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S. Schneider

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15. SUBJECT TERMS

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					Tonny Hawkins
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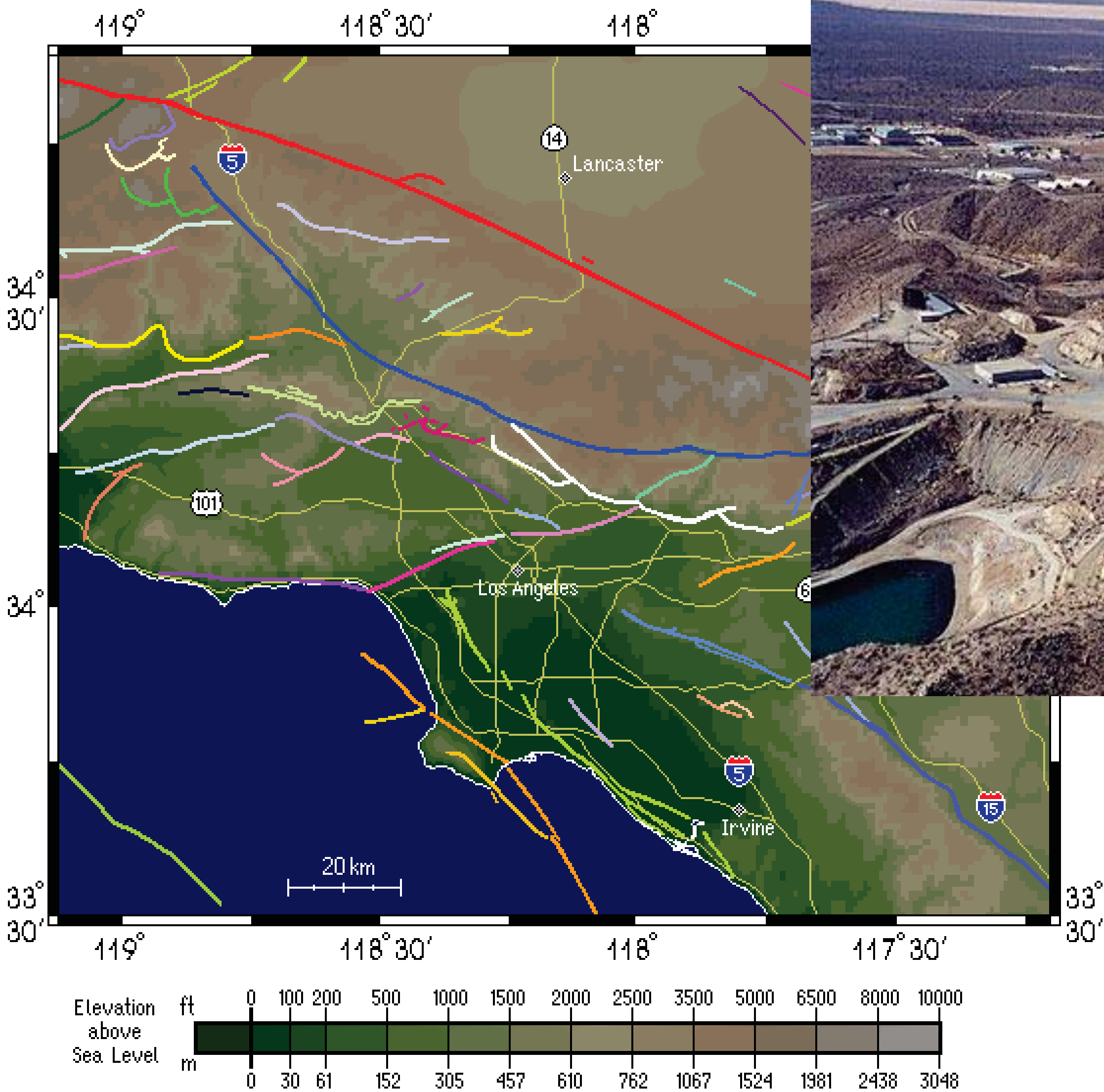
IONIC LIQUID FUELS FOR ADVANCED PROPELLANTS

Pasadena, December 2012

S. Schneider
Edwards AFB, CA

Where are we located?

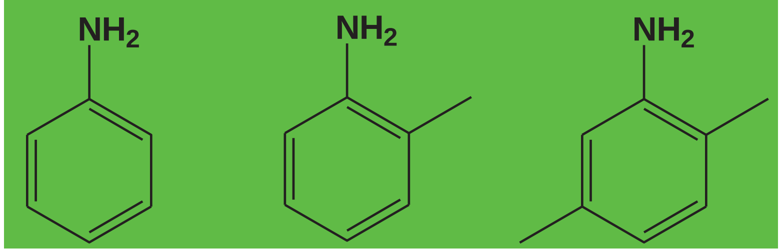


- Images: Southern California Earthquake Data Center, California Institute of Technology; The Center for Land Use Interpretation

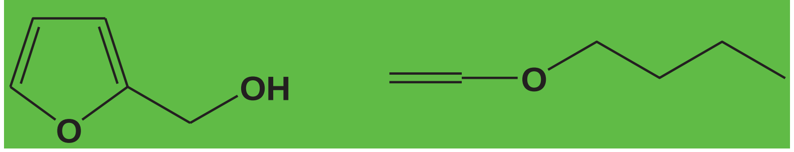
The beginning - A world without hypergols

Engineers
commercially available, off the shelf

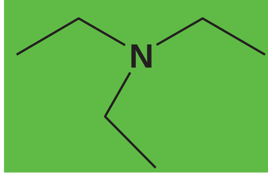
aromatic Amines



ethers



aliphatic amines

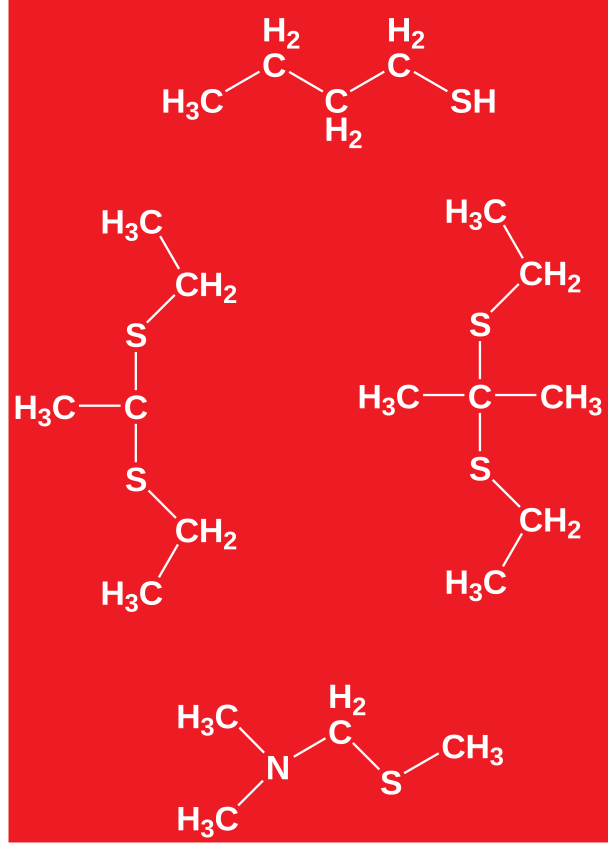


tertiary > secondary > primary

heterocyclic amines

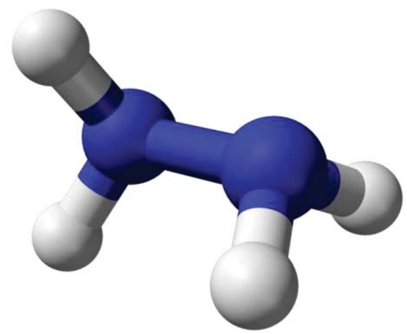
Chemists
designing new propellants with desired properties

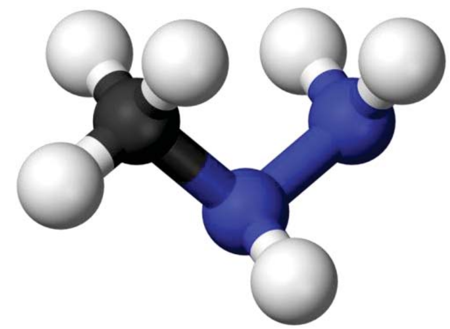
sulfur compounds



Creativity of a Chemist has no limits

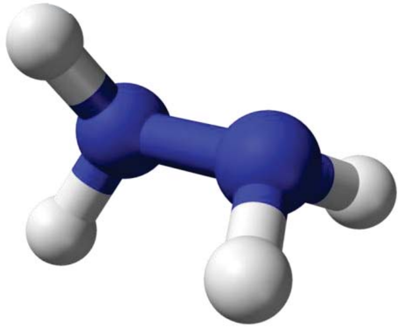
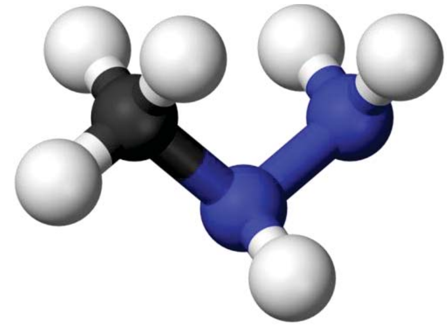
All work became obsolete by hydrazine





	Hydrazine	Monomethylhydrazine
Molecular formula	N_2H_4	$CH_3(NH)NH_2$
Appearance	Colourless liquid	Colourless liquid
Density	1.00 g/cm^3 (anhydrous) 1.03 g/cm^3 (hydrate)	0.88 g/cm^3
Melting point	1 °C (anhydrous) -51.7 °C (hydrate)	−52 °C
Boiling point	114 °C (anhydrous) 119 °C (hydrate)	87 °C
Solubility in water	miscible	very soluble
Viscosity	0.876 cP(25 °C)	0.855 cP(20 ºC)

Hydrazine – Why is it or why it became a problem chemical*

Hydrazine	Monomethylhydrazine
	

- Chemical workers accidentally exposed to high hydrazine vapor concentrations during the 1950's have not shown a higher mortality in the exposed group when compared to workers employed in other industrial positions.
- Hydrazine permissible limit concentration was lowered in 1995 from 0.1 to 0.01 ppm by conservative toxicologists to avoid law suits similar to those against the asbestos industry.

E.W. Schmidt, E.J. Wucherer *Proc. 2nd Int. Conference on Green Propellants for Space Propulsion ESA Sp-557* **2004**.

Pitfalls for the development of new propellants*

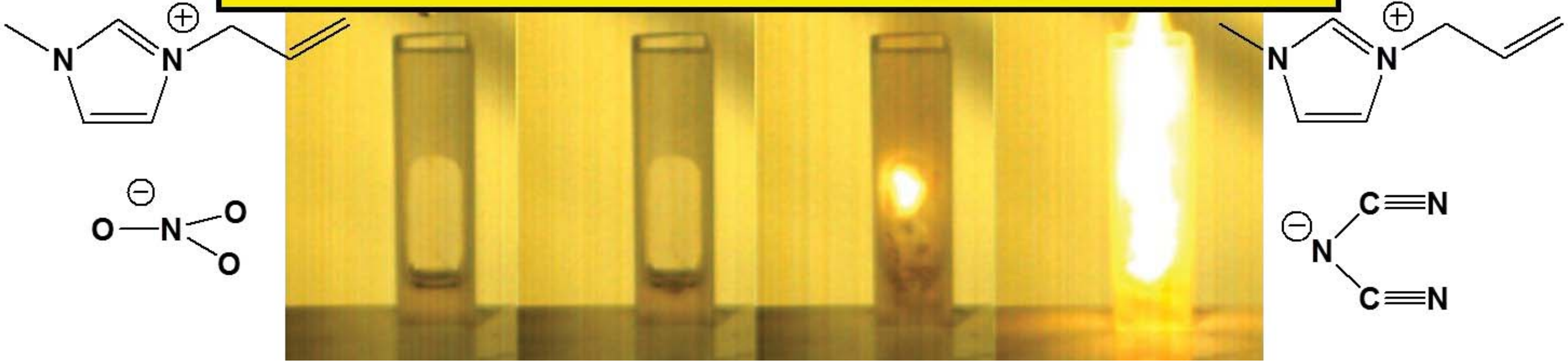
- ❑ Cost of the propellant
- ❑ Cost of monitoring the health of fueling / defueling crew
- ❑ Cost of disposal of residual

- ❑ We expect lower cost with lower toxicity fuels, but we don't know at this point and only future experience will show
- ❑ After a long development effort we may find that the non-toxic alternative is not as benign as we hoped for

E.W. Schmidt, E.J. Wucherer *Proc. 2nd Int. Conference on Green Propellants for Space Propulsion ESA Sp-557* **2004**.

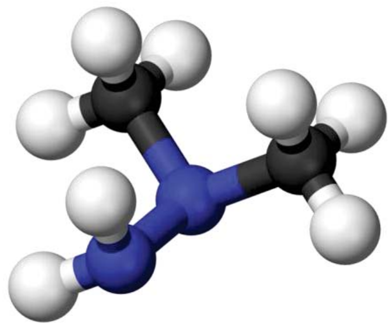
Particle free Combustion for Space Propulsion

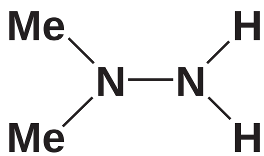
Oxygenated	**Fuel-Rich**
Oxidizer: White fuming nitric acid	
Not Hypergolic	***Hypergolic***; ID ≈ 43.0 ms



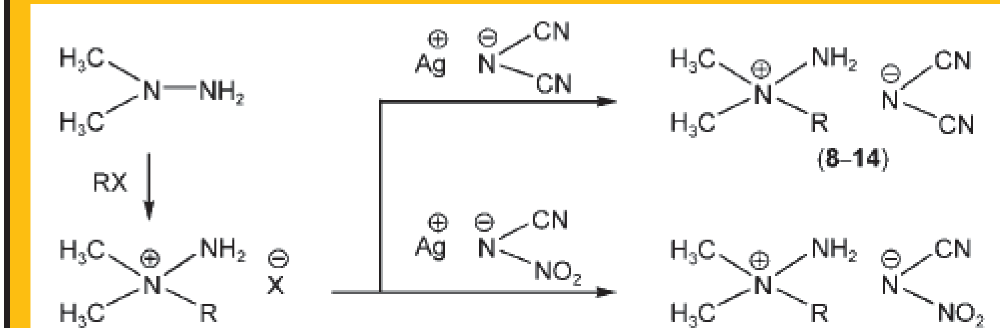
- **The development of cationic structures, who allow for fast, hypergolic ignition with common oxidizers independent of the accompanying anion.**
- **The inability to endow the cation with a hypergolic "trigger" narrows the synthetic design space available for hypergolic fuels and blocks another possible avenue for the promotion of rapid ignition.**

Transform a hypergolic neutral into an aprotic IL e.g. N,N-Dimethylhydrazinium





Properties	
Molecular formula	$C_2H_8N_2$
Molar mass	60.1 g/mol
Density	0.793 g/cm^3
Melting point	−57 °C
Boiling point	63 °C

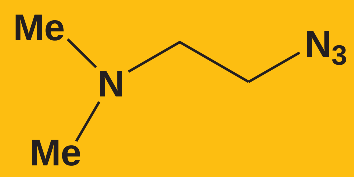


$T_m(T_g)$[a] [°C]	T_d[b] [°C]	ρ[c] [g cm^{-3}]	η[d] [mPas]	ID[e] [ms]
60.5	253.5	1.10	–	58
30.9	267.1	1.06	67.5	22
20.4	263.3	1.01	113.9	46
–	199.2	1.05	78.6	24
–	174.3	1.13	228.6	30
–	236.0	1.15	161.8	40
–	144.8	1.17	1057.0	1286
35.2	292.4	1.24	–	126
25.4	296.9	1.17	–	198
9.0	285.5	1.11	119.5	228
–	208.2	1.16	84.9	130
–	189.3	1.21	269.8	134
–	269.1	1.26	185.9	247
–	193.5	1.28	1310.0	1642

Oxidizer: White fuming nitric acid

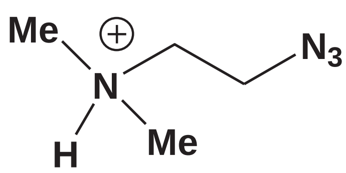
Y. Zhang, Y. Guo, Y.-H. Joo, J. M. Shreeve Chem. Eur. J. **2010**, *16*, 3114.

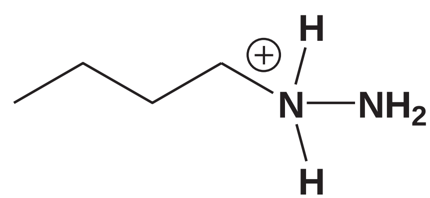
Transform a hypergolic neutral into a protic IL e.g. DMAZ, hydrazine

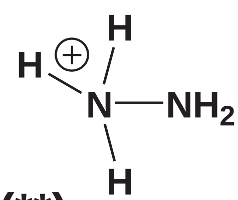


- **Protic ILs exist as neutral molecules in the gas phase!**
- **Find neutral, known hypergols and convert to protic Ils.**

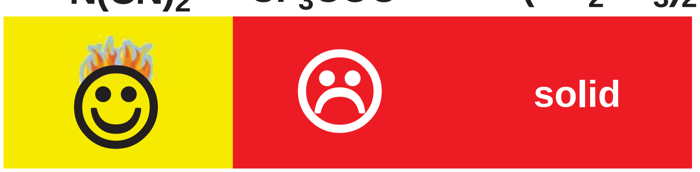
Emel'yanenko, V.N.; Verevkin, S.P.; Heintz, A.; Voss, K.; Schulz, A. J. Phys. Chem. B **2009**, 113(29), 9871-9876.
Leal J.P.; Esperancüa J.M.S.S.; da Piedade M.E.M.; Lopes J.N.C. ; Rebelo L.P.N; Seddon K.R. Phys. Chem. A **2007**, 111, 6176-6182.



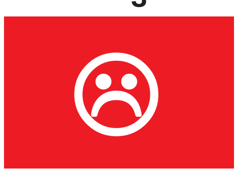




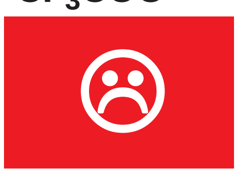
(*) ⊖ $N(CN)_2$ | ⊖ CF_3COO | ⊖ $N(SO_2CF_3)_2$



⊖ NO_3



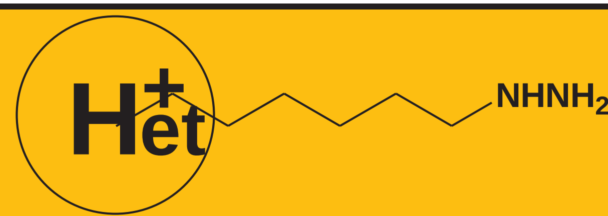
(**) ⊖ CF_3COO



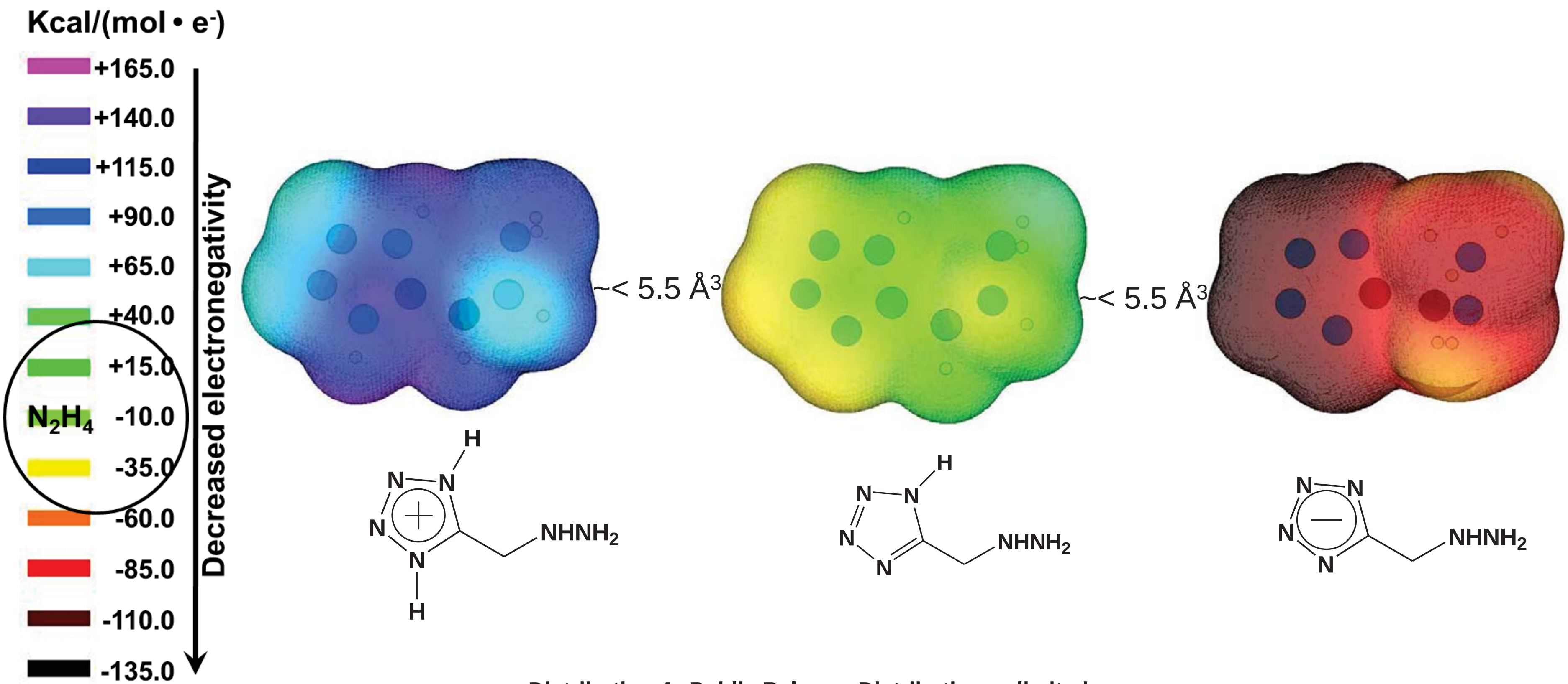
*Schneider, S.; Dambach, E.; Hawkins, T.; Rosander M. Proceedings of the COIL-3 conference (3rd Congress on Ionic Liquids), Cairns, Australia, May 31-June 4, **2009**.

Nicolich, Steven M.; Paraskos, Alexander J.; Doll, Daniel W.; Lund, Gary K.; Balas, Wendy A. **U.S. Pat. Appl. Publ. (2008), US 2008251169
Bargamova, M. D.; German, L. S.; Mysov, E. I.**Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1989), (5), 1215-16.**

Tunable Hybrid Materials

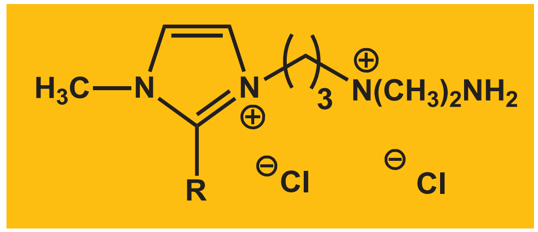


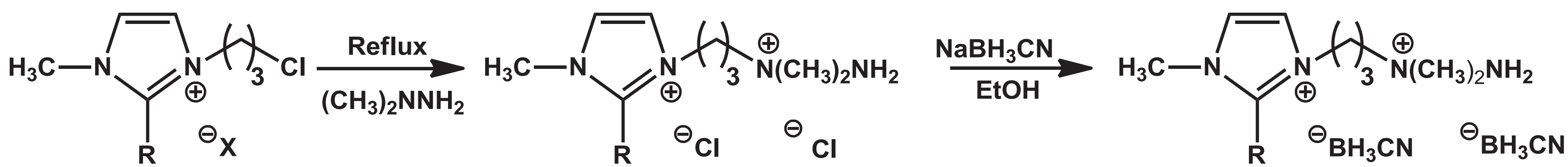
- Combining in one hybrid material the facile ignition characteristics of the hydrazines with the desirable properties of ILs, especially their density and low vapor toxicity.

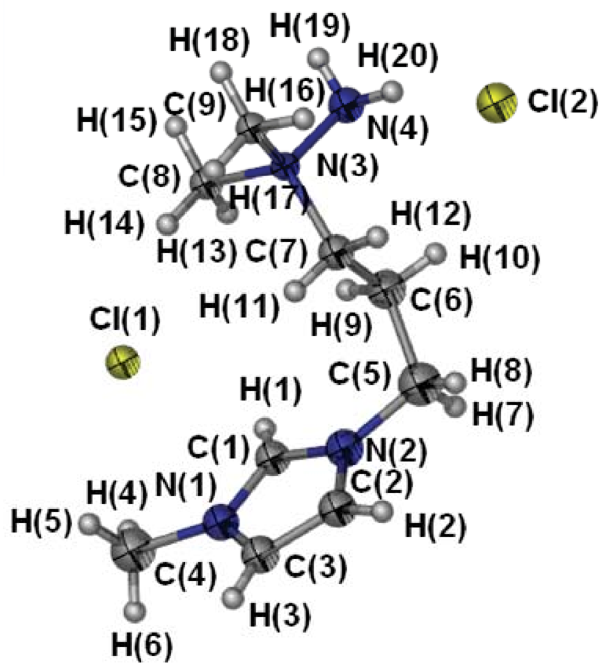


Distribution A: Public Release, Distribution unlimited

Unsymmetrical dimethylhydrazine Ionic Liquid

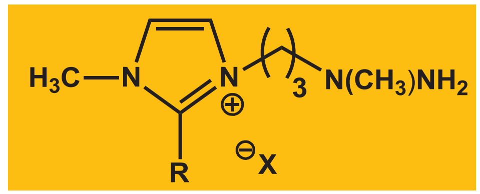


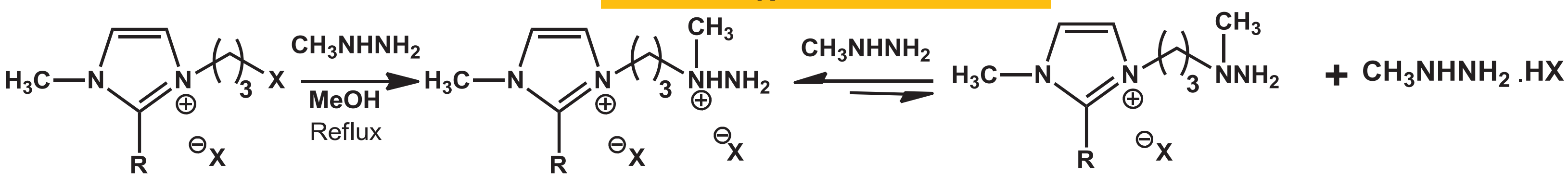


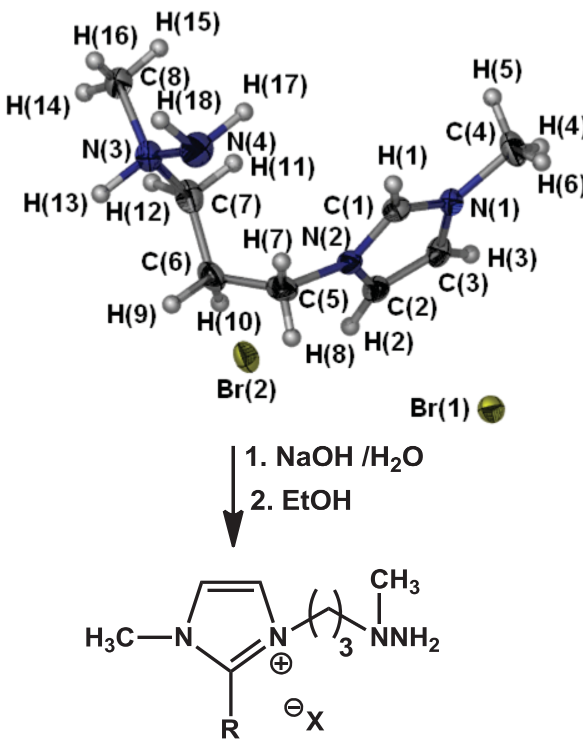


- BH_3CN salt is a glassy solid as expected for a dicationc species.

Monomethylhydrazine Ionic Liquid

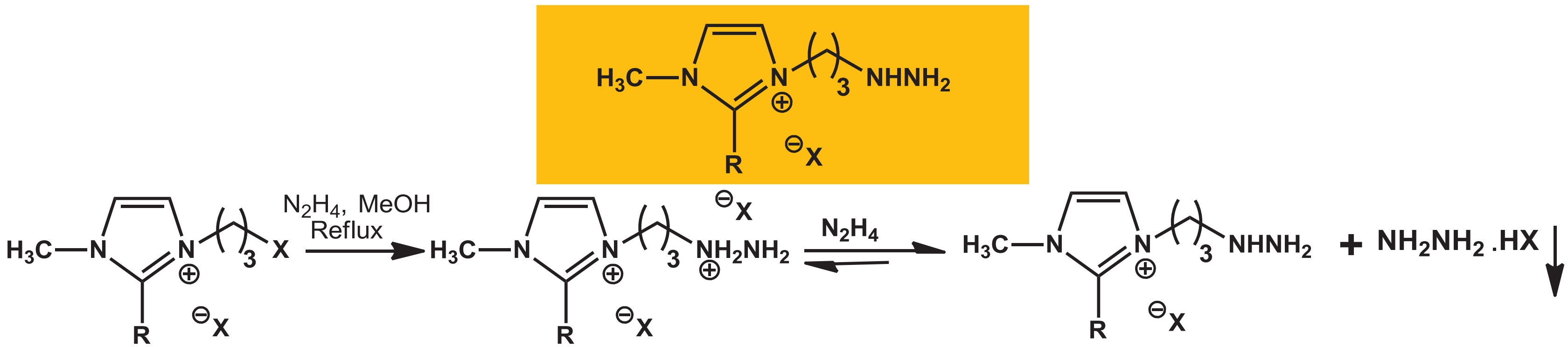


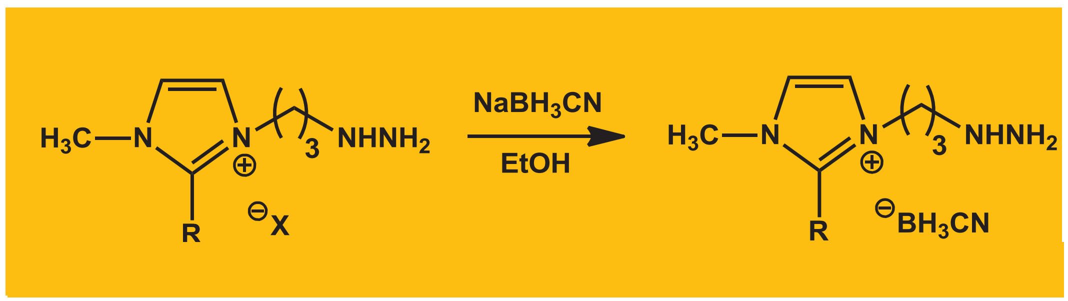




- So far, only isolated as a mixture of mono and dihalide salts.
- No precipitate formed in presence of MMH

Hydrazine Ionic Liquid





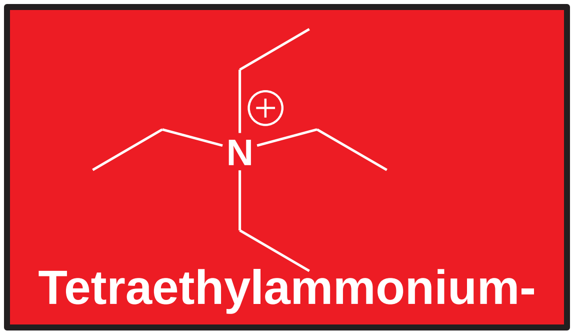
- ❑ Unacceptably high viscosity of hydrazino-functionalized imidazolium CBHs render them unusable as propellants.
- ❑ Initial drop tests with HNO_3 revealed a much longer ID time than obtained with simple alkyl substituted imidazolium CBHs.
- ❑ High viscosity is probably due to strong cation and anion interactions of the hydrazino group.

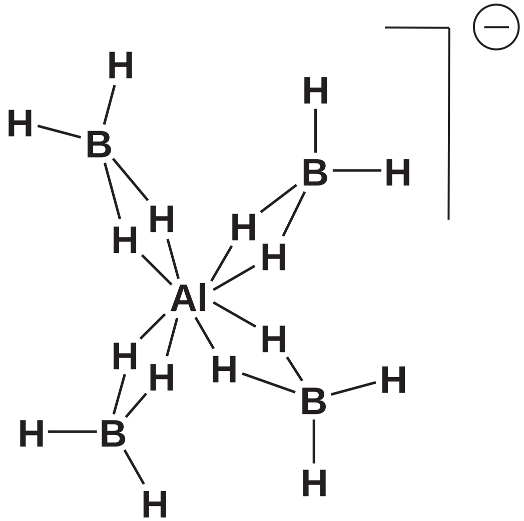
Performance!

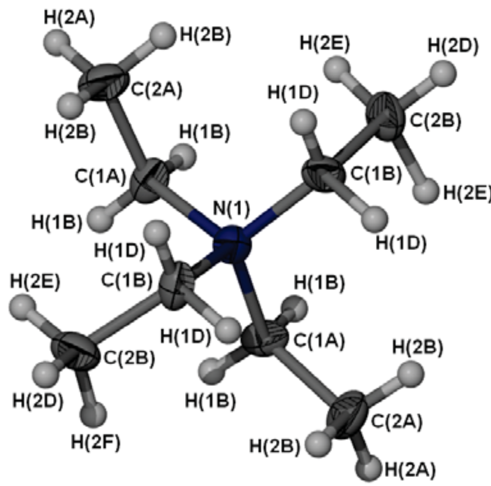
- Besides environmental friendliness, low toxicity, and overall operability, performance levels must be comparable with current propellant combinations such as hydrazine and N_2O_4.

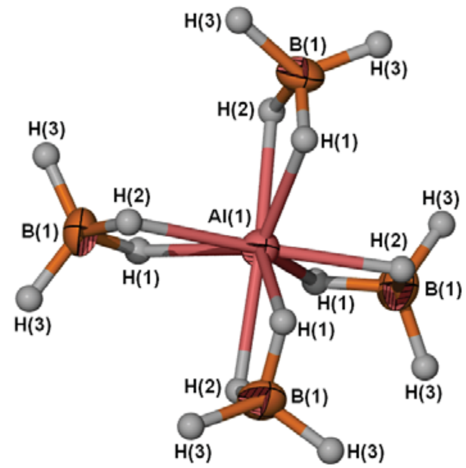
- A high fuel performance can be fostered by light metals with large combustion energies and relatively light products.
- Elements with considerable performance advantages and nontoxic products are aluminum and boron.
- The need for light combustion products through the production of hydrogen gas and water vapor is fulfilled by a high hydrogen content.

Tetraethylammonium tetrakis(tetrahydroborato)aluminate









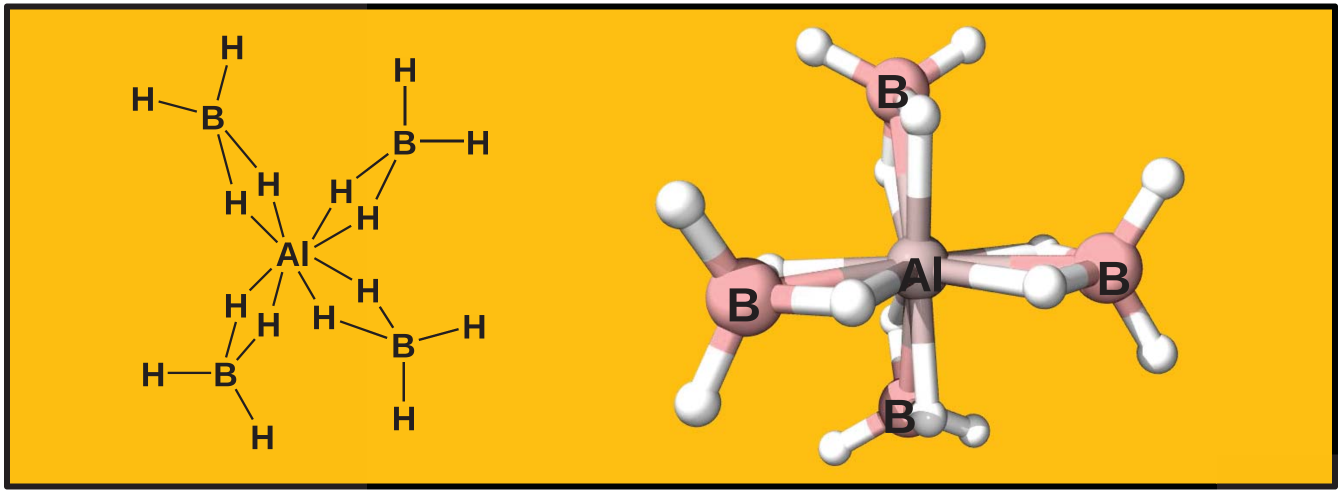
$C_8N_1H_{36}Al_1B_{4,}$ 216.60 g/mol, ρ = 0.81 g/cm^3

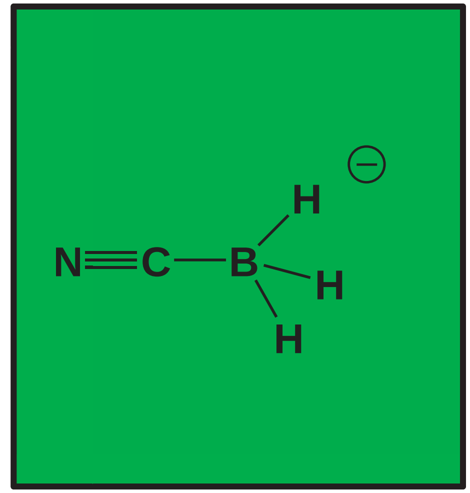
decomposition onset ~ 150°C

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

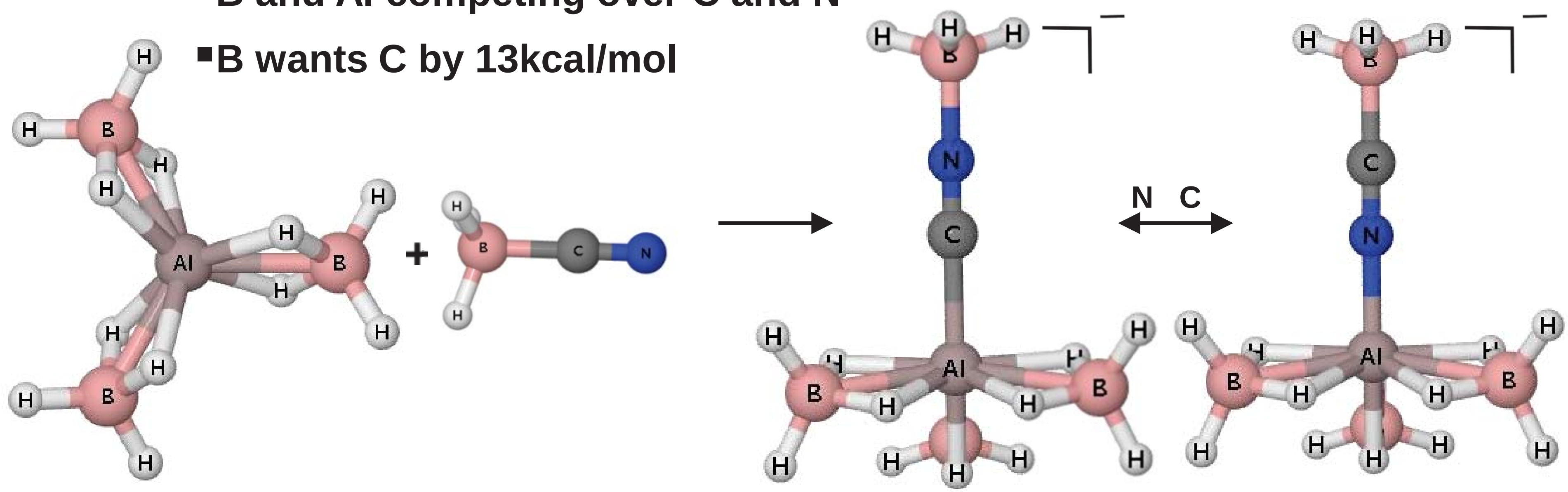
~ 99% more H than LH_2/mL

Anion Alteration

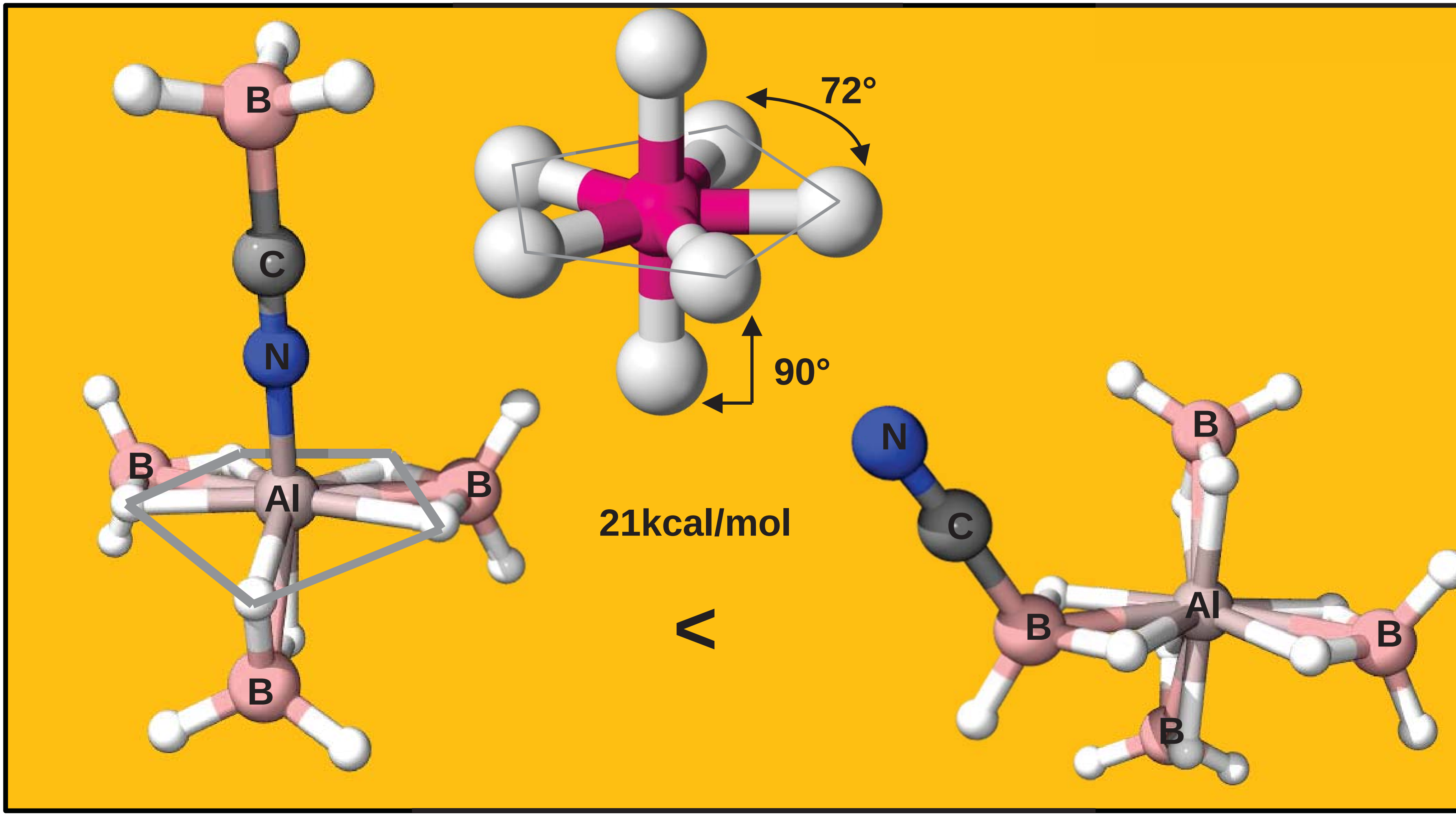




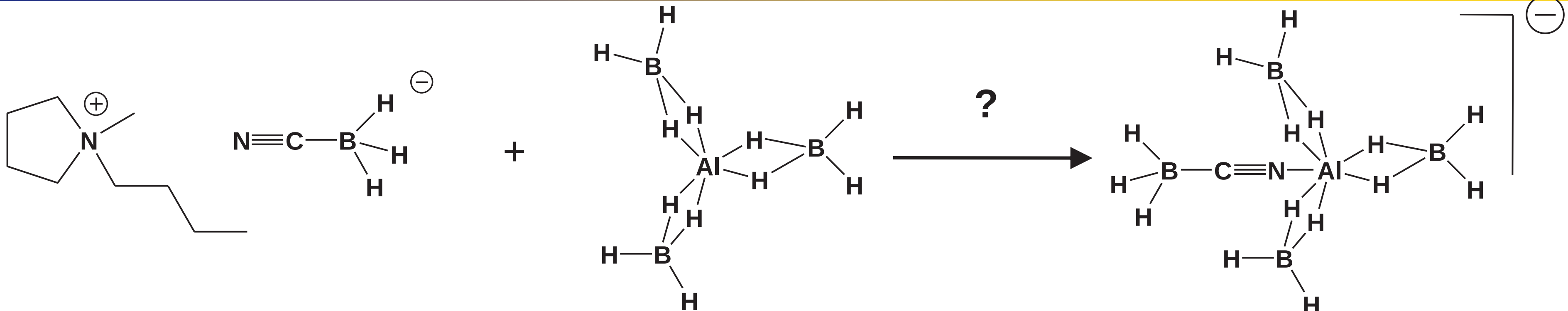
- B and Al competing over C and N
- B wants C by 13kcal/mol

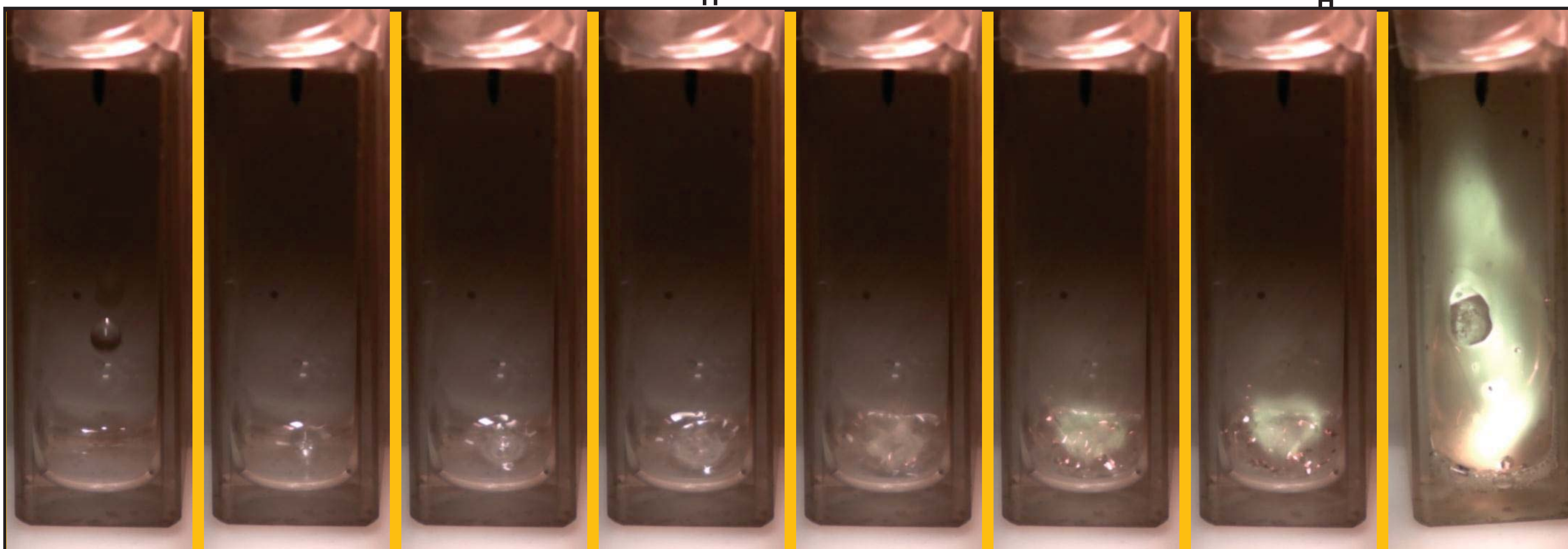


Cyanoborohydride coordination



Methyl butyl pyrrolidinium CBHABH

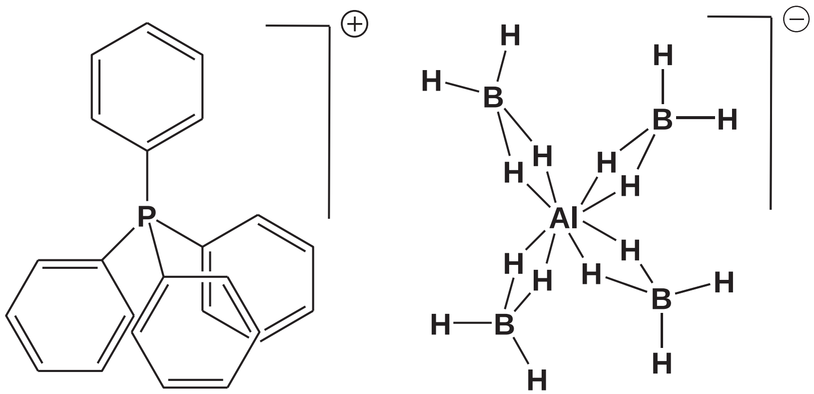


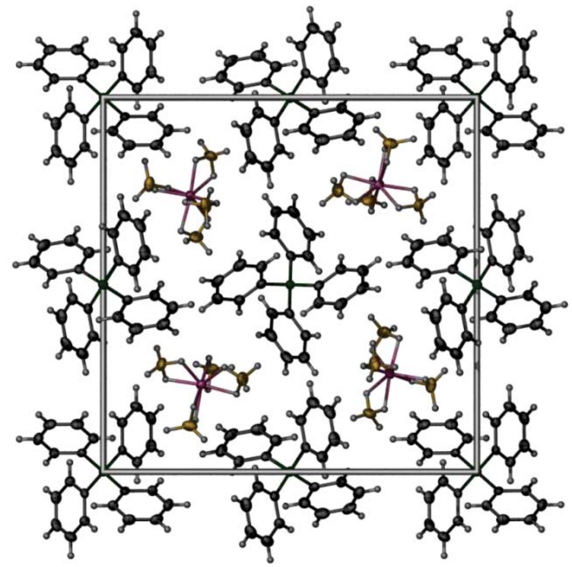


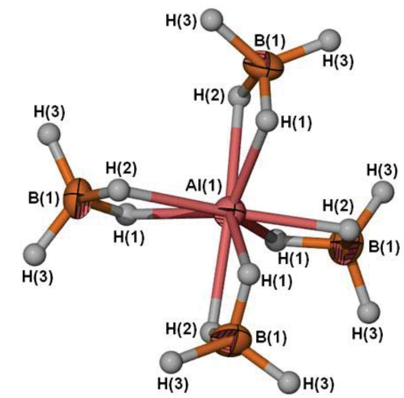
t = -14 | t = 0 | t = 1 | t = 2 | t = 3 | t = 4 | t = 5 | t = 76 ms

Oxidizer 90% H_2O_2

Surprise!
tetrakis(tetrahydroborato)aluminates



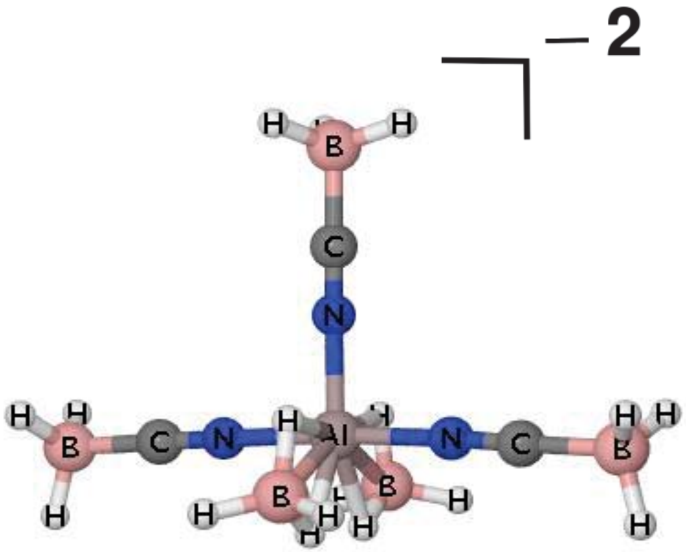


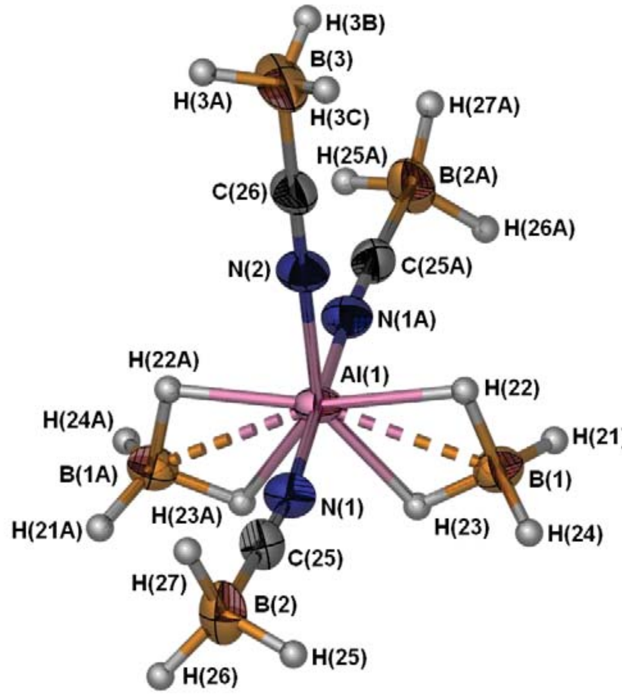


$BH_3CN^- + Al(BH_4)_3 \longrightarrow BH_4^- + Al(BH_4)_2BH_3CN$

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

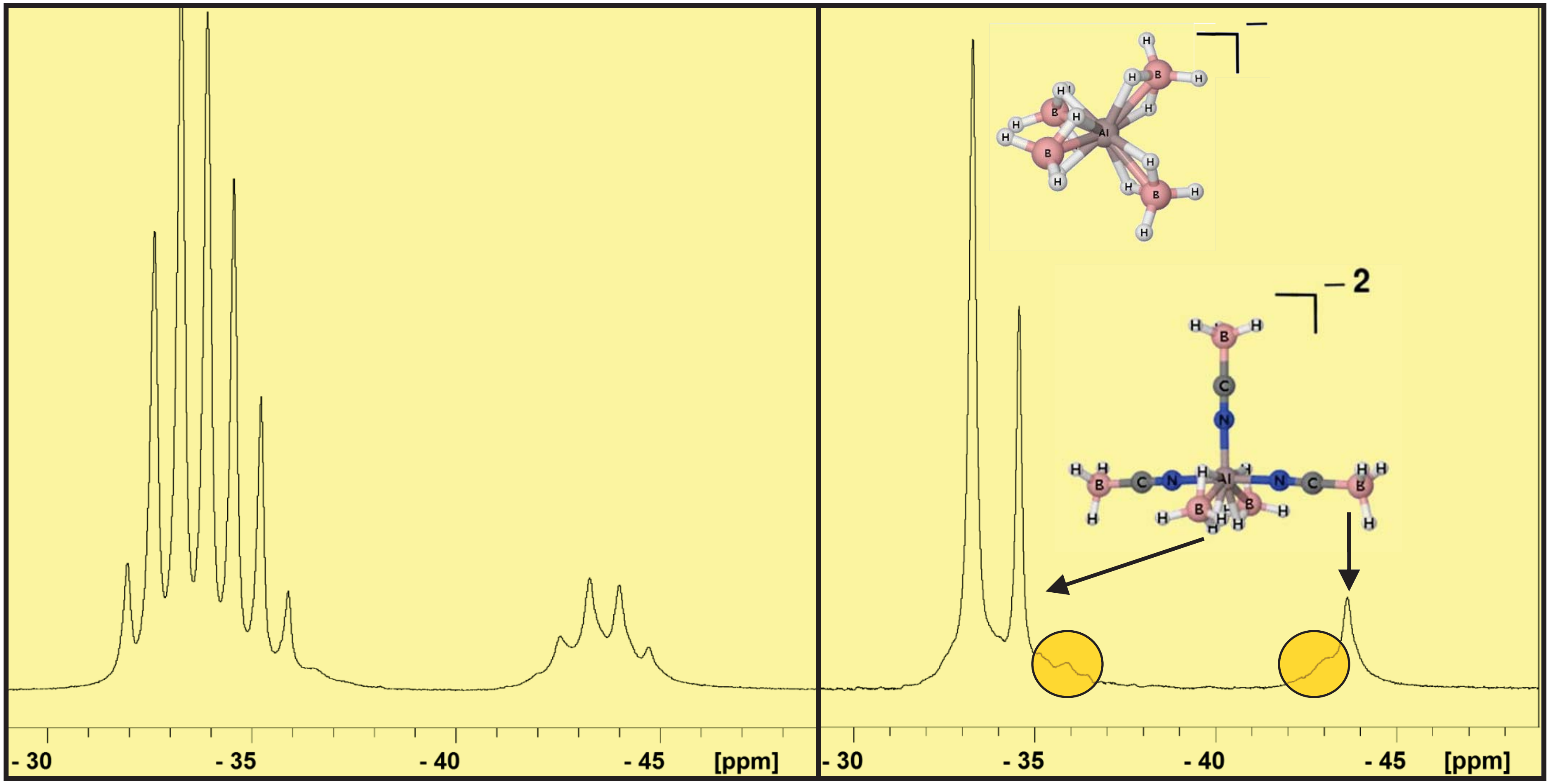
What happened to $Al(BH_4)_2BH_3CN$?



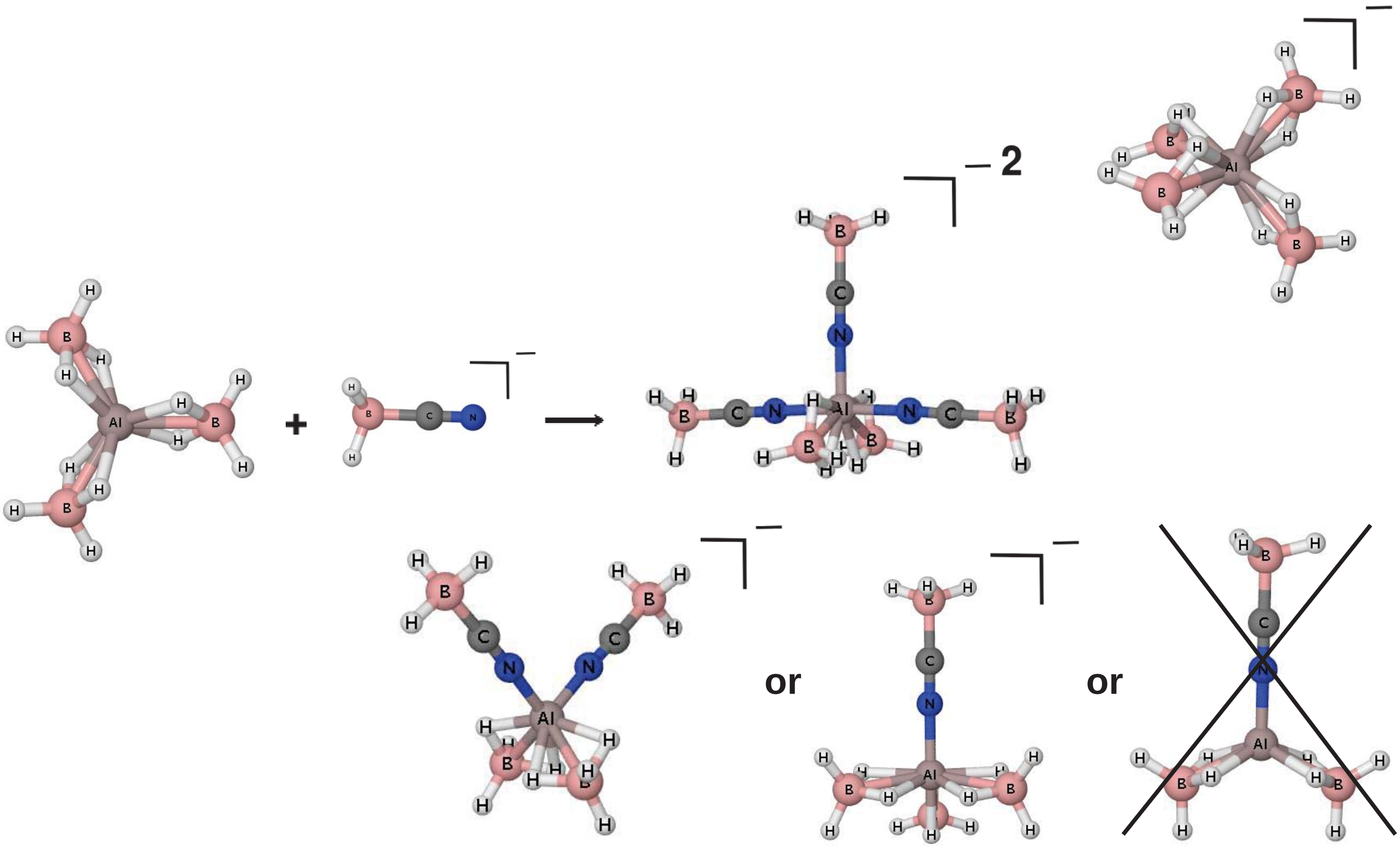


$BH_3CN^- + Al(BH_4)_3$	$\longrightarrow$	$BH_4^- + Al(BH_4)_2BH_3CN$
$BH_4^- + Al(BH_4)_3$	$\longrightarrow$	$Al(BH_4)_4^-$
$Al(BH_4)_2BH_3CN + 2\ BH_3CN^-$	$\longrightarrow$	$Al(BH_4)_2(BH_3CN)_3^{2-}$
$3\ BH_3CN^- + 2\ Al(BH_4)_3$	$\longrightarrow$	$Al(BH_4)_4^- + Al(BH_4)_2(BH_3CN)_3^{2-}$

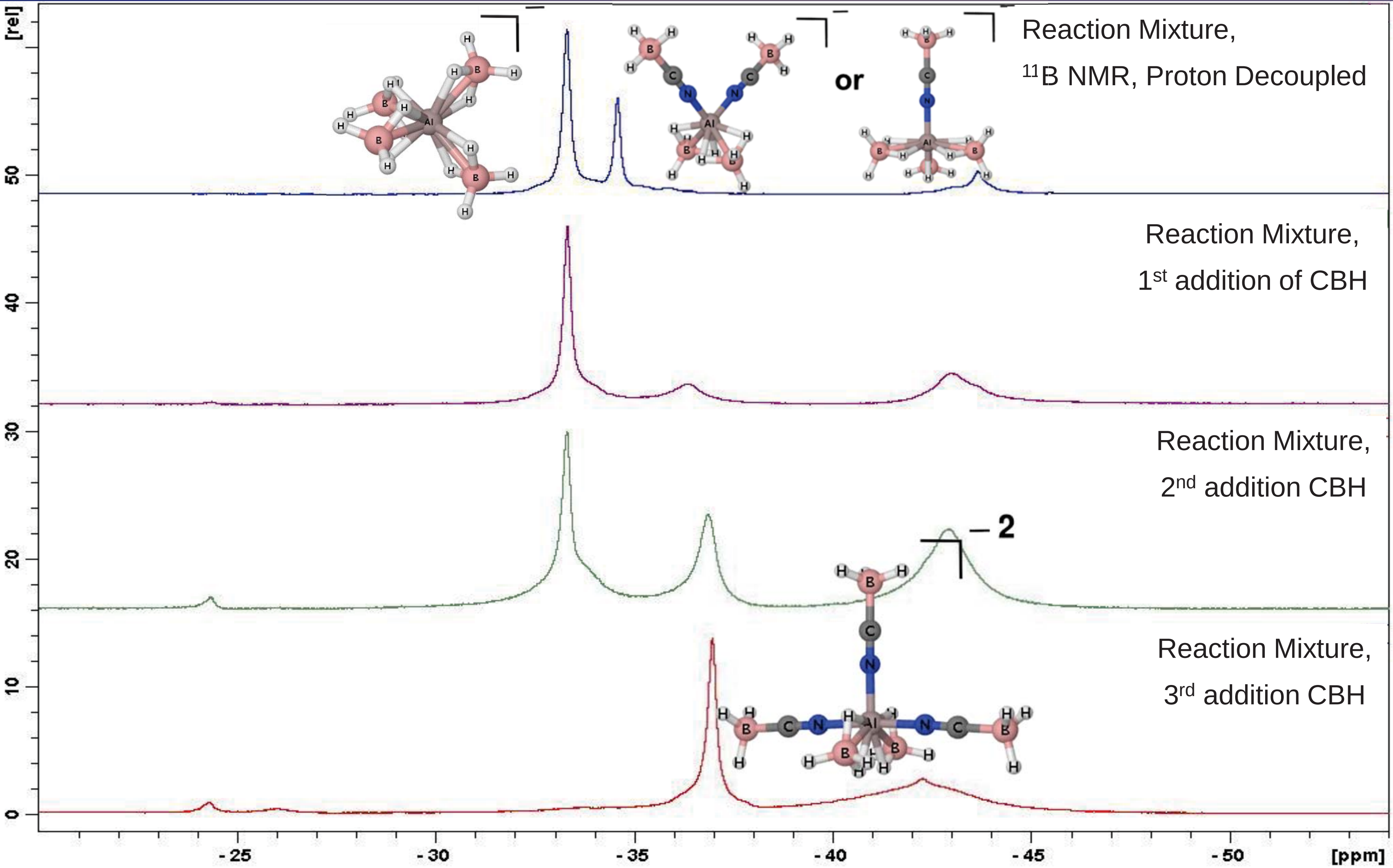
11B NMR of reaction mixture



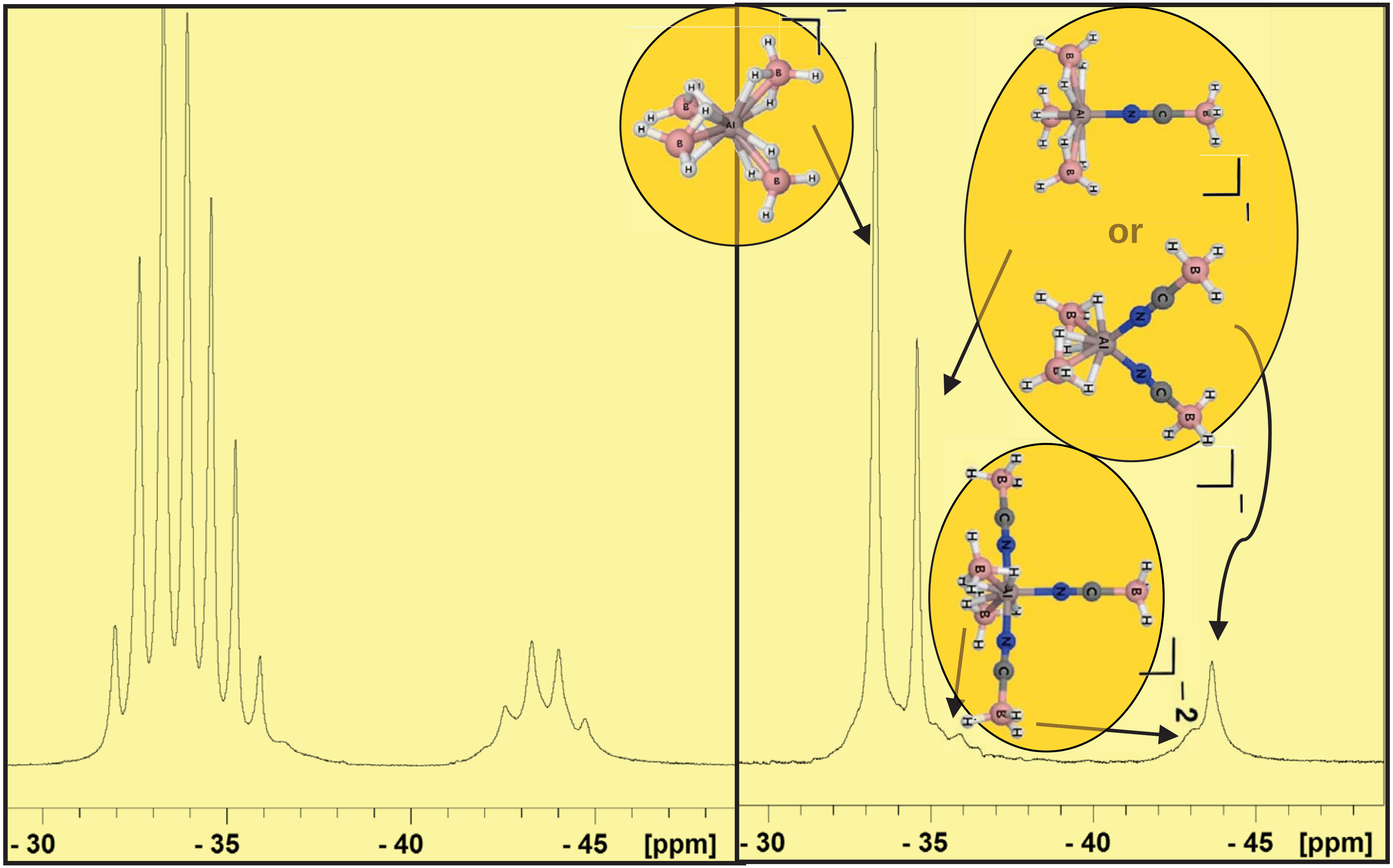
Maybe Chemistry is more complicated



Spiking reaction mixture with CBH



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**

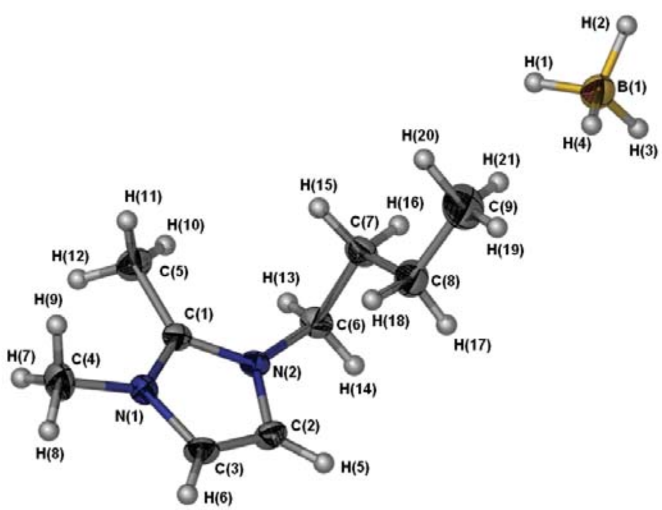
Lack of heterocyclic BH_4 salts

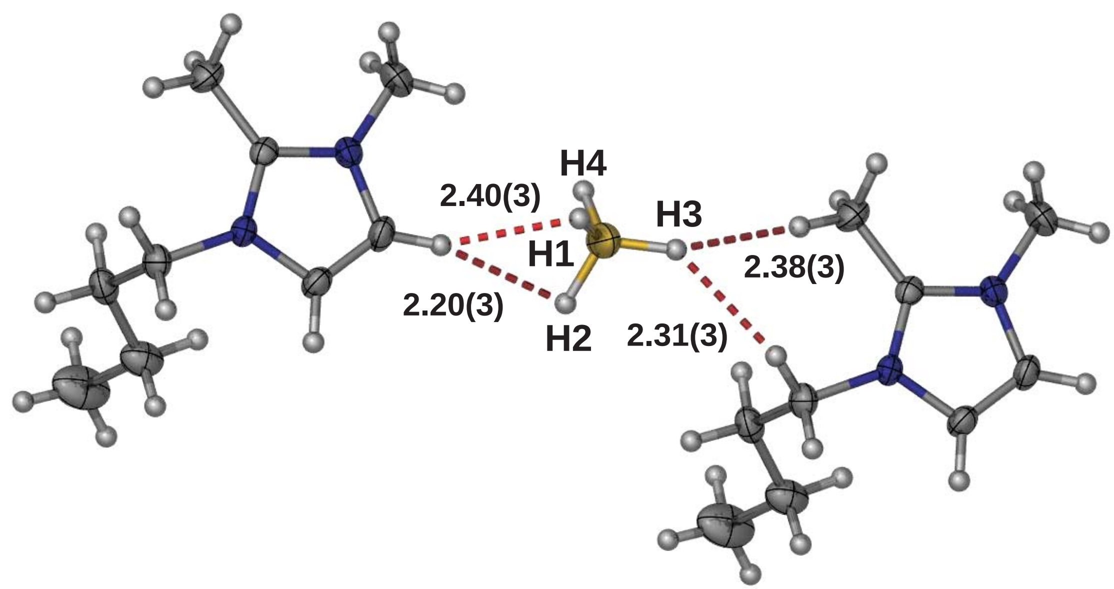
- **Published routes to BMIM BH_4 used IL halide in acetonitrile or CH_2Cl_2**
- **This work could not be reproduced and only yielded material with substantial halide content**

  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**





Summary and Conclusion

PARTICLE FREE COMBUSTION

- **Search for cationic structures, who allow for fast, hypergolic ignition with common oxidizers independent of the accompanying anion continues.**

METAL HYDRIDES

- **Aluminumborohydride is a rich scaffold for new complexed anions**
- **The reactivity of aluminum borohydride is not easily predictable**
- **New synthetic routes to heterocyclic BH_4 salts open new possibilities**

- **The clearly extensive design space of *IONIC LIQUIDS* carries the hope for new liquid propellant fuels which can meet and beat todays hydrazines.**

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