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14. ABSTRACT

The low vapor toxicity of ionic liquids (ILs) make them attractive replacements for hydrazine in rocket applications. However, ILs will fail to fulfill their revolutionary promise unless toxic oxidizers like HNO_3 or N_2O_4 can be replaced with safer alternatives. By their very nature all rocket oxidizers are hazardous and so reducing those hazards, even though the resulting materials might not be completely harmless, is at the heart of green initiatives in propulsion. The corrosivity of nitric acid is well known and while N_2O_4 is much less corrosive it combines high toxicity with high vapor pressure. A significant step to a lower toxicity bipropulsion system would be the demonstration of hypergolicity (spontaneous ignition) between an IL and a safer oxidizer. Outside of cryogens high performing hydrogen peroxide seems to be especially promising, with its less toxic vapor and corrosivity and its environmentally benign decomposition products. Up to now, no IL has been reported to be hypergolic with H_2O_2. Design strategies for prospective ILs are discussed.

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Green Hypergolics

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Green Hypergolic Bipropellants: H_2O_2 / Hydrogen-Rich Ionic Liquids**

Stefan Schneider, Tom Hawkins, Yonis Ahmed, Michael Rosander, Jeff Mills and Leslie Hudgens*

While today's rocket propulsion community strives for environmental friendliness, low toxicity and overall operability, it also seeks to maintain a performance level comparable with current propellant combinations like hydrazine and N_2O_4. Keeping performance high, while lowering hazards is extremely difficult.

By their very nature all rocket oxidizers are hazardous and so reducing those hazards, even though the resulting materials might not be completely harmless, is at the heart of green initiatives in propulsion. The corrosivity of nitric acid is well known and while N_2O_4 is much less corrosive it combines high toxicity with high vapor pressure. A significant step to a lower toxicity bipropulsion system would be the demonstration of hypergolicity (spontaneous ignition) between an ionic liquid (IL), a paragon of low vapor toxicity, and a safer oxidizer. Outside of cryogens high performing hydrogen peroxide seems to be especially promising, with its less toxic vapor and corrosivity and its environmentally benign decomposition products[1] which make handling the oxidizer considerably less difficult than N_2O_4 or nitric acid.

On the fuel side, high performance can be fostered by light metals with large combustion energies and relatively light products. Elements with considerable performance advantages and non-toxic products are aluminum and boron. High hydrogen content fulfills the need for light combustion products through the production of hydrogen gas and water vapor. Aluminum and boron are well known for their ability to serve as hydrogen carriers in neutral and ionic molecules. Defense research in the 1960's focused extensively on the development of hydrogen-containing fuels with boron, aluminum and other metals[2] but was mainly concerned with neutral compounds which have profound vapor toxicity. Their rich anionic chemistry combined with the design flexibility of ILs presage novel materials having the potential to overcome problems which caused these promising propellants to be abandoned.

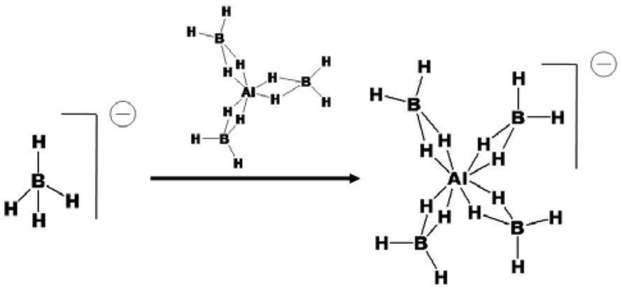
Up to now, no IL has been reported to be hypergolic with H_2O_2 and first generation hypergolic ILs based on dicyanamide, nitrocyanamide and azide anions lack high hydrogen content.[3] We tested ILs from each class with 90% and 98% H_2O_2 and all failed to ignite. This is hardly surprising since fuels hypergolic with nitric acid vastly outnumber those igniting with N_2O_4 and for a long time hydrazine was the only fuel hypergolic with H_2O_2.[4]

Since solutions of Li-Al hydrides and $LiBH_4$ in ethers have demonstrated H_2O_2 hypergolicity,[5] one might expect the same from ILs with metal hydride anions. However, developing energetic room temperature ILs (RTILs) with metal hydride anions bears a number of technical challenges. Simple metal hydride anions are poor liquefying agents. Furthermore, heterocyclic, unsaturated salts featuring imidazolium, triazolium, pyridinium and other common IL cations, are reduced by BH_4^-,[6] negatively affecting their thermal stability.

Thus, saturated ammonium/heterocyclic cations might be better candidates for RTIL metalhydrides and indeed there are two patents involving quaternary ammonium aluminum hydrides.[7] Examples included tri-octyl-n-propyl ammonium AlH_4^- (mp. 65-66°C) and tri-octyl-methyl ammonium AlH_4^- (viscous liquid). While these data are tantalizing, a cation that yields a stable, free-flowing RTIL with a simple metal hydride might not be easily found.

Another approach to liquefying metalhydrides is to replace hydrogen atoms with other groups. 1-butyl-2,3-dimethylimidazolium cyanoborohydride (CBH) is reported to be a low viscosity IL.[8] We prepared a variety of new CBH ILs and Shreeve *et al.* prepared novel dicyanoborohydrides (DCBH) ILs.[9] While all of them are fast igniting with nitric acid, our tests with CBH ILs and H_2O_2 revealed excessive ignition delays of several seconds. Since we also obtained negative results with 1-butyl-3-methyl-imidazolium $B(CN)_4$ it is probable that DCBH ILs are equally unsuitable.

Yet another approach would be to combine an IL with aluminum borohydride (ABH) to form complex anions like $Al(BH_4)_4^-$ (Scheme 1). Tetrabutyl ammonium (TBA) $Al(BH_4)_4^-$, has a melting point of 50°C, 75°C lower than the uncomplexed borohydride.[10] Noeth *et al.* reported tri-octyl-n-propyl ammonium $Al(BH_4)_4^-$ as a "viscous oil crystallizing very slowly."[11]



Scheme 1. Generic method for preparing ABH-containing anions.

In view of the advantages of high hydrogen content, RTILs containing $Al(BH_4)_4^-$ anions may be viewed as a densified form of hydrogen stabilized by metal atoms. The volumetric hydrogen contents of tetraethylammonium- (TEA) and TBA-$Al(BH_4)_4$[10] are 99% and 68% higher than that of liquid hydrogen.

Here we report on our first efforts to prepare RTIL borohydrides with subsequent conversion to $Al(BH_4)_4^-$ RTILs and the reactivity of both toward oxidizers including hydrogen peroxide.

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[**] The authors gratefully acknowledge the Air Force Office of Scientific Research, Dr. M. Berman and Dr. M. Gembicky Bruker AXS Inc. for helping refining the X-ray data

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

We repeated a published preparation of TEA $Al(BH_4)_4^-$,[10] a solid with a decomposition point of 150°C, obtaining its X-ray crystal structure for the first time. (Figure 1).

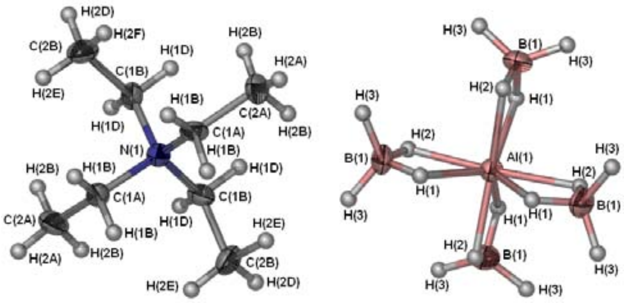
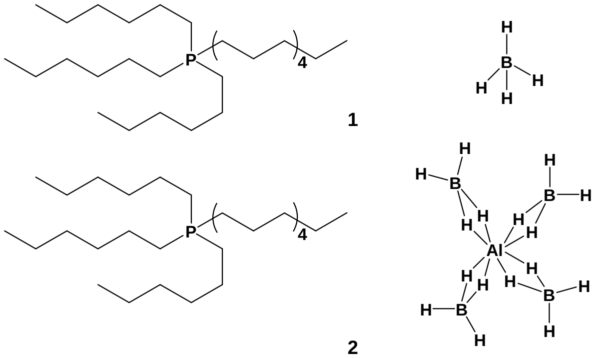


Figure 1. ORTEP diagram of the cation and anion of TEA $Al(BH_4)_4$ (Disorder removed for clarity).

The trihexyl-tetradecyl-phosphonium (THTDP) cation has been used to transform fullerenes into RTILs and forms liquids with BH_3Cl^-.[12, 13] THTDP Cl is also soluble in most organic solvents, enabling facile, quantitative anion exchange of Cl^- for BH_4^- and making this cation an appealing component for our initial research. The new material THTDP BH_4 (**1**) is a viscous RTIL and was characterized by NMR and Raman spectroscopy. Subsequent reaction with a slight excess of ABH produced, in quantitative yield, the first RTIL (**2**) incorporating a $Al(BH_4)_4^-$ anion (Scheme 2). (**2**) is colorless and free-flowing (Figure 2) and was characterized by NMR and Raman spectroscopy, mass balance and hydrogen analysis.



1

2

Scheme 2. Novel borohydride ILs (**1**) (top), (**2**) (bottom).

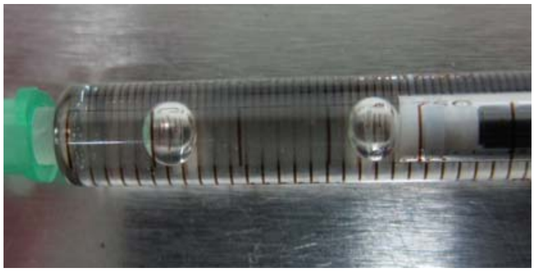


Figure 2. A 250μL syringe filled with (**2**) (Note two air bubbles)

Vibrational spectroscopy proved especially useful as the cation and anion stretch vibrations do not overlap and the ν_{BH} of (**1**) are easily distinguished from those of (**2**) (Figure 3).

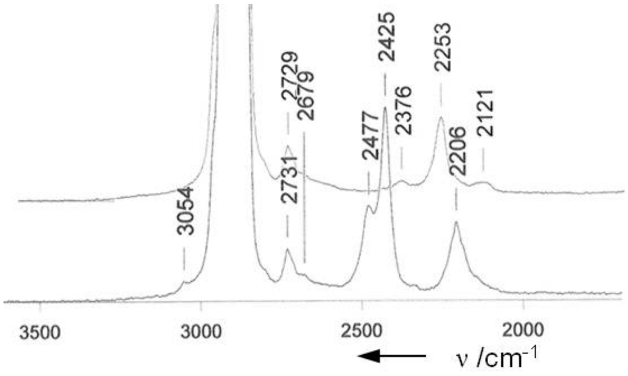


Figure 3. Raman spectra of (**1**) (upper) and (**2**) (lower) (only ν_{CH} and ν_{BH} region is shown).

These new materials were then subjected to drop tests to determine their reactivity with common propulsion oxidizers including 90% and 98% H_2O_2 (Table 1). While (**1**) dropped onto H_2O_2 only lights after 3s the ignition delay of (**2**) was quite short. Additionally, in contrast to hypergolic dicyanamide ILs that display changes in delay times (WFNA) from 30ms to 1000ms upon reversal of oxidizer and fuel, ignition of (**2**) is equally fast either way.

Table 1. Drop test results of (**2**) on four oxidizers (N_2 atmosphere) [a]

Fuel\Oxidizer	90%H_2O_2	98%H_2O_2	N_2O_4	WFNA[c]
(**2**)	Ignition	Ignition	Ignition	Explosion
Ignition Delay	< 30ms	< 30ms	-[b]	-

[a] for details see supplemental material [b] IL ignited with N_2O_4 vapors before liquids combined [c] White Fuming Nitric Acid

These simple drop tests only place upper limits on the ignition delays because ignition may be initiated by hydrogen, which burns with a nearly invisible flame. However, these tests do demonstrate that a RTIL with a complex ABH anion is universally reactive with traditional rocket oxidizers including lower hazard H_2O_2. Furthermore, this new class of ILs holds the potential for enabling high-performing, non-cryogenic, green bipropulsion for the first time.

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[1] J.J. Rusek, N. Anderson, B.M. Lormans, N.L. Purcell, US Patent 5932837, **1999**

[2] A. Dequasie, in *The Green Flame*, American Chemical Society, Washington DC, **1991.**

[3] a) S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau, G. Drake, *Energy Fuels* **2008**, *22*, 2871-2872; b) H. Gao, Y.-H. Joo, B. Twamley, Z. Zhou, J. M. Shreeve, *Angew. Chem.* **2009**,

121, 2830-2833; *Angew. Chem. Int. Ed.* **2009**, *48*, 2792-2795; Y. Zhang, H. Gao, Y. Guo, Y.-H. Joo, J. M. Shreeve, *Chem. Eur. J.* **2010**, *16*, 3114-3120; c) L. He, G. Tao, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2010**, 16, 5736-5743; d) Y. H. Joo, H. Gao, Y. Zhang, J. M. Shreeve, *Inorg. Chem.* **2010**, *49*, 3282-3288.

[4] J. D. Clark, *Ignition! An Informal History of Liquid Rocket Propellants*, Rutgers University Press, New Brunswick, **1972**.

[5] 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**.

[6] a) T. Isida, T. Akiyama, N. Mihara, S. Kozima, K. Sisido, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1250-1253; b) E.F. Godefroi, *J. Org. Chem.* **1968**, *33*, 860-862.

[7] a) R. Ehrlich, US Patent, 3417119, **1968**; b) A.A. Hinckley, US Patent 3072698, **1963**.

[8] H. Schottenberger, G. Bentivoglio, M. Rauch, W. Porcham, G. Winkler, G. Nauer, R. Krendelsberger, H.-P. Martinz, Patent WO2006053362, **2006**.

[9] a) S. Schneider, T. Hawkins, M. Rosander, Y. Ahmed, J. Mills, *Prepr. Symp. - Am. Chem. Soc., Div. Fuel Chem.***2010**, *55*, 158; b) Y. Zhang, J. M. Shreeve, *Angew. Chem.* **2011**, *123*, 965-967; *Angew. Chem. Int. Ed.* **2011**, *50*, 935-937.

[10] L.V.Titov, L.A. Gavrilova, E.R. Eremin, S.S. Mishchenchuk, V.Y. Rosolovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.***1971**, *6*, 1354-1356 and references cited therein.

[11] H. Noeth, M. Ehemann, *Chem. Commun.* **1967**, *14*, 685-686.

[12] R.E. DelSesto, C.A. Corley, D.S. Dudis, A.T. Yeates, J.S. Wilkes *ECS Trans.* **2007**, *3*, 33-39.

[13] T. Ramnial, M.K. Hauser, J.A.C. Clyburne, *Aust. J. Chem.* **2006**, *59*, 298-301.

Green Hypergolics

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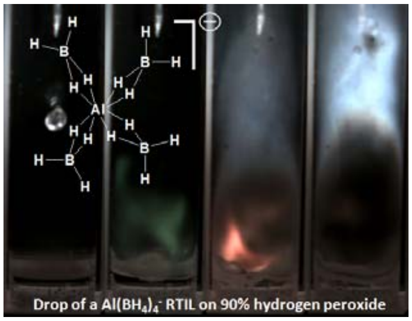
Green Hypergolic Bipropellants: H_2O_2 / Hydrogen-Rich Ionic Liquids



Drop of a $Al(BH_4)_4^-$ RTIL on 90% hydrogen peroxide

The low vapor toxicity of ionic liquids (ILs) make them attractive replacements for hydrazine in rocket applications. However, ILs will fail to fulfil their revolutionary promise unless toxic oxidizers like HNO_3 or N_2O_4 can be replaced with safer alternatives. H_2O_2 has long been considered as such but until now no suitable ILs were available. The ILs presented here are hypergolic with H_2O_2 and hydrogen rich, helping to boost performance.

Supporting Information

Green Hypergolic Bipropellants: H_2O_2 / Hydrogen-Rich Ionic Liquids**

Stefan Schneider,* Tom Hawkins, Yonis Ahmed, Michael Rosander, Jeff Mills and Leslie Hudgens

Experimental Section.

Caution! Aluminumborohydride is highly volatile and highly pyrophoric. While no accidents or mishaps occurred during work with this material extreme care should be taken handling aluminumborohydride and its solutions. Handling of high concentration hydrogenperoxide (>90%) should also only be attempted after receiving specific safety training from the supplier. Proper protective measures (safety shields, face shields, leather gloves, and protective clothing such as heavy leather welding suits) should be used at all times. Ignoring safety precautions can lead to serious injuries!

General. Starting materials, trihexyltetradecyl-phosphonium chloride, sodium borohydride (≥99%), lithium borohydride (purum, ≥95.0%), n-propyl amine, dichloromethane (anhydrous, ≥99.8%), toluene (anhydrous, 99.8%), Celite® and WFNA (puriss. p.a., ACS reagent, fuming, ≥99.5%) were purchased from Aldrich Chemical Company, Inc. and were used without further purification. Aluminumborohydride was prepared according to a literature procedure.[1] Ampules of deuterated solvents were purchased from Cambridge Isotope Laboratories Inc.. 90% and 98% H_2O_2 were obtained from FMC Peroxygens and NO_2 from MATHESON. Nonvolatile solids and liquids were handled in the dry nitrogen atmosphere of a glovebox. The ^{1}H and ^{13}C, spectra were recorded on a 400 MHz Ultrashield™ spectrometer at room temperature with samples dissolved in CD_2Cl_2 or $CDCl_3$ using 5mm NMR tubes. The ^{1}H and ^{13}C spectra were referenced to external/internal samples of TMS. ^{11}B and ^{31}P NMR spectra were referenced to $[BF_3(OEt_2)]$ and 85% H_3PO_4 respectively. Raman spectra were recorded in the range 4000-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. 5mm glass NMR tubes were used as sample containers. Decomposition onsets were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 Differential Scanning Calorimeter. Measurements were carried out at a heating rate of 10°C/min in sealed aluminum pans with a nitrogen flow rate of 20mL/min. The reference sample was an empty Al container which was sealed in the nitrogen atmosphere of a glove box. Elemental analyses were performed out on a PerkinElmer 2400 Series II CHNS/O elemental analysis instrument equipped with S2AD6 Autobalance.

Trihexyltetradecyl-phosphonium borohydride (1). In a one neck round bottom flask sodium borohydride (0.48g, 12.69mmol) was dissolved in 25mL of n-propyl amine and the clear solution was transferred into a flame dried Schlenk flask containing a teflon coated stir bar. To this, a solution of trihexyltetradecyl-phosphonium chloride (5.00g, 9.63mmol) in propyl amine (25mL) was added and the resultant white suspension was stirred for 12-16h at ambient temperature. The reaction mixture was concentrated and the residue diluted with dichloromethane (50-70mL). The dichloromethane suspension was stirred for 15-30min, filtered through celite and concentrated leaving behind a colorless hygroscopic oil. Yield 3.60g, 75%; melting point (peak): +5°C; decomp. onset +95°C; Raman (500mW, 25°C, cm^{-1}) ν = 2927(88), 2894(100), 2874(98), 2854(64), 2729(11), 2375(4), 2253(15), 2121(3), 1441(17), 1369(3), 1305(11), 1219(3), 1175(3), 1115(4), 1078(6), 1065(6), 1031(4), 967(3), 892(6), 872(6), 849(6), 735(3), 671(6), 404(4), 185(8), 121(12), 86(68); ^{1}H NMR (CD_2Cl_2, 400 MHz), δ[ppm] 2.34 - 2.27 (m, 8H), 1.53 – 1.29 (m, 48H)), 0.95-0.89 m, 12H), 0.15–(-)0.46 (m, 4H, J = 82Hz, BH_4); ^{13}C NMR (CD_2Cl_2, 100 MHz), δ[ppm] 31.90, 31.04, 30.85, 30.71, 30.53, 30.38, 29.67, 29.63, 29.53, 29.34, 29.31, 28.92, 22.67, 22.35, 21.75, 21.71, 19.34, 18.87, 13.88, 13.72; ^{31}P NMR (CD_2Cl_2, 162 MHz), δ[ppm] 36.6; ^{11}B NMR (CD_2Cl_2, 128 MHz), δ[ppm] -38.2 (quintet, J = 82 Hz, BH_4); Found: C, 76.38; H, 13.82; N, 0.14. Calc. for $C_{32}H_{72}B_1P_1$: C, 77.07; H, 14.55; N 0.00.

Trihexyltetradecyl-phosphonium tetrakis(tetrahydroborato)aluminate (2). 4.14g (8.22mmol) of (1) were dissolved in 8.80g of dry toluene. The solution was transferred into a flame dried Schlenk flask and connected to a glass vacuum line. 1.03g of aluminum borohydride (10.79mmol) together with an additional 80.20g of dry toluene were condensed to the frozen solution of (1) at -196°C. The mixture was allowed to warm to ambient temperature agitated multiple times and kept overnight. All volatiles were removed in a dynamic vacuum with gentle heating up to 45°C. The volatiles were collected in a cold trap and weighed after warm up. A total of 89.25g were recovered indicating a quantitative uptake of aluminumborohydride by (1). 4.93g of a clear, colorless, free-flowing, hygroscopic liquid were left behind; decomp. onset >150°C; Raman (500mW, 25°C, cm^{-1}) ν = 3053(3), 2934(79), 2904(100), 2874(74), 2858(73), 2731(8), 2679(4), 2477(15), 2425(30), 2338(3), 2206(12), 1617(1), 1592(1), 1441(18), 1411(4), 1344(3), 1311(8), 1266(3), 1211(1), 1171(4), 1114(4), 1077(4), 1065(4), 1029(3), 1002(4), 970(3), 893(4), 875(4), 847(4), 807(3), 741(1), 669(4), 440(12), 243(6), 165(9), 121(12), 86(64); ^{1}H NMR ($CDCl_3$, 400 MHz), δ[ppm] 2.12 -2.05 (m, 8H), 1.52 – 1.26 (m, 48H)), 0.93 - 0.86 (m, 28H, with overlapping $(BH_4)_4$ signal); ^{13}C NMR ($CDCl_3$, 400 MHz), δ[ppm] 31.94, 30.90, 30.68, 30.54, 30.35, 30.20, 29.71, 29.67, 29.63, 29.51, 29.38, 29.26, 28.82, 22.71, 22.30, 21.60, 21.56, 19.25, 18.78, 14.15, 13.92; ^{31}P NMR ($CDCl_3$, 162 MHz), δ[ppm] 37.0; ^{11}B NMR ($CDCl_3$, 128MHz), δ[ppm] -32.8 (quintet, J = 85 Hz, BH_4)

A hydrogen analysis of (**2**) was carried out similar to the procedure described in [1]. Three separate samples of 489, 518 and 524mg were hydrolyzed with water in a closed vacuum system. A sample was placed in a glass Schlenk vessel equipped with a Kontes-style valve and connected to a glass vacuum line. From a second vessel water was then condensed to the reaction vessel at liquid nitrogen temperature. The mixture was allowed to warm to ambient temperature. Assuming that any gas produced was H_2 that came from the hydrogens in the $Al(BH_4)_4$ anion, the measured pressure and the volume of the vacuum system were used to calculate the molar quantity of H_2. Found: 15.7 per mole (**2**); calculated: 16.0 mole.

X-ray Analyses. The single-crystal X-ray diffraction data were collected on a Bruker 3-circle-platform diffractometer equipped with a SMART APEX 2 detector with the χ-axis fixed at 54.74° and using CuK_α radiation from a fine-focus tube. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. The data collection as well as structure solution and refinement were carried out using standard procedures with the APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, and SHELXTL software packages and programs.[2] Crystal data and refinement details of crystals of TEA $Al(BH_4)_4$ are given in Table 1. Crystallographic data are also available in CIF-format.

[1] J.-C. Zhao, D.A. Knight, G.M. Brown, C. Kim, S.-J. Hwang, J.W. Reiter, R.C. Bowman Jr., J.A. Zan, J.G. Kulleck *J. Phys. Chem.* **2009**, *113*, 2-11.

[2] APEX2 V.2.1-4, SMART V.5.622, SAINT 7.24A, SADABS, SHELXTL ed.; Bruker-AXS, INC.: Madison, WI USA, 2007.

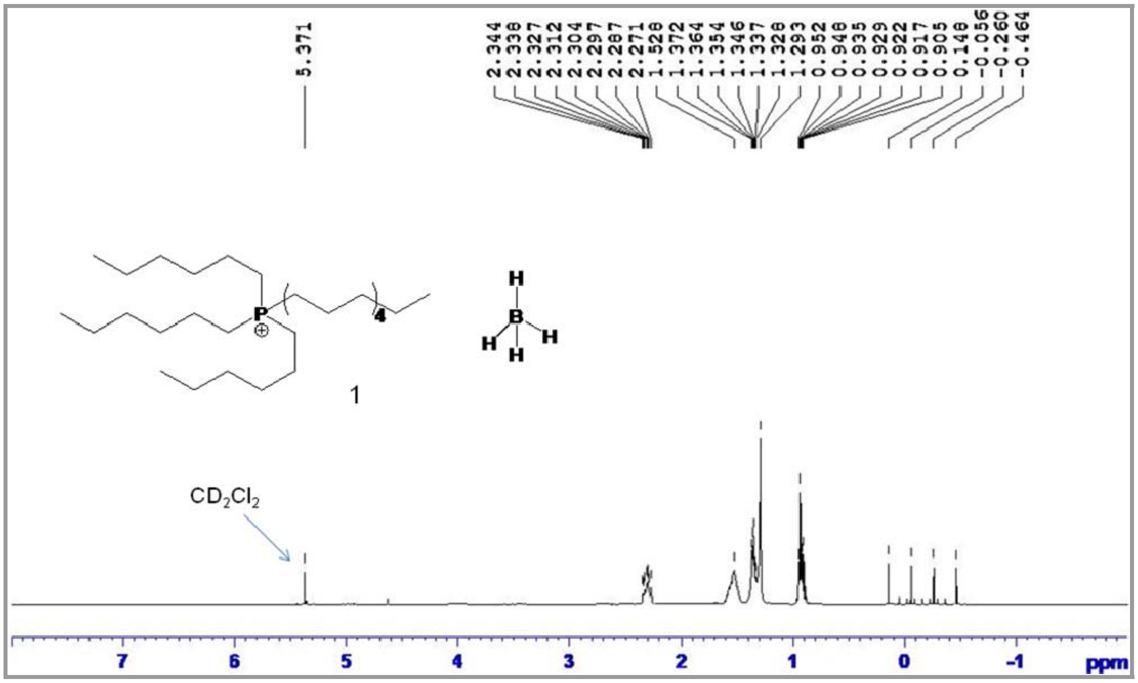


Figure S1. ^{1}H NMR of (1) in CD_2Cl_2.

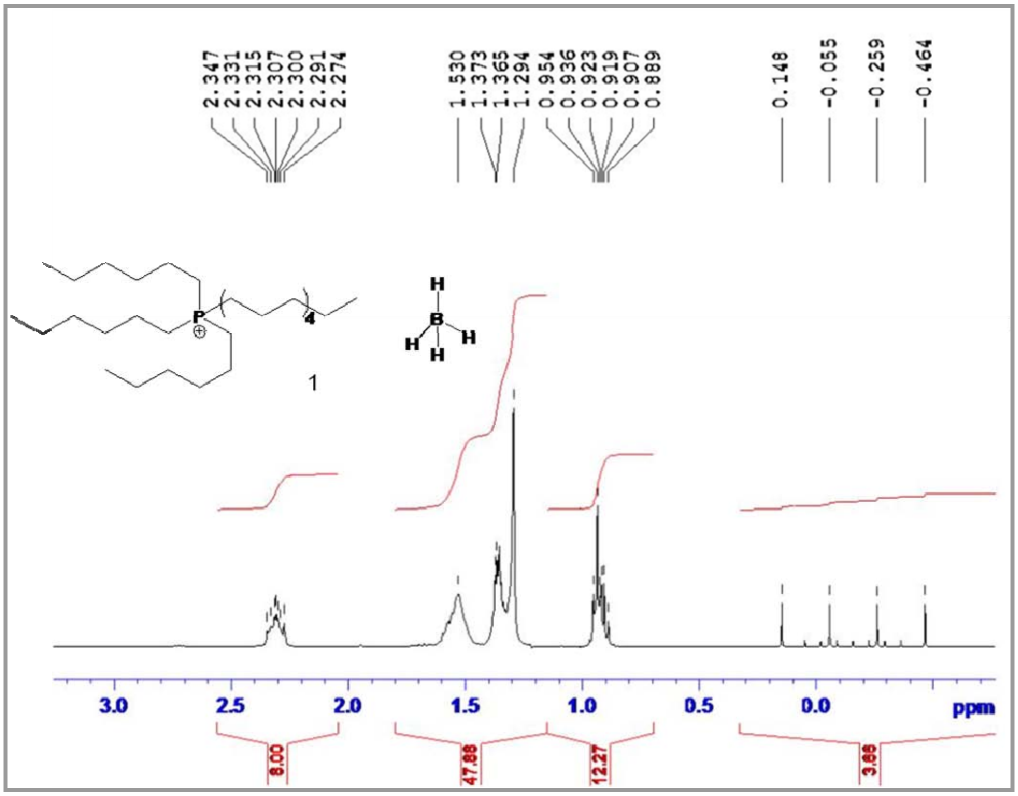


Figure S2. ^{1}H NMR of (1) in CD_2Cl_2 (expanded).

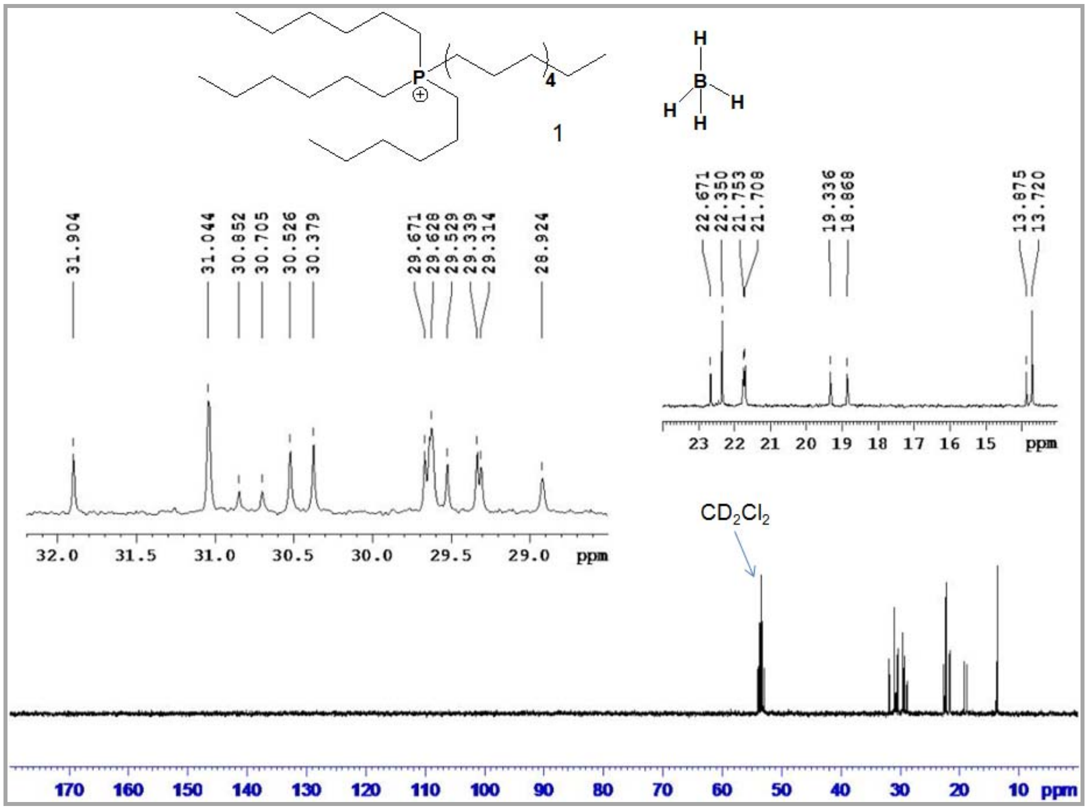


Figure S3. ^{13}C NMR of (1) in CD_2Cl_2.

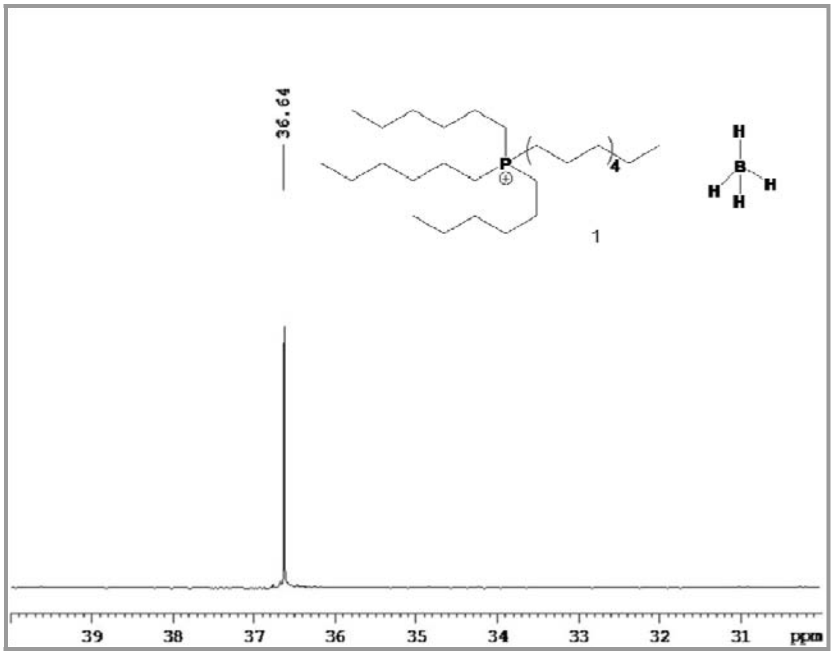


Figure S4. ^{31}P NMR of (1) in CD_2Cl_2.

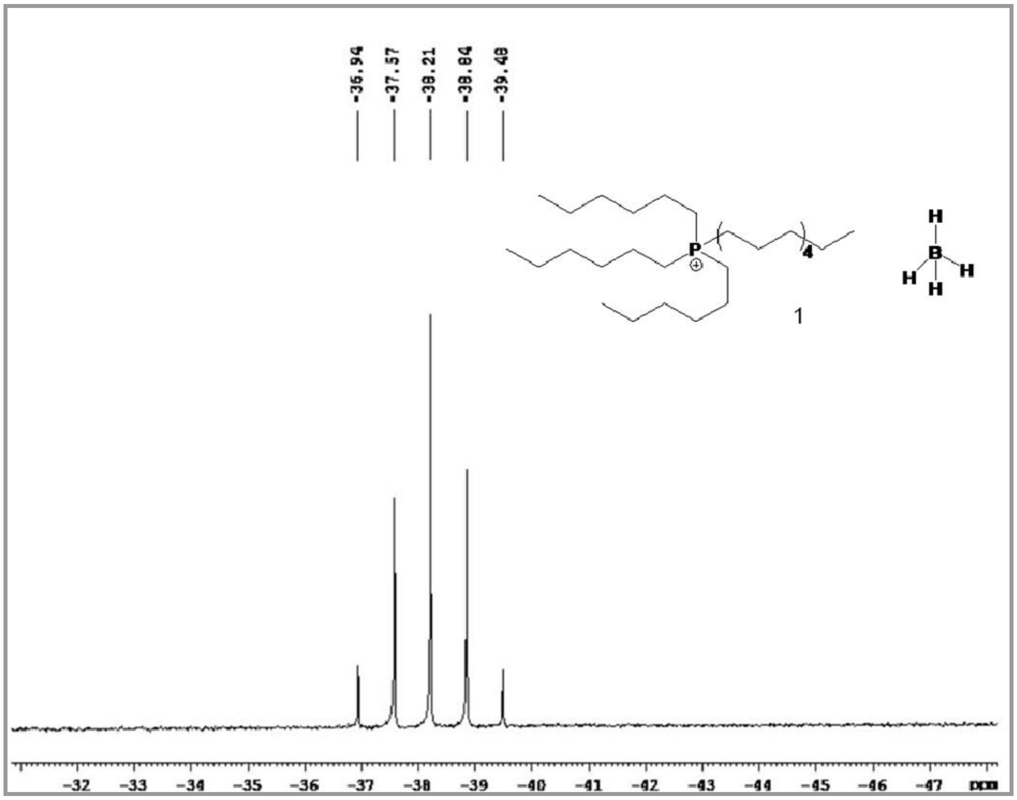


Figure S5. ^{11}B NMR of (1) in CD_2Cl_2.

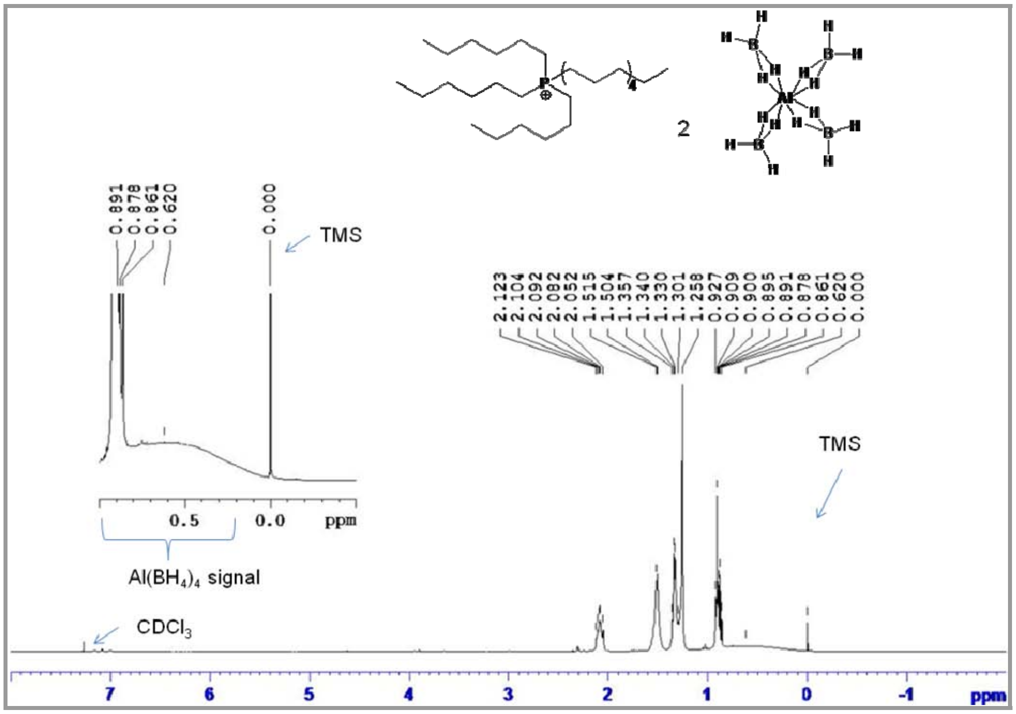


Figure S6. ^{1}H NMR of (2) in CDCl$_3$.

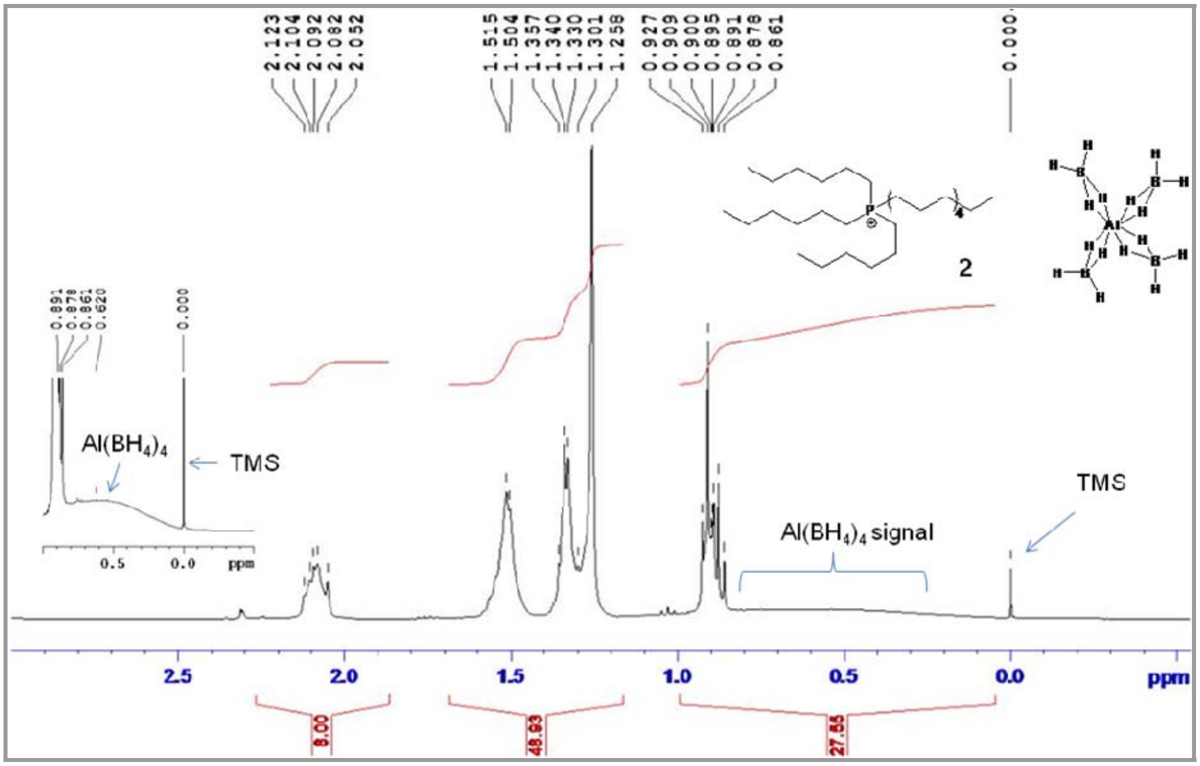


Figure S7. ^{1}H NMR of (2) in CDCl$_3$ (expanded).

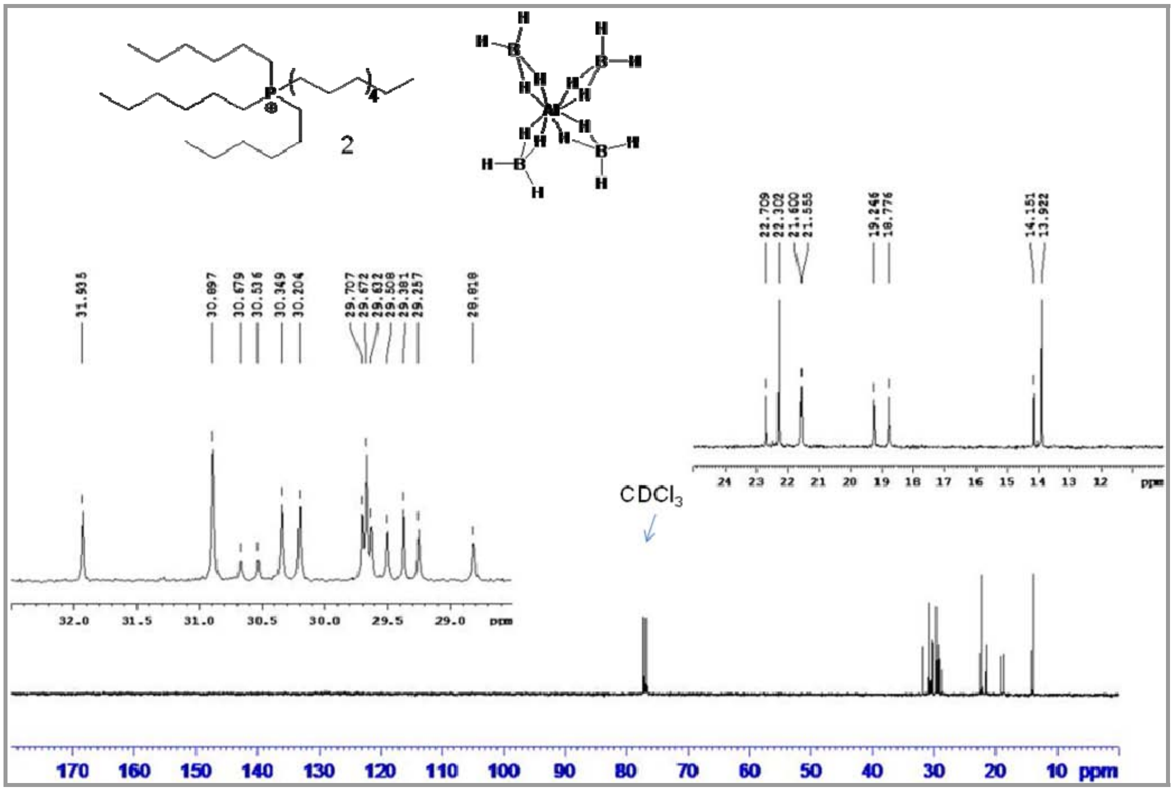


Figure S8. ^{13}C NMR of (2) in CDCl$_3$.

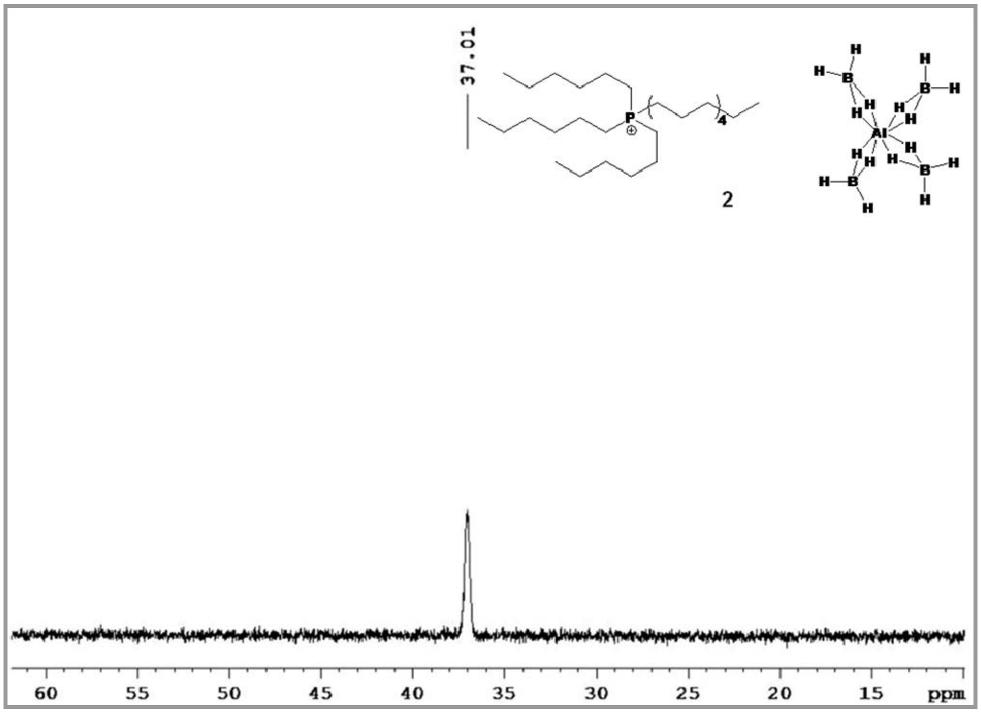


Figure S9. ^{31}P NMR of (2) in CDCl$_3$.

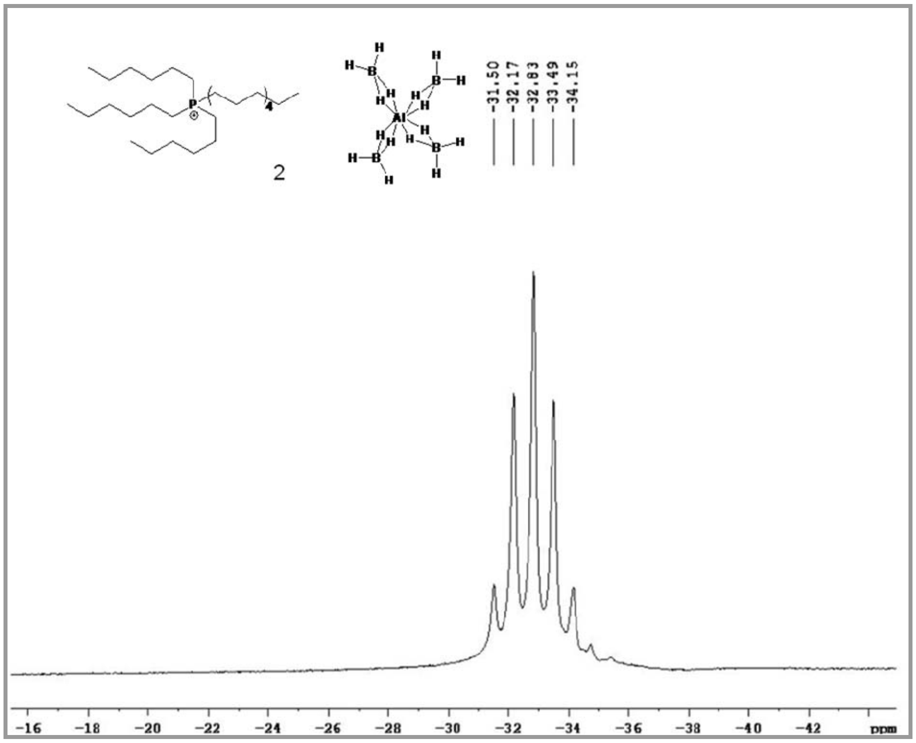


Figure S10. ^{11}B NMR of (2) in $CDCl_3$.

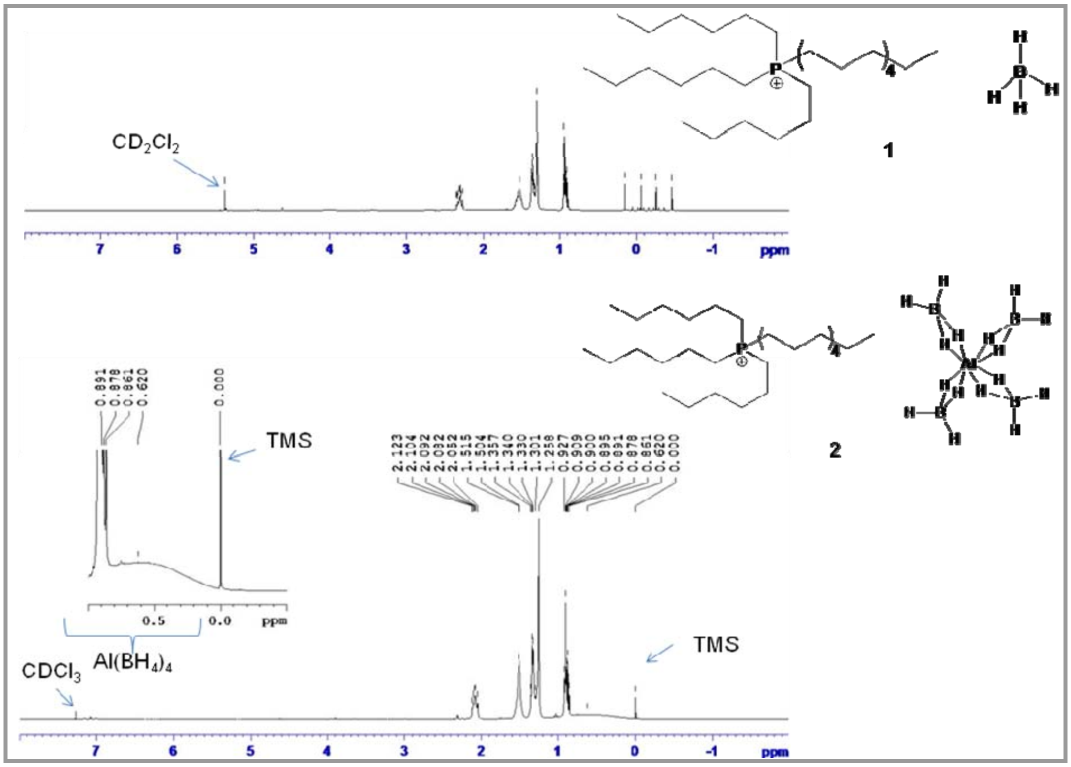


Figure S11. ^{1}H NMR of (1) in CD_2Cl_2 and ^{1}H NMR of (2) in $CDCl_3$ for direct comparison.

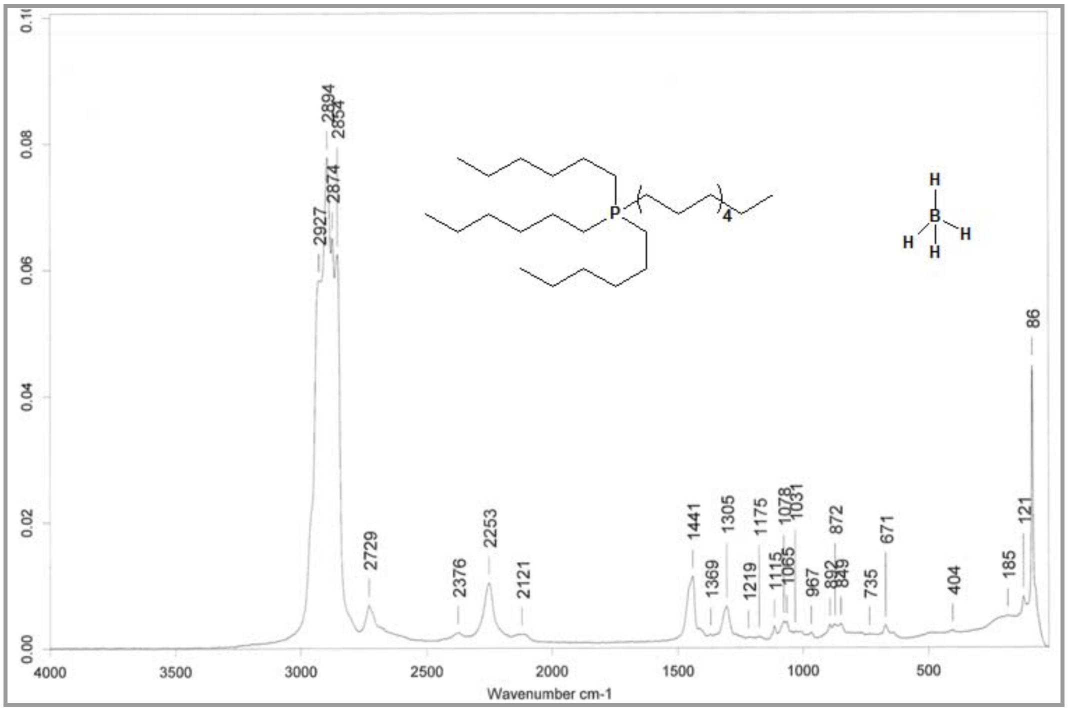


Figure S12. Raman of (**1**); clear colorless liquid; 5mm NMR tube; 500mW; 1000 scans.

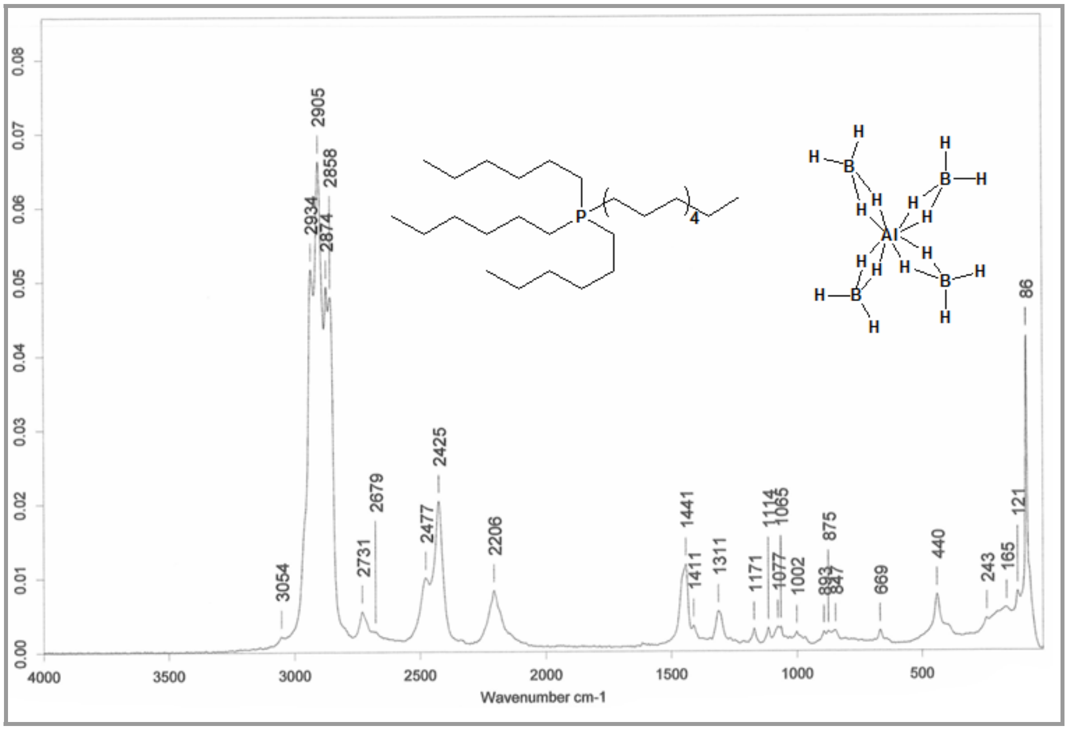


Figure S13. Raman of (2); clear colorless liquid; 5mm NMR tube; 500mW; 1000 scans.

Table S1 Crystal and structure refinement data for TEA $Al(BH_4)_4$**.**

	TEA $Al(BH_4)_4$
Formula	$C_8H_{36}Al_1B_4N_1$
Space group	P_4/nmm tetragonal
a (Å)	12.0311(2)
b (Å)	12.0311(2)
c (Å)	5.8672(1)
α, β, γ(°)	90
$V/Å^3$	849.26(2)
$\rho_{calc.}/g\ cm^{-3}$	0.847
Z	2
Formula weight	216.60
μ/mm^{-1}	0.778
Temperature (K)	173(2)
λ(CuKα)	1.54178
Crystal size	0.20 x 0.15 x 0.10
Theta range θ/°	5.20 to 71.63
Index range	$-14\leq h\leq 13$, $-14\leq k\leq 14$, $-6\leq l\leq 7$
Reflection collected	6610
Independent [R(int)]/	492 [0.0356]
Obs. refl. ([I > 2.0 σ(I)])	446
F(000)	248
GooF	1.171
R_1, wR [I > 2σ(I)]	0.0318, 0.0818
R_1, wR_2 (all data)	0.0351, 0.0842
L.diff. peak/hole $eÅ^3$	0.17 and -0.15
Absorption correct.	multiscan SADABS
T_{min}, T_{max}	0.860, 0.926
Data/restraints/param.	492/0/52
Refinement method	Full-matrix least squares on F^2

$R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{½}$

CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/ data_request/cif.

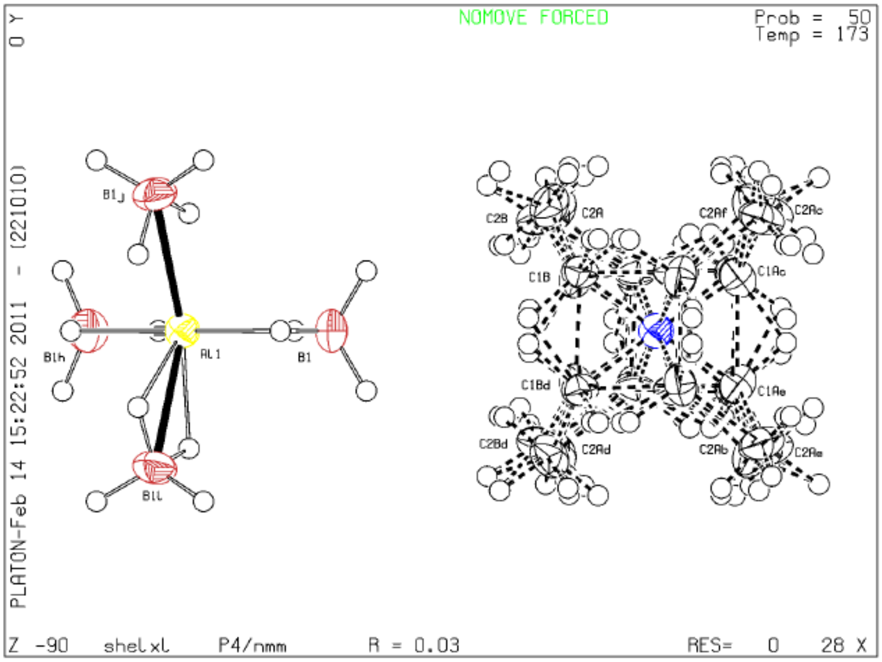


Figure S14. ORTEP diagram showing conformation and atom numbering scheme of the individual cation and anion present in the asymmetric unit of TEA $Al(BH_4)_4$.

Table S2. Drop test results of selected IL dicyanamides, nitrocyanamides and azides on oxidizer.

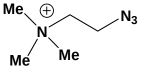
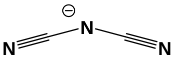
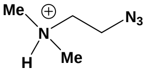
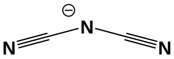
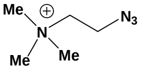
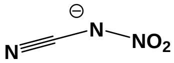
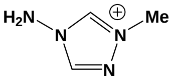
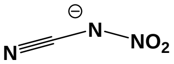
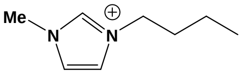
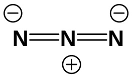
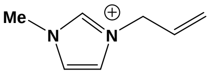
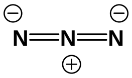
cation	anion	90% H_2O_2	98% H_2O_2
		No ignition	No ignition
		No ignition	No ignition
		No ignition	No ignition
		No ignition	No ignition
		No ignition	No ignition
		No ignition	No ignition

Table S3. Drop test results of selected IL cyanoborohydrides, tetracyanoborohydrides and (**1**) on oxidizer.

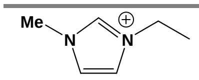
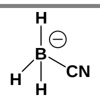
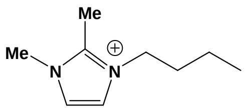
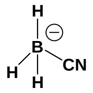
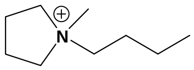
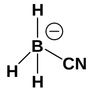
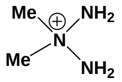
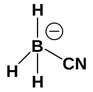
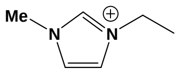
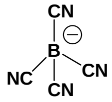
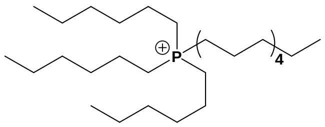
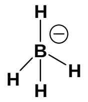
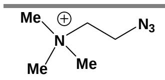
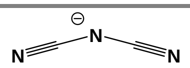
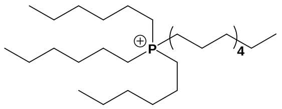
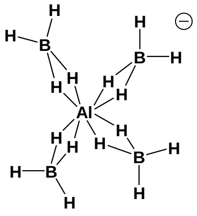
cation	anion	90% H_2O_2	98% H_2O_2
		> 1s	> 1s
		> 3s	> 3s
		> 3s	> 3s
		> 3s	> 3s
		No ignition	No ignition
		> 3s	> 3s

Table S4. Ignition delay times of selected fuel on oxidizer tests and reverse tests of oxidizer on fuel.

cation	anion	Fuel on WFNA	WFNA on Fuel	Fuel on 90%H_2O_2	90%H_2O_2 on Fuel
		~ 30ms	> 1s	No ignition	No ignition
		Explosion	Explosion	< 30ms	< 30ms

Additional material. 4 video files are uploaded for further consideration.

90H2O2onR4PABH.wmv	drop of 90% H_2O_2 on (**2**)
R4PABHon90H2O2.wmv	drop of (**2**) on 90% H_2O_2
R4PABHonNTO.wmv	attempt to drop (**2**) on liquid N_2O_4
R4PABHonWFNA.wmv	drop of (**2**) on WFNA

The hygroscopic nature of (**2**) required samples to be prepared inside the dry atmosphere of a glove box. Oxidizer or fuel (**2**) (250μL used) was placed in a cuvette (1cm x 1cm x 3cm) and the counterpart was loaded into a 250μL syringe with a 21G needle. Cuvettes were then sealed with Parafilm®. Cuvettes were placed in a sample holder and the syringe was attached to a syringe pump. The syringe was lowered until the needle tip pushed through the Parafilm®. Flowrates were either 0.03 mL/min or 0.13mL/min. High speed movies were recorded with a Redlake, MotionPro® Y-series 3 camera at 1000frames/s. Ignition delay times were determined by counting the frames between the droplet first hitting the surface and the sign of the first visible flame.

In case of N_2O_4 the first material exiting the syringe needle immediately reacted with N_2O_4 vapors which filled the entire cuvette. Instead of a clean drop this led to a slowly growing "stalactite" with a continuously forming partially oxidized outer crust and liquid material in the core. Finally ignition occurred between the liquid fuel and the oxidizer vapors.