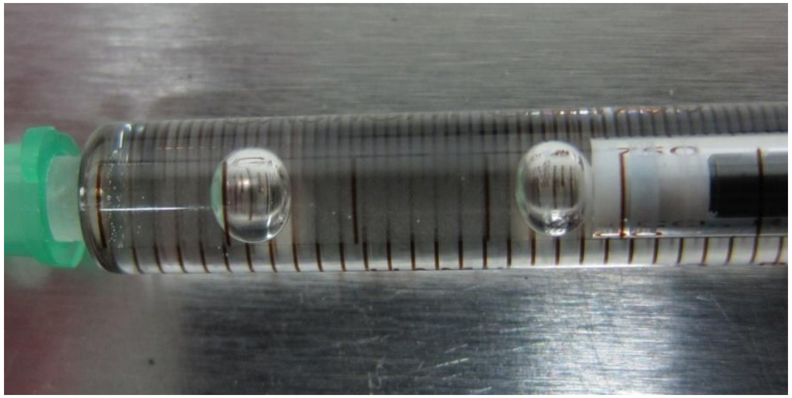
**m.p. 124-128 °C**

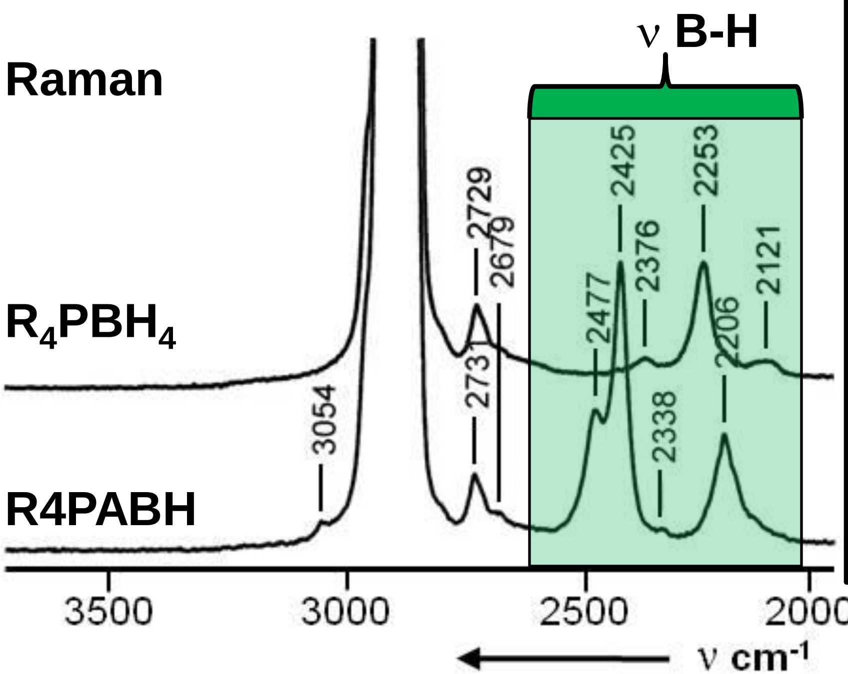


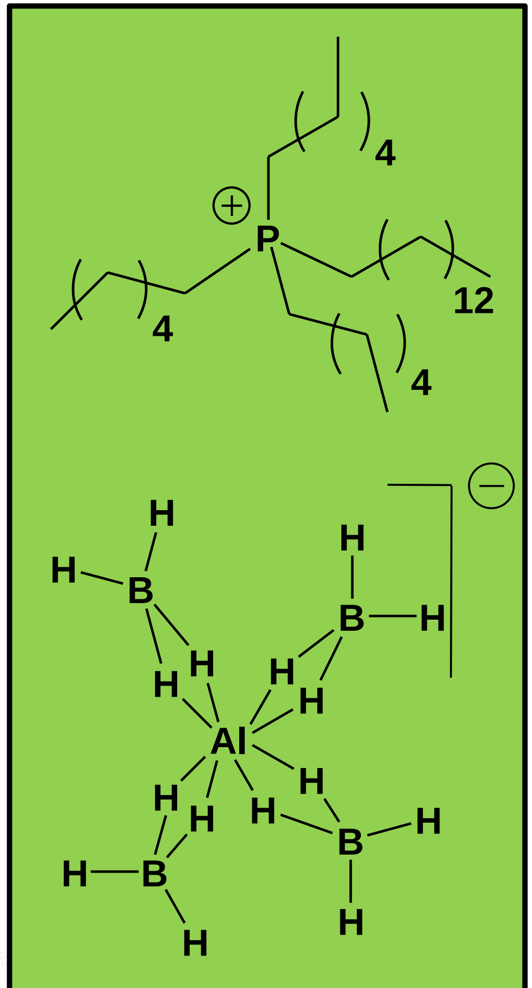
**m.p. 50 °C**

**Melting point depression of 75 °C.**

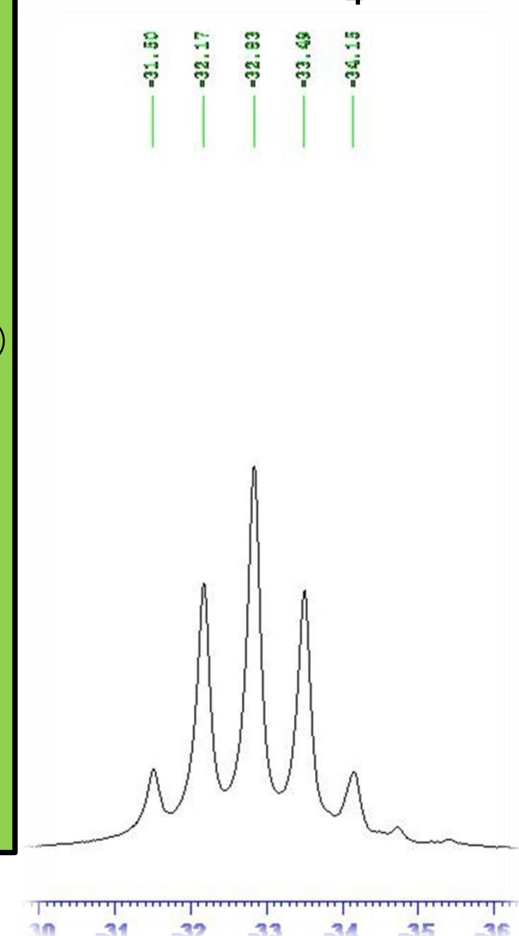
# *Trihexyltetradecylphosphonium tetrakis(tetrahydroborato)aluminate*



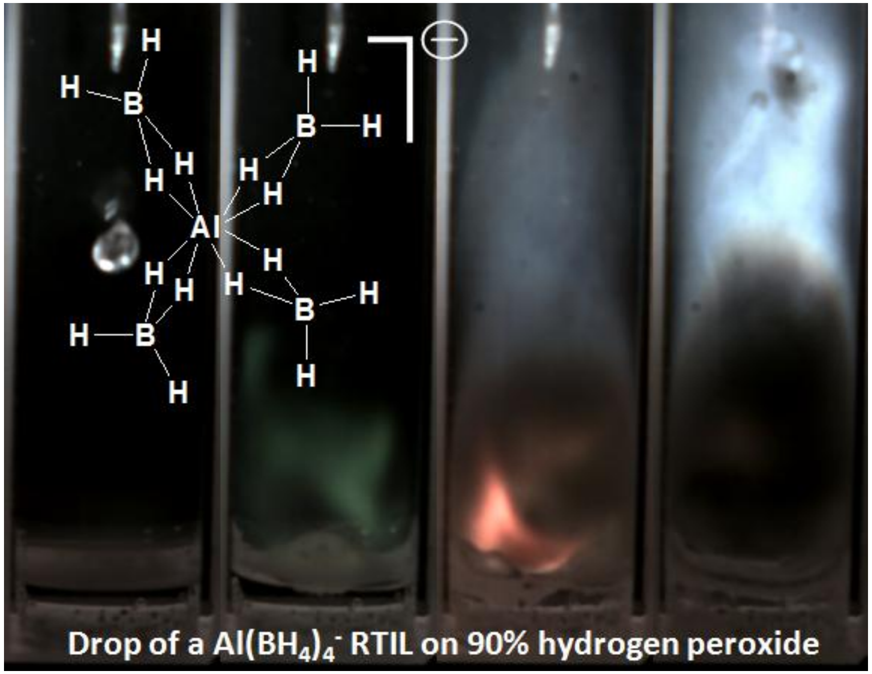



$^{11}B$ NMR of $R_4PABH$



# Drop Test Results with Hydrogen Peroxide and other Oxidizer

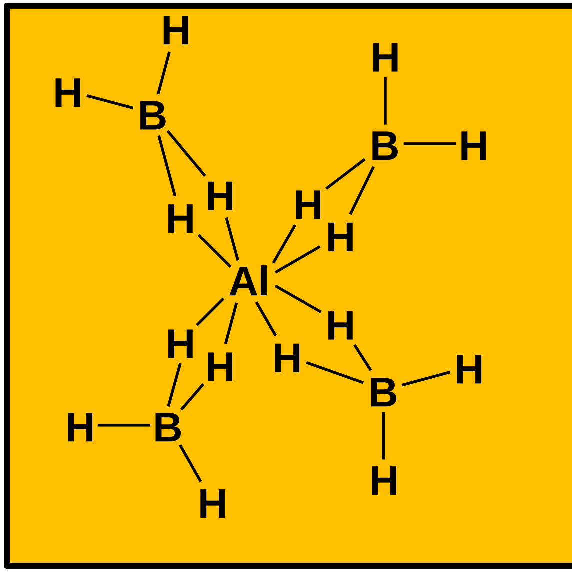


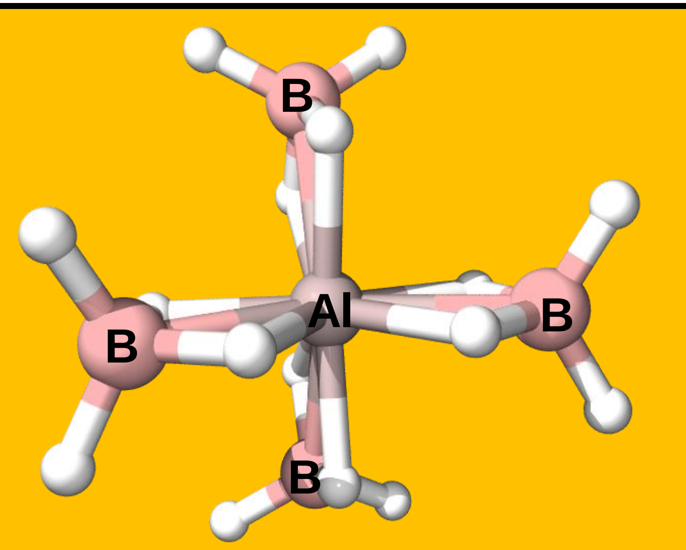

| Fuel\Oxidizer | 90%$H_2O_2$ | 98%$H_2O_2$ | $N_2O_4$ | WFNA |
|---|---|---|---|---|
| $R_4P\ Al(BH_4)_4$ Ignition Delay | Ignition < 30ms | Ignition < 30ms | Ignition Vapor ignition | Explosion - |

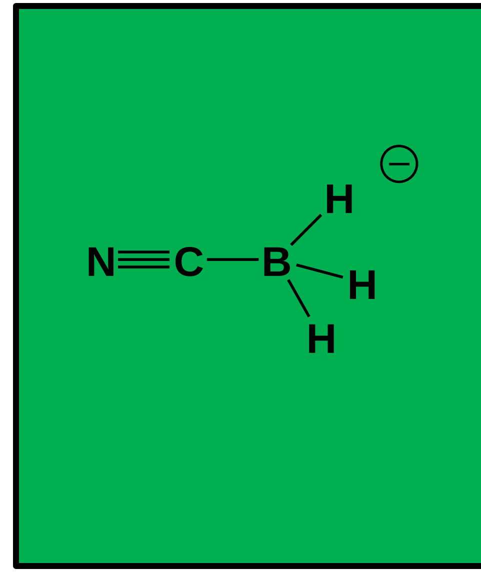
**Green Bipropellants: Hydrogen-Rich Ionic Liquids that Are Hypergolic with Hydrogen Peroxide**

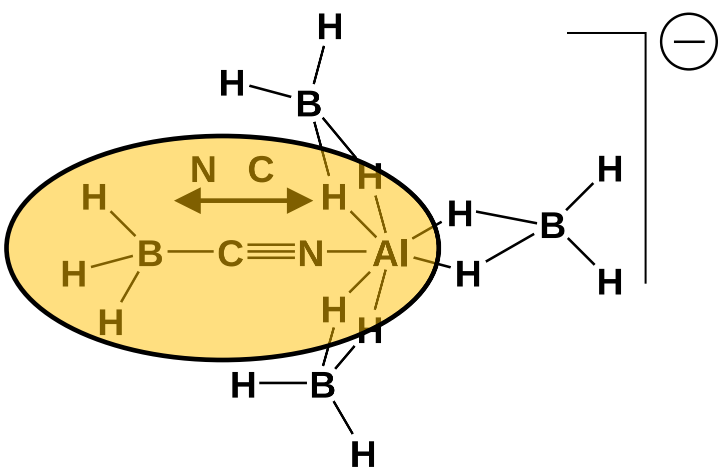
Stefan Schneider, Tom Hawkins, Yonis Ahmed, Michael Rosander, Leslie Hudgens, Jeff Mills Angew. Chem. Int. Ed. **2011**, *50*, 5886.

# *Anion Alteration*



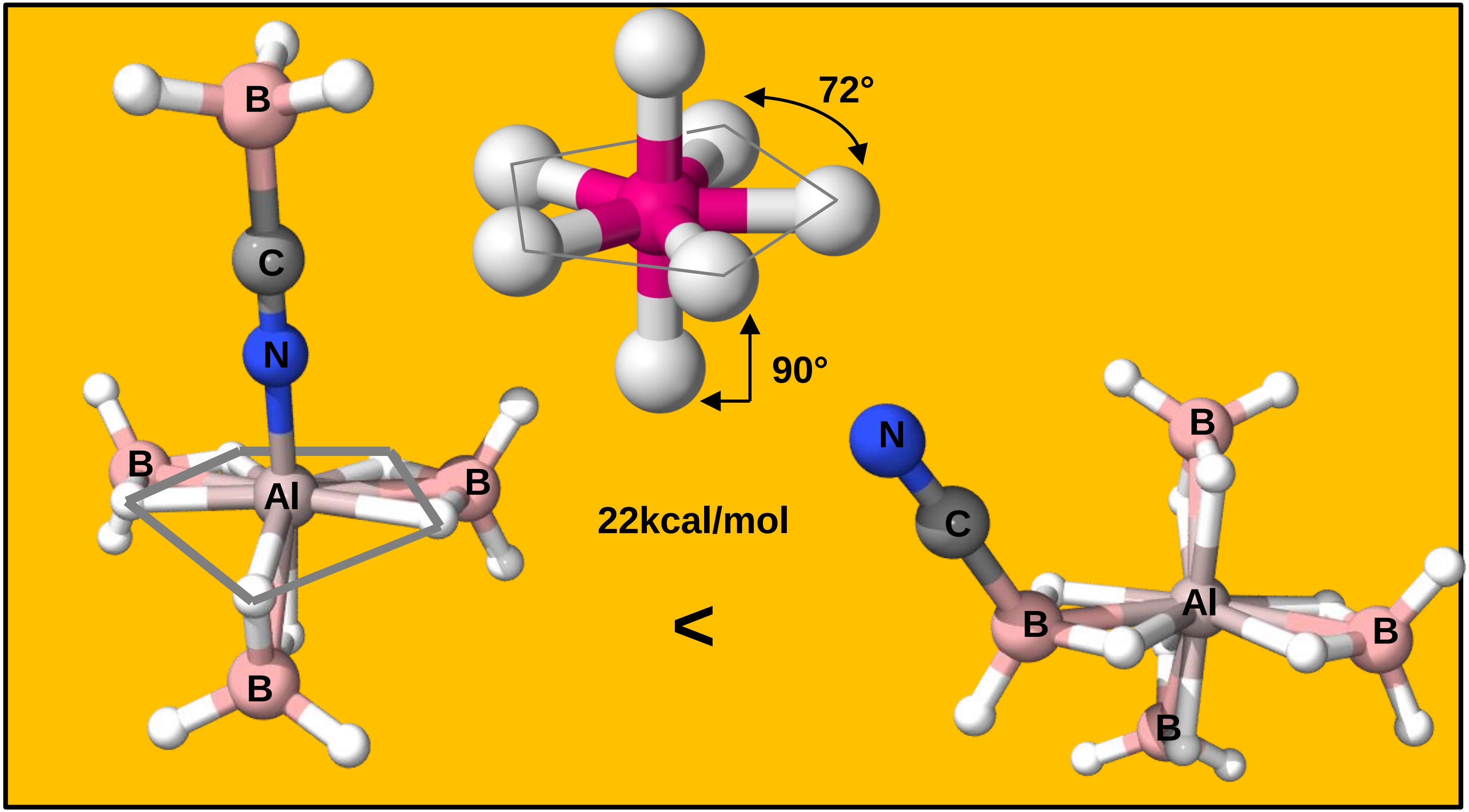




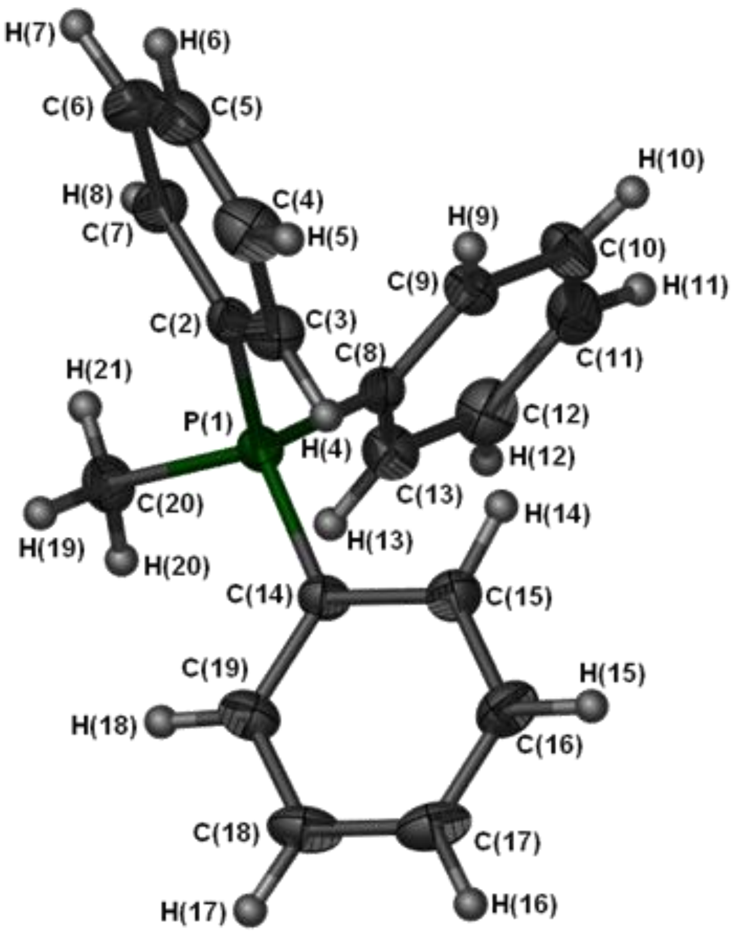


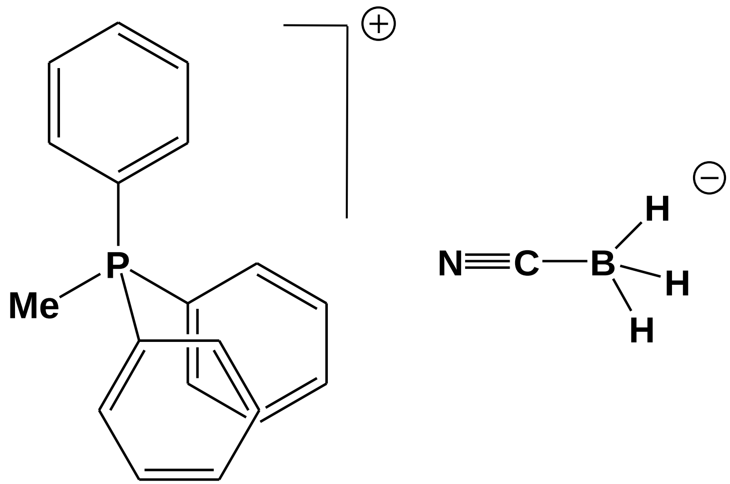
- B and Al competing over C and N
- B wants C by 14kcal/mol

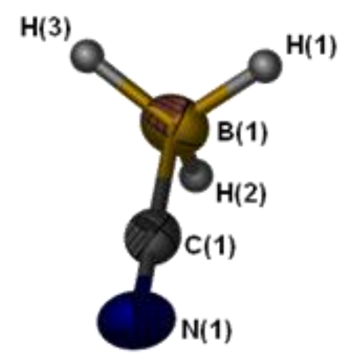
# Cyanoborohydride coordination



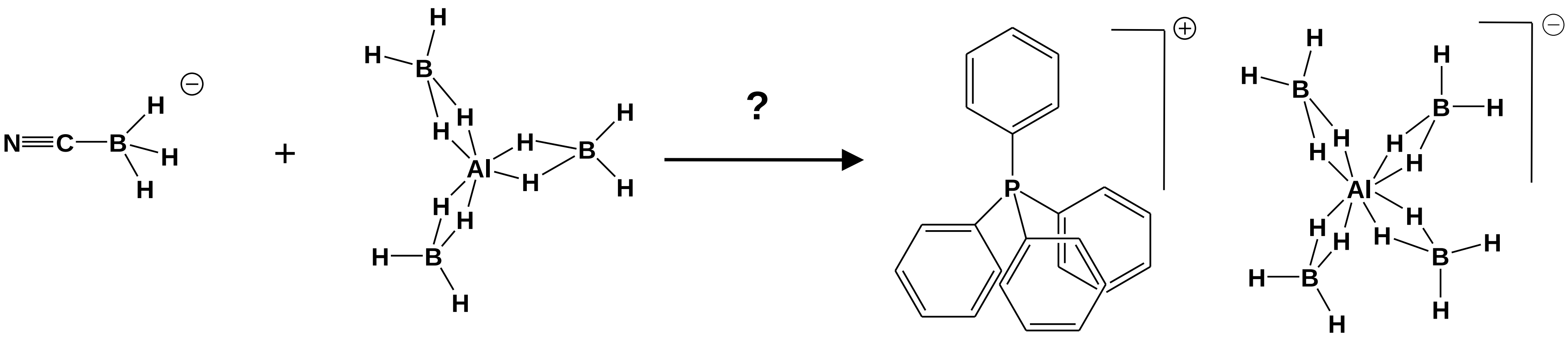
# X-ray crystal structure analyses as tool of characterization

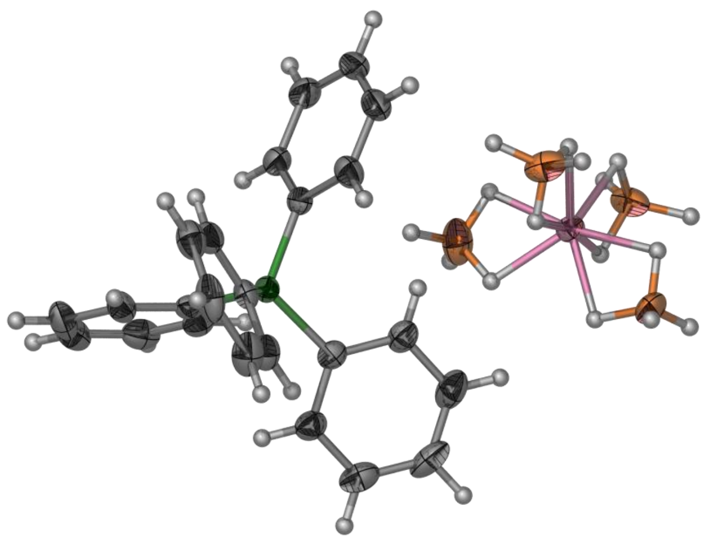


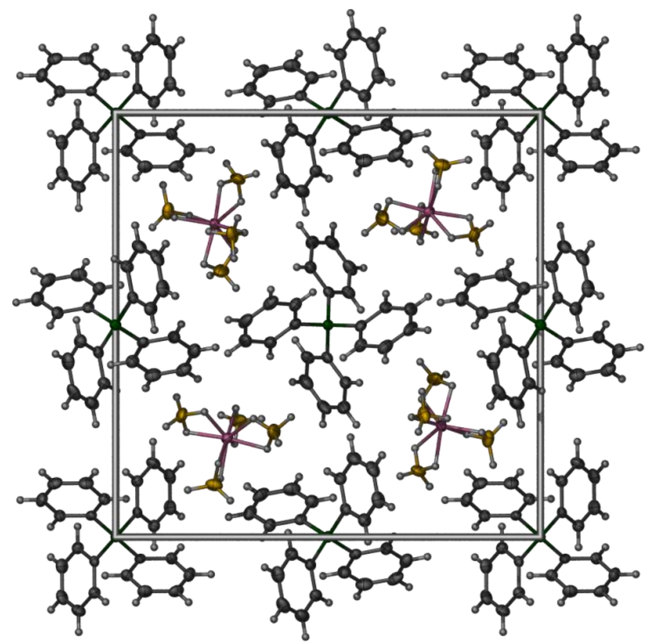



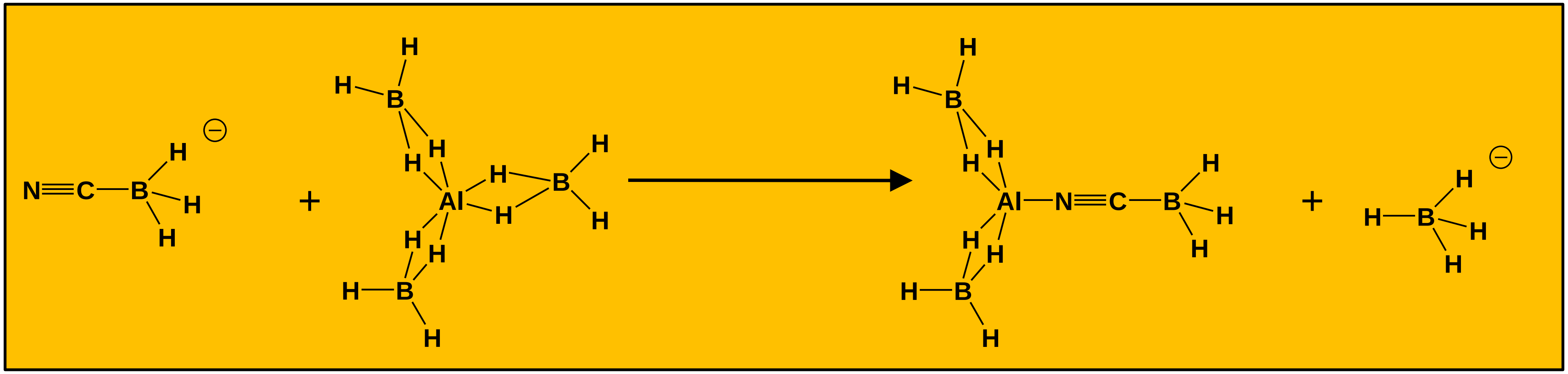
# Surprise! An all borohydride anion

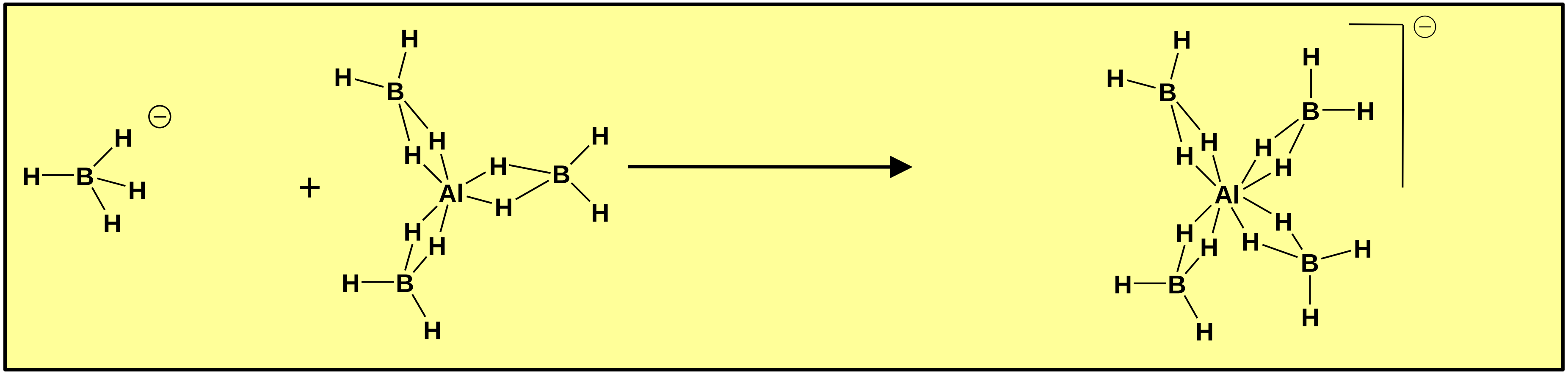




# A general path to tetrakis(tetrahydroborato)aluminates?





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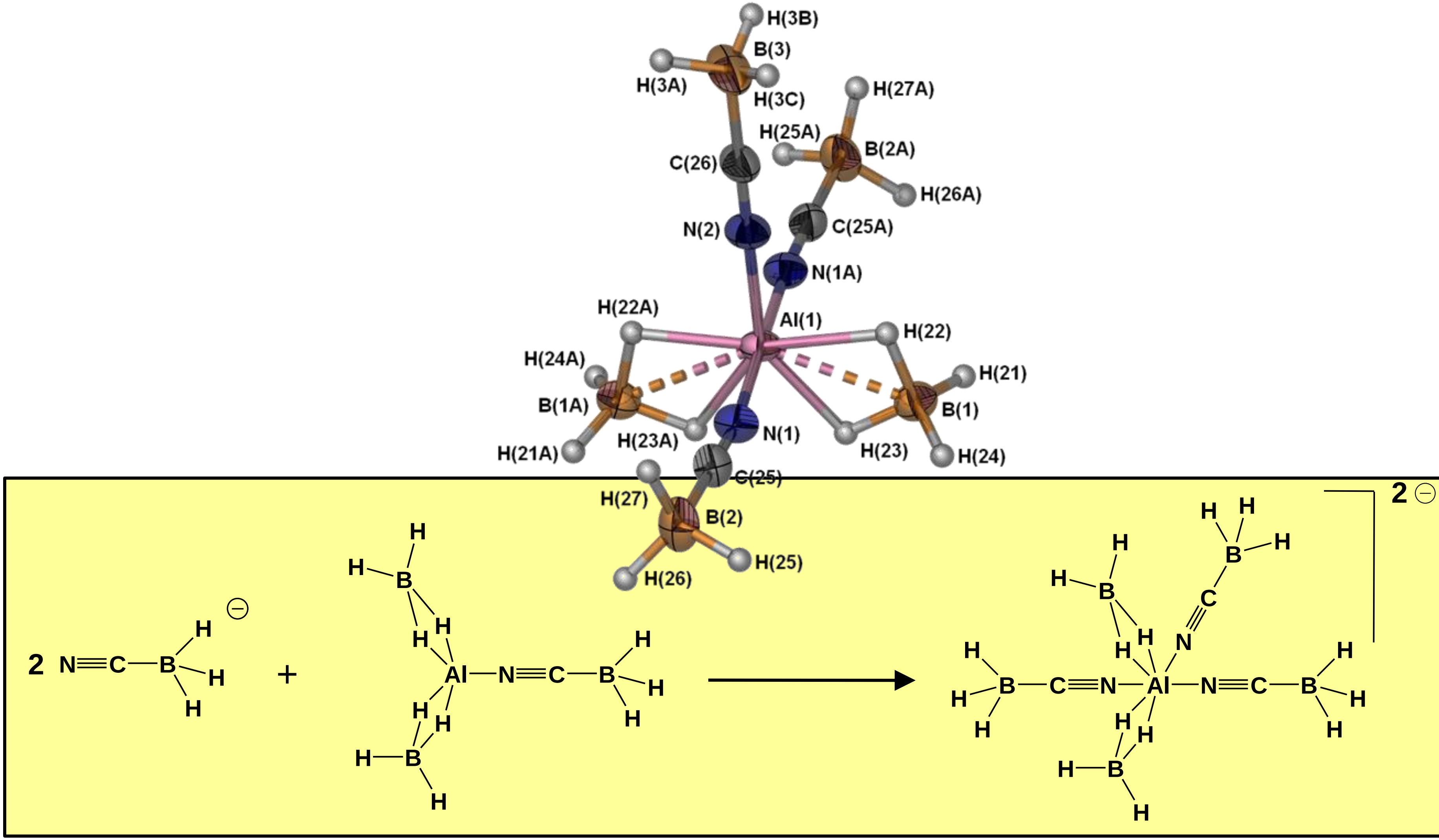
# What happened to $Al(BH_4)_2BH_3CN$




**DISTRIBUTION A: Approved for public release; Distribution unlimited**

# A reaction pathway based on x-ray structures

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

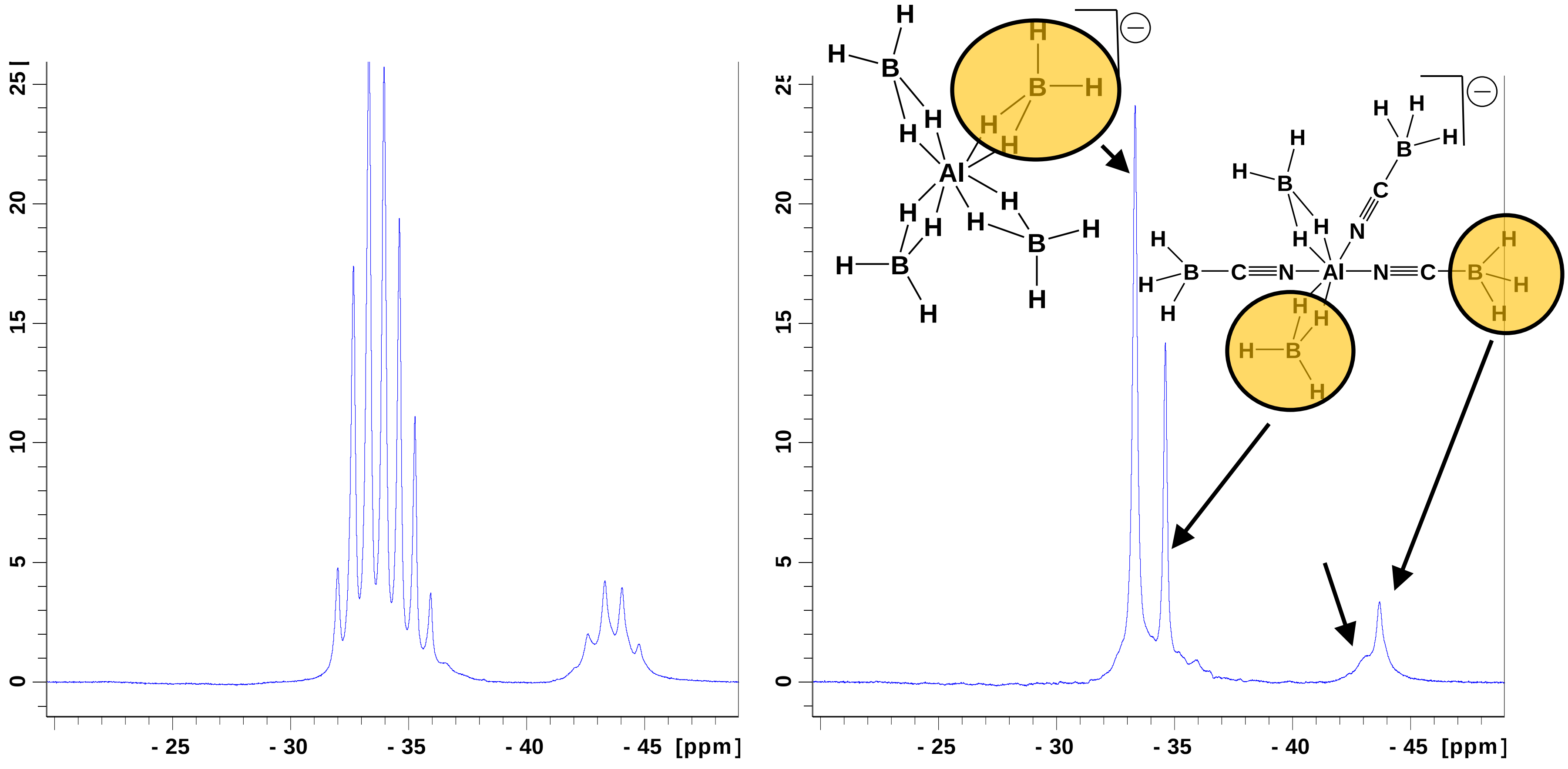
$$BH_4^- + Al(BH_4)_3 \longrightarrow Al(BH_4)_4^-$$

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

---

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

# 11B NMR of reaction mixture

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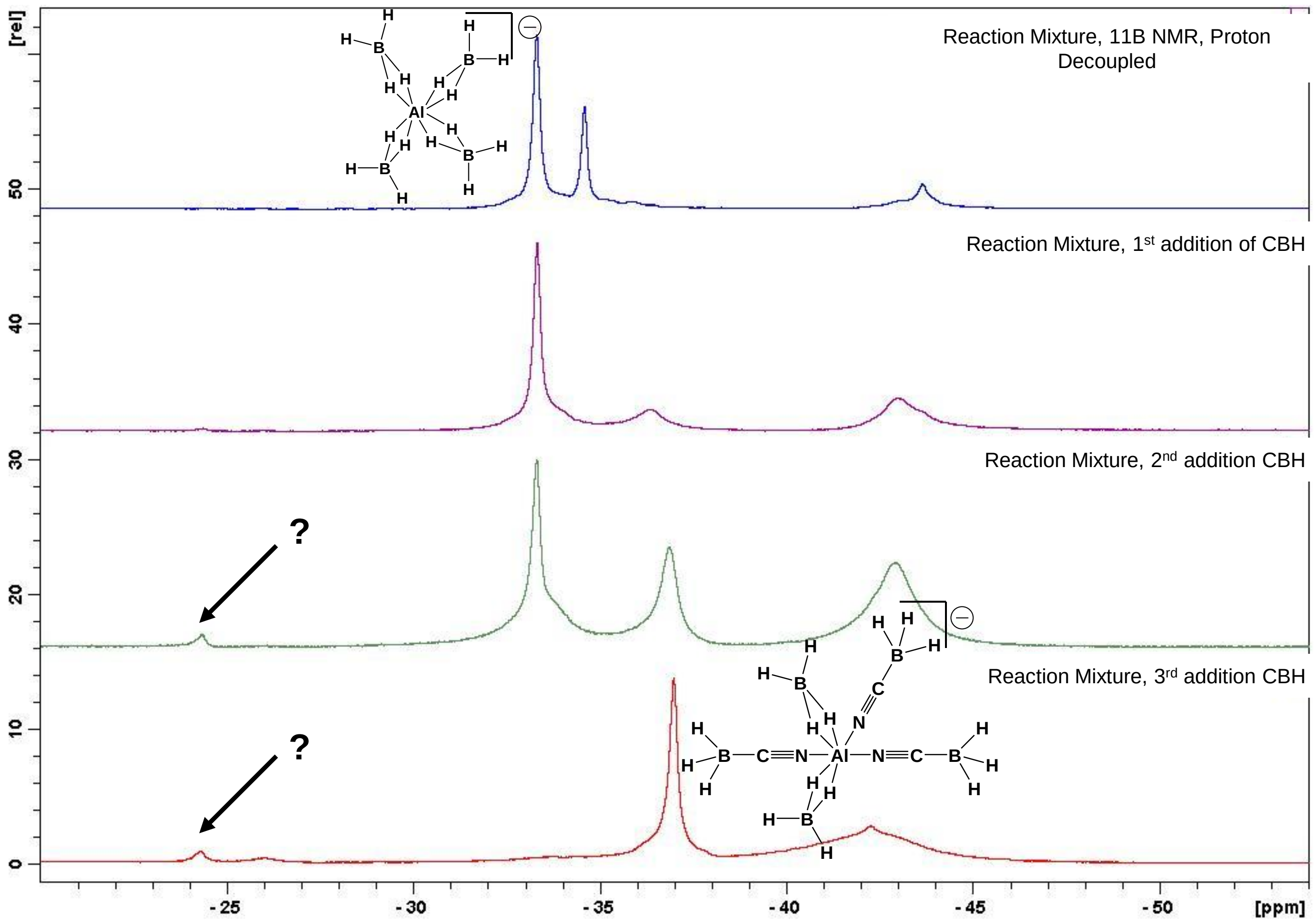
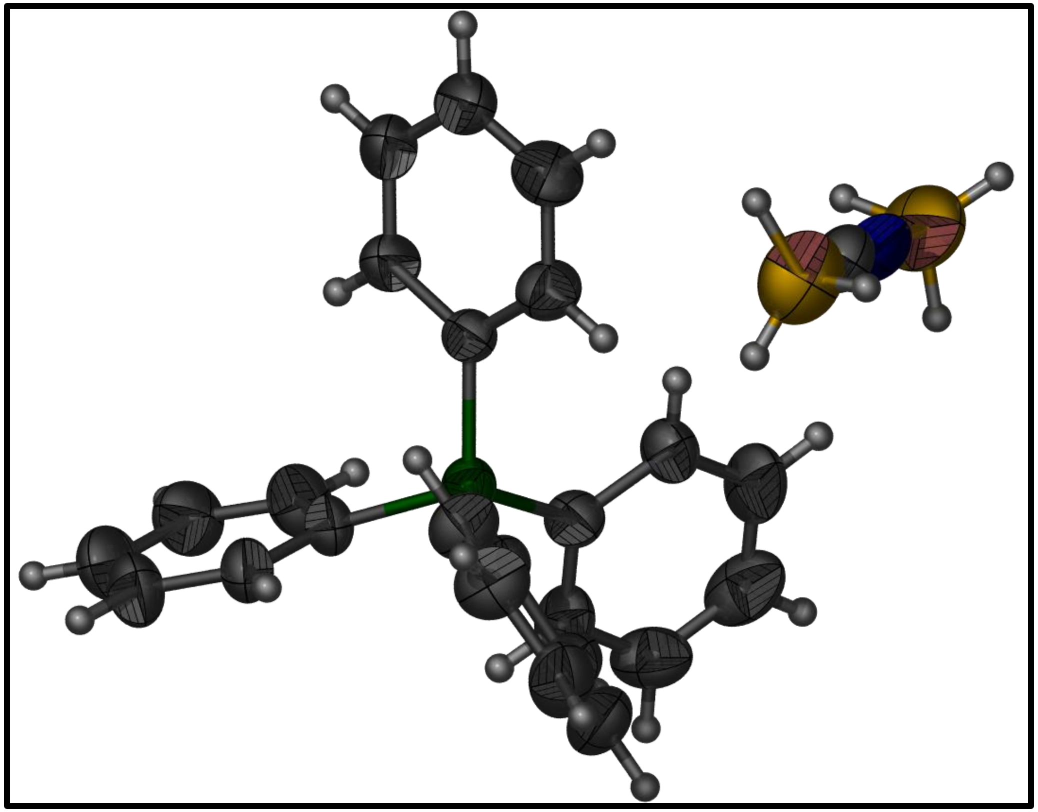
# Spiking reaction mixture with CBH

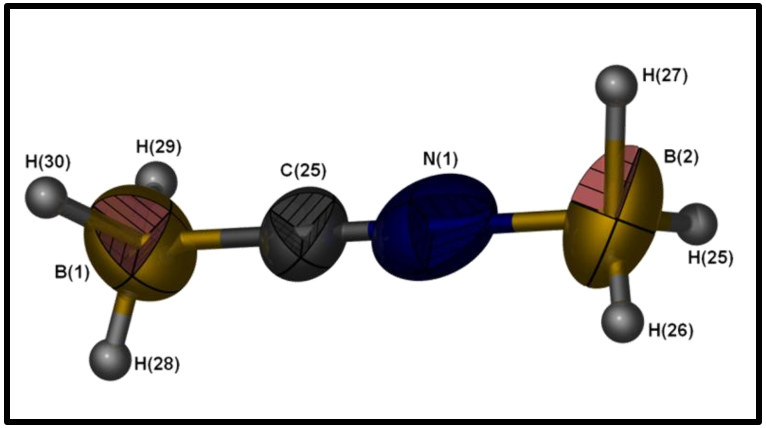


# Single crystal X-ray structure analysis provided the answer

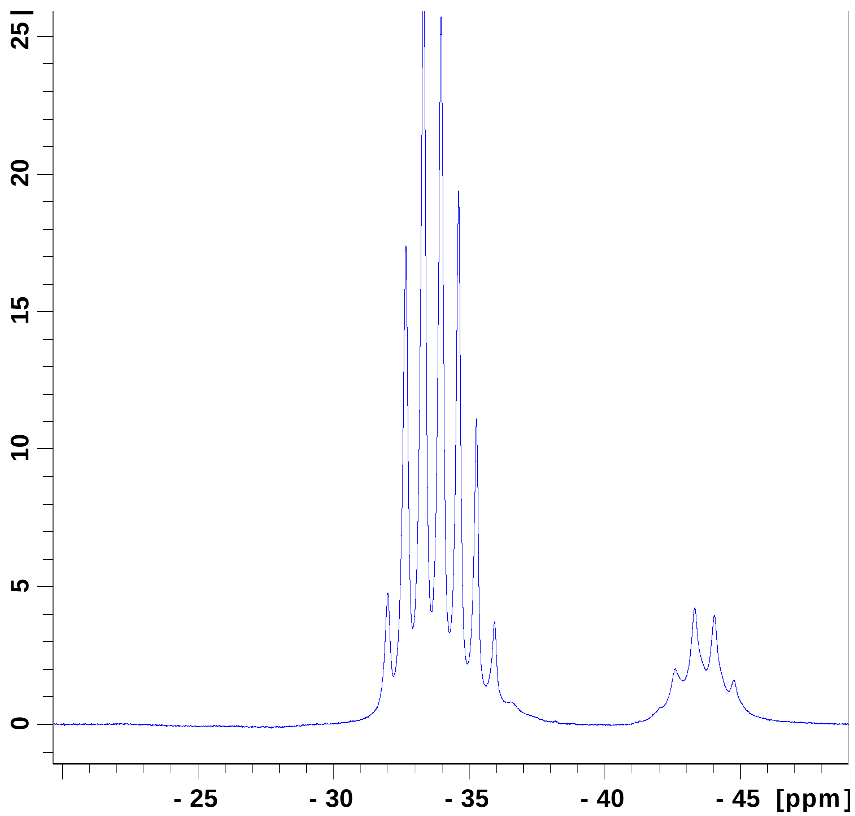
- A total of four different crystal shapes were identified under a microscope.
- Super thin plates are not a preferred crystal shape for X-ray analysis.

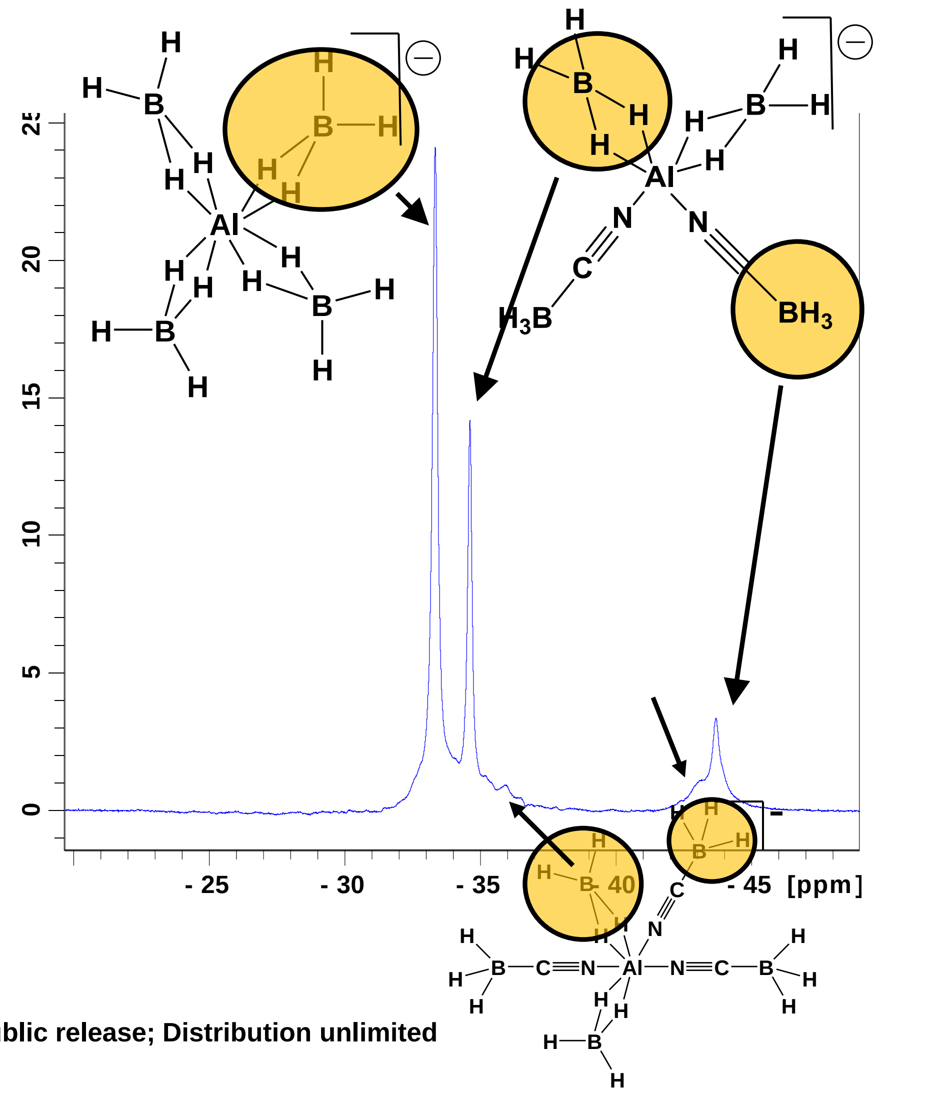


Anion enlarged and rotated



# The real picture of the crude reaction mixture

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# Heat of reaction calculations

$$4\,Al(BH_4)_3 + 4\,[NCBH_3]^- \xrightarrow{-116.5} 2\,[Al(BH_4)_4]^- + [Al(NCBH_3)_3(BH_4)_2]^{2-} + Al(NCBH_3)(BH_4)_2$$

$$[NCBH_3]^- + Al(BH_4)_3 \xrightarrow{+19.0} Al(NCBH_3)(BH_4)_2 + [BH_4]^-$$

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$$2\,Al(BH_4)_3 + 2\,[NCBH_3]^- \xrightarrow{-96.3} [Al(BH_4)_4]^- + [Al(NCBH_3)_2(BH_4)_2]^-$$

$$Al(BH_4)_3 + [NCBH_3]^- \xrightarrow{-48.6} [Al(NCBH_3)_2(BH_4)_2]^-$$

$$[Al(NCBH_3)_2(BH_4)_2]^- + [NCBH_3]^- \xrightarrow{+3.4} [BH_4]^- + [Al(NCBH_3)_2(BH_4)_2]^-$$

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$$[Al(NCBH_3)_2(BH_4)_2]^- + [CNBH_3]^- \xrightarrow{+16.3} [Al(NCBH_3)_3(BH_4)_2]^{2-}$$

* All values are kcal/mol, gas phase

# The current reaction sequence

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

$$[Al(BH_4)_4]^- + [Al(BH_4)_2(NCBH_3)_2]^- \xrightarrow{\text{exc } NCBH_3^-} [Al(BH_4)_2(NCBH_3)_3]^{2-}$$

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


* 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

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