# Cleaner Propellants

# Towards Safer Rocket Fuels: Hypergolic Imidazolylidene-Borane Compounds as Replacements for Hydrazine Derivatives

Shi Huang,<sup>[a]</sup> Xiujuan Qi,<sup>[b]</sup> Tianlin Liu,<sup>[a]</sup> Kangcai Wang,<sup>[a]</sup> Wenquan Zhang,<sup>[a]</sup> Jianlin Li,<sup>[c]</sup> and Qinghua Zhang<sup>\*[a]</sup>

**Abstract:** Currently, toxic and volatile hydrazine derivatives are still the main fuel choices for liquid bipropellants, especially in some traditional rocket propulsion systems. Therefore, the search for safer hypergolic fuels as replacements for hydrazine derivatives has been one of the most challenging tasks. In this study, six imidazolylidene-borane compounds with zwitterionic structure have been synthesized and characterized, and their hypergolic reactivity has been

# Introduction

With the rapid development of aerospace technologies, various chemically-propelled rockets have been invented and applied for space exploration over the past decades.<sup>[1–3]</sup> In some liquid rocket engines that are still in use today, hydrazine and its derivatives are still widely used as the chemical propulsion fuels in some bipropellant systems. However, these hydrazine derivatives are acutely toxic, highly volatile, carcinogenic substances and consequently have high handling costs. Against such a context, there is increasing demand in developing greener and safer rocket fuels as replacements for hydrazine derivatives.<sup>[4,5]</sup> Thus, exploring safer hypergolic fuels has become an area of intense research.

In recent years, a new concept of hypergolic liquids (HILs) has emerged and shown great promise as relatively greener rocket fuels owing to their unique properties including low vapor pressure, high thermal stability, high density, and ultrafast ignition delay (ID) times, etc.<sup>[6-11]</sup> These properties can well

studied. As expected, these compounds exhibited fast spontaneous combustion upon contact with white fuming nitric acid (WFNA). Among them, compound **5** showed excellent integrated properties including wide liquid operating range (-70-160 °C), superior loading density (0.99 g cm<sup>-3</sup>), ultrafast ignition delay times with WFNA (15 ms), and high specific impulse (303.5 s), suggesting promising application potential as safer hypergolic fuels in liquid bipropellant formulations.

satisfy the requirement of developing safer liquid hypergolic fuels. For instance, Schneider et al. and Shreeve et al. described several imidazolium dicyanamide (DCA) and nitrocyanamide (NCA) HILs and studied their hypergolic reactivity with the white fuming nitric acid (WFNA).<sup>[12,13]</sup> These hypergolic ionic liquids exhibited relatively routine ignition performance, for example, their ID times were commonly longer than 30 ms. In order to achieve superior hypergolic reactivity, a wide variety including [BH<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup>,<sup>[14]</sup> of borohydride-rich anions  $[BH_{3}CN]^{-,[15]} \ [BH_{4}]^{-,[16]} \ [BH_{3}(CN)BH_{2}(CN)]^{-,[17]} \ and \ [Al(BH_{4})_{4}]^{-,[18]}$ have been developed and used for the construction of new high-performance HILs (Figure 1). As expected, these borohydride-rich HILs showed significantly enhanced ID performance and most examples gave the ID times of <20 ms with WFNA as the oxidizer. However, the majority of them suffered from the problem of poor water stability due to the high reactivity of their anions. Although it has been demonstrated that introducing two cyano groups into the borohydride structure can



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significantly improve anionic water stability (e.g. [BH<sub>2</sub>(CN)<sub>2</sub>]<sup>-</sup> and [BH<sub>3</sub>(CN)BH<sub>2</sub>(CN)]<sup>-</sup>), the difficulty in synthesizing these cyano-rich borohydride salts decreases their practical application values.

Against this background, we tried to develop new hypergolic compounds with low ID times and good water stability as replacements for toxic hydrazine-based fuels. It is known that N-heterocyclic carbenes (NHCs) have received significant attention in the fields of both organometallic chemistry and catalysis.<sup>[19-22]</sup> Due to the lone pair of electrons on the carbon atom in the structure, NHCs are capable of combining the unoccupied orbital of borane (BH<sub>3</sub>) to form stable NHC-borane adducts. These NHC-borane compounds represent a new "clean" class of reagents with moderate reductive ability.<sup>[23]</sup> Due to their intrinsic reducing properties, violent exothermic redox reactions will occur when the NHC-boranes come into contact with strong oxidizers such as WFNA. In this violent process, gaseous reactive species (e.g., radicals, carbenes, etc.) may be produced, which easily initiate a spontaneous combustion. To the best of our knowledge, so far there are no examples of using NHC-borane compounds as safer hypergolic fuels in liquid bipropellants.

In our continuous efforts to develop safer hypergolic fuels, in this study six imidazolylidene-borane compounds were synthesized in moderate yields, and their hypergolic reactivity with the oxidizer of WFNA was investigated. As shown in Scheme 1, the imidazolium halides can be readily synthesized



Scheme 1. Synthesis of imidazolylidene-borane compounds.

according to literature methods,<sup>[24,25]</sup> followed by reactions with sodium borohydride in toluene. Six imidazolylideneborane compounds were obtained (1-6) in moderate yields ranging from 63-76%. In these NHC-borane compounds, the {BH<sub>3</sub>} moiety is directly connected to the 2-position of imidazolylidene. More importantly, all these NHC-borane compounds showed expected hypergolic reactivity upon contact with WFNA as the oxidizer, demonstrating their potential application as safer hypergolic fuels or additives in liquid bipropellant formulations.

# **Results and Discussion**

Except for compound 1 with a melting point of 141°C, the other five imidazolylidene-borane compounds (2-6, Scheme 1) showed relatively low melting points of <50°C and three compounds with unsymmetrical substituents (3, 4, and 5) are liquids at room temperature ( $T_q = -70$  °C). All these new NHCborane compounds were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, IR, elemental analysis, and ESI-HRMS, etc. The characterization data support the expected structure and their high purities (see the characterization data and NMR spectra in the Supporting Information).

#### Structural analysis

The X-ray crystallographic analysis shows that 1 crystallizes in the monoclinic space group  $P2_1/m$  (no. 11) with lattice parameters: a = 7.1421(7), b = 7.0068(10), c = 7.2312(7) Å;  $\beta = 106.516(12)^{\circ}$ ; V = 349.86(4) Å<sup>3</sup>; Z = 2;  $\rho = 1.044$  g cm<sup>3</sup>. In its structural data, the bond length of C2-B1 is 1.596 Å. No typical hydrogen bonds are present in the molecule<sup>[26]</sup> (the crystallographic data are summarized in the Supporting Information). In addition, the structure of 1 was also simulated by theoretical computations. Electrostatic potential analysis (Figure 2a)



Figure 2. a) Electrostatic potential surfaces of compound 1 at the B3LYP/6-31+G (d,p) level, 0.004 electron/bohr isosurface, energy values -0.06172 to +0.06172H. Color coding: red, negative; green, neutral; blue, positive. b) Hirshfeld charges for 1 at the B3LYP/6-31 + G(d,p) level. The red and green of the ruler (from left to right) indicate regions of more negative and positive Hirshfeld charges, respectively.

reveals that there is obvious charge separation in this molecule, that is, the negative charge is assembled in the {BH<sub>3</sub>} moiety, whereas the positive region is delocalized around the imidazolium ring. The Hirshfield charge on the site of molecule was calculated by B3LYP/6-31+G (d, p).<sup>[27]</sup> From Figure 2b and Table S2 (Supporting Information), it has been clearly demonstrated that in the structure of 1, the {BH<sub>3</sub>} moiety possesses more negative charge (-0.456 e) and the imidazolium ring shows a more positive charge (0.456 e). In combination with the analysis of the electrostatic potential and Hirshfeld charge, it can be concluded that this class of NHC-boranes has typical characteristics of zwitterionic structures.

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## Thermal properties, density, and viscosity

Physicochemical properties of six imidazolylidene-boranes (1–6) were measured and studied. First, their thermal properties including melting point, glass transition temperature and thermal stability were measured and comparatively studied. From the viewpoint of practical applications, low melting points and high thermal decomposition temperatures make for ideal liquid fuels, while they can be safely stored and handled over a wide range of liquid operating temperatures. From Table 1, three compounds **3–5** are liquids at room tem-

Table 1. Physicochemical properties of imidazolylidene-borane.							
Entry	$T_{g}^{[a]}[^{\circ}C]$	$T_{d}^{[b]}[^{\circ}C]$	$\rho^{\rm [c]}[\rm gcm^{-3}]$	ற <sup>[d]</sup> [mPa]	$\Delta_{\rm f} H^{\rm [e]}[\rm kJmol^{-1}]$	ID <sup>[f]</sup> [ms]	<i>I</i> <sub>sp</sub> <sup>[g]</sup> [s]
1	141	188	1.0560	_	61.61	2	304.6
2	45	190	1.0274	-	29.06	100	200.5
3	-70	172	0.9604	29	8.30	35	308.1
4	-70	208	0.9273	31	-14.93	38	304.0
5	-70	160	0.9887	26	145.21	15	303.5
6	41	186	1.0280	-	-5.25	79	305.1
UDMH	-57	64 <sup>[h]</sup>	0.79	0.51	53.28	4.8	313.6

[a] Melting point/glass transition temperature. [b] Thermal decomposition temperature. [c] Density at 25 °C. [d] Viscosity at 25 °C. [e] Heat of formation. [f] Ignition-delay time with WFNA, 1 was tested as a solid. [g] Vacuum specific impulse (CEA400); pressure 0.95 MPa; area expansion ratio of nozzle 70; oxidizer N<sub>2</sub>O<sub>4</sub> (equivalence ratio = 1.0). [h] Boiling point.

perature with glass-transition temperatures ( $T_g$ ) of -70 °C, while compounds **1**, **2**, and **6** are solids at room temperature. The high melting points may be partly due to their structural symmetry or relatively short alkyl substituents on the imidazo-lium ring. Furthermore, their thermal stabilities were also evaluated. As shown in Table 1, compounds **1–6** showed high decomposition temperatures ( $T_d$ ) ranging from 160 to 208 °C, in which **4** gave the highest  $T_d$  value of 208 °C (Figure 3), while **5** showed the lowest  $T_d$  value of 160 °C. When compared to unsymmetrical dimethylhydrazine (UDMH,  $T_g = -57$  °C and b.p. = 64 °C), it is obvious that these imidazolylidene-borane compounds have a much wider liquid operating range and are therefore safe to operate.



Figure 3. TGA graph of 4.

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Density is an important indicator for evaluating the energy level of propellant fuels. In general, a fuel with higher density means higher loading capacity in the fuel tank and, therefore, higher energy contribution in the propulsion process. The densities of the six imidazolylidene-borane compounds ranged from 0.93 to  $1.06 \text{ g cm}^{-3}$ , which are much higher than the  $0.79 \text{ g cm}^{-3}$  of UDMH; this suggests that these imidazolylideneborane compounds as potential fuels have higher loading capacities than hydrazine-based fuels in propellant tanks. Among them, **1** had the highest density of  $1.06 \text{ g cm}^3$ , whereas **4** had the lowest density of  $0.93 \text{ g cm}^3$ . On the other hand, the

> low viscosity of hypergolic fuels is highly desirable for the mixing and mass-transfer operation with the oxidizer in the thrust chamber. Among these NHCborane compounds, three liquid compounds **3–5** exhibited relatively low viscosities ranging from 26– 31 MPa, in which **5** had the lowest viscosity (26 MPa).

## Water stability

For rocket fuels, water stability is very important for actual applications, including manufacture, storage, transportation, and ignition processes.<sup>[28,29]</sup> To our knowledge, the majority of known HILs with ultrafast ID times (e.g., <20 ms) have shown very poor water stability and typical examples include the  $[AI(BH_4)_4]^-$ based HILs.<sup>[18]</sup> and the  $[BH_4]^-$ -based HILs.<sup>[16]</sup> With sev-

eral exceptions, some [BH<sub>2</sub>CN<sub>2</sub>]<sup>-</sup>-based HILs reported by the Shreeve' group<sup>[14]</sup> showed both good hydrolytic stability and very short ID times. In this study, the water stability of these imidazolylidene-borane compounds was also evaluated. The NMR experiments have demonstrated that these compounds showed good water stability. For example, when 1 was dissolved and stored in deuterium oxide at room temperature for a month, no obvious chemical degradation was observed from the <sup>1</sup>H NMR spectra (Figure 4), providing convincing evidence for the high water stability of these compounds. This has also demonstrated that this imidazolylidene-borane framework can



**Figure 4.** Hydrolytic experiment of 1 by <sup>1</sup>H NMR: a) stored in deuterium oxide at room temperature for 30 min; b) stored in deuterium oxide at room temperature for a week; c) stored in deuterium oxide at room temperature for a month.

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play a role in stabilizing the  $\{BH_3\}$  moiety like the cyano group, thereby improving the water stability of  $\{BH_3\}$ -containing structures.

### Theoretical study

The enthalpy calculations were performed with the Gaussian 09 (Revision D.01) suite of programs.<sup>[30]</sup> The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using the B3LYP functional with the 6-31 + G (d,p) basis set.<sup>[31]</sup> Single-point energies were calculated at the MP2/6-311 + +G (d, p) level. Atomization energies for the molecules were obtained by the G2 ab initio method. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The isodesmic reactions (Scheme 2) were carried out to obtain the gas-phase heats of



Scheme 2. Isodesmic reactions for the HOFs calculation of imidazolylideneborane compounds.

formation of these boranes compounds. The solid-state enthalpy of formation for six NHC-borane compounds was calculated by subtracting the heat of sublimation from the calculated gas-phase heat of formation. Employing Trouton's rule, the heat of sublimation was calculated based on the decomposition temperature according to Equation (1).<sup>[32]</sup>

$$\Delta H_{\rm sub} = 188 \,\mathrm{J}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1} \times T \tag{1}$$

From Table 1, the  $\Delta H_{\rm f}$  values of six NHC-borane compounds ranged from -14.93 to 145.21 kJ mol<sup>-1</sup>, in which **5** gave the highest  $\Delta_{\rm f}H$  value which is much higher than that of UDMH (53.28 kJ mol<sup>-1</sup>). Analyzing the influences of different substituents on heats of formation, the allyl of imidazolylidene in **5** shows a more positive influence than other alkyl substituents such as the methyl, ethyl, and butyl, etc., perhaps due to the fuel-rich characteristic of the allyl group, which is in agreement with the results reported in the literature.<sup>[15]</sup>

Specific impulse  $(I_{sp})$  is very indicative of the efficiency of a chemical propellant and helps in the design of the rocket

engine.<sup>[33,34]</sup> It is highly desirable for the  $I_{sp}$  value of a propellant fuel to be as high as possible. The  $I_{sp}$  values of new hypergolic fuels were also calculated by professional CEA400 software at  $\varepsilon = 70$ , considering the variation of specific heat ratio with temperature.<sup>[35,36]</sup> As listed in Table 1, the vacuum  $I_{sp}$  values of NHC-borane adducts vary from 200.5–308.1 s. Among the compounds **1–6**, **1** and **3–6** exhibited the relatively high vacuum  $I_{sp}$ values of > 300 s, demonstrating their promising potentials as high-performance green fuels in formulating the future hypergolic liquid bipropellants.

#### Hypergolic test

As potential hypergolic fuels, evaluating the hypergolic reactivity with bipropellant oxidizers is very important since it determines whether these fuels are suitable for practical propulsion applications. In general, hypergolic reactivity is estimated by recording the ID times. Ultra-short ID times usually indicate very fast ignition rates of hypergolic fuels with the oxidizer. In this study, a droplet test was performed to evaluate the hypergolic reactivity of compounds 2–5. Each sample was measured three times and averaged so the degree of variability was in a reasonable range ( $\pm 3$  ms). A high-speed camera was used to record the ID times as show in Figure 5 (the time between the initial contact between fuels and oxidant and the flame appears).



Figure 5. Drop test setup used to measure the ID times.

A series of high-speed camera (2000 fps) photos of **5** is shown in Figure 6. When the liquid drop of **5** contacted the pool surface of WFNA, an intense reaction occurred and spontaneous ignition was observed. The drop tests showed that these compounds exhibited very short ID times ranging from 2–100 ms. When compared with the widely used UDMH (4.7 ms), **1** showed a shorter ID time. However, the high melting point of **1** limits its direct application as a liquid fuel. Fortunately, liquids **3–5** also showed very short ID times ranging from 15–38 ms, which can well meet the requirements of liquid hypergolic fuels with desired ID time of < 30 ms. Among them, **5** showed the shortest ID time of 15 ms, which

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Figure 6. High-speed camera photos that show a spatially resolved ignition event for a droplet of 5 falling into 100% HNO<sub>3</sub>.

may be attributed to the fuel-rich allyl substituent in the structure. For the liquid compound **5**, its low  $T_g$  (-70 °C), high thermal stability ( $T_d$  = 160 °C), short ID time (15 ms), high specific impulse (303.5 s), and low volatility makes it a potentially safer fuel to replace hydrazine derivatives in liquid bipropellants.

# Conclusions

In summary, six imidazolylidene-borane compounds were synthesized and characterized. These compounds exhibited good water-stability and hypergolic reactivity with WFNA as the oxidizer. As a potential hypergolic fuel, compound **5** showed excellent properties including a low melting point, high thermal stability, low viscosity, and a very short ID time, and therefore has potential as a hypergolic fuel in bipropellant formulations.

# **Experimental Section**

## Chemicals

The organic solvents were of analytical grade. 1-Methylimidazole (99%), 1-ethylimidazole (99%), 1-propylimidazol, 1-butylimidazole (99%), and 1-allylimidazole (99%) were purchased form Sigma-Aldrich. Iodomethane (99%), iodoethane (99%), and sodium borohydride (97%) were purchased from J&K Scientific. All of the chemicals were used without further purification.

#### Synthesis of imidazolylidene-borane compounds

lodomethane or iodoethane (1.2 equiv) was added slowly in portions to a dichloromethane solution of the appropriate imidazole (5 M) over the course of 15–30 min. The reaction mixture was allowed to stir for 1 h, after which time the mixture was concentrated by rotary evaporation. Then, the remaining residue was washed by ethyl acetate three times and dried under vacuum to give the salt sample. The sample was used directly. Then a 250 mL flask was charged with 100 mmol of imidazolium salt and 100 mL of toluene, and then 120 mmol of sodium borohydride was added into it. The flask was fitted with a cold water condenser and placed in an oil bath at 125 °C for 18–24 h. After which time, the reaction solvent was cautiously decanted from the insoluble mixture, and the remaining residue was extracted with hot toluene. The solvent was then filtered through a pad of silica gel. After evaporation of the solvent, crude compounds were purified by silica gel column chromatography or recrystallization.

## Synthesis of compound 1

As a general procedure, 22.4 g (100 mmol) 1,3-dimethylimidazolium iodide and 4.68 g (120 mmol) sodium borohydride was stirred for 18 h at 125 °C to afford crude product. The crude product was recrystallized from water to give the pure product **1** as a white solid. Yield: 70%; m.p. 144 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.69– 1.33 (m, 3 H, BH<sub>3</sub>), 3.74 (s, 6 H, CH<sub>3</sub>), 6.81 ppm (s, 2 H, CH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 119.95, 35.96 ppm; IR (KBr):  $\tilde{\nu}$  = 3133, 3167, 3051, 2985, 2953, 2275, 1574, 1479, 1445, 1266, 1232, 1187, 1122, 876, 736, 702, 655 cm<sup>-1</sup>; HRMS (ESI): *m/z*: calcd for C<sub>5</sub>H<sub>10</sub>BN<sub>2</sub>: 109.0937 [*M*]<sup>+</sup>; found: 109.0935; elemental analysis calcd (%) for C<sub>5</sub>H<sub>11</sub>BN<sub>2</sub>: C 54.61, H 10.08, N 25.47; found: C 54.56, H 10.25, N 25.58.

### Synthesis of compound 2

As a general procedure, 23.8 g (100 mmol) 1-methy-3-ethyl imidazolium iodide and 4.68 g (120 mmol) sodium borohydride was stirred for 18 h at 125 °C to afford the crude product, which was purified by column chromatography (20% EtOAc/hexane) to afford **2** as a white solid. Yield: 68%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.70–1.40 (m, 6H, CH<sub>3</sub>, BH<sub>3</sub>), 3.73 (s, 3H, CH<sub>3</sub>), 4.16 (q, 2H, CH<sub>2</sub>), 6.85 ppm (d, 2H, CH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.33–172.02,120.18, 118.17, 43.72, 35.79, 15.46 ppm; IR (KBr):  $\vec{\nu}$  = 3161, 3123, 2973, 2933, 2873, 2275, 1574, 1479, 1441, 1273, 1229, 1131, 753 cm<sup>-1</sup>; HRMS (ESI): *m/z*: calcd for C<sub>6</sub>H<sub>12</sub>BN<sub>2</sub>:123.1094 [*M*]<sup>+</sup>; found: 123.1089; elemental analysis calcd (%) for C<sub>6</sub>H<sub>13</sub>BN<sub>2</sub>: C 58.12, H 10.57, N 22.59; found: C 57.98, H 10.68, N 23.12.

## Synthesis of compound 3

As a general procedure, 25.2 g (100 mmol) 1-methy-3-propyl imidazolium iodide and 4.68 g (120 mmol) sodium borohydride was stirred for 18 h at 125 °C to afford the crude product, which was purified by column chromatography (20% EtOAc/hexane) to afford **3** as a colorless liquid. Yield: 64%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.75–1.35 (m, 6H, CH<sub>3</sub>, BH<sub>3</sub>), 1.80 (m, 2H, CH<sub>2</sub>), 3.73 (s, 3H, CH<sub>3</sub>), 4.06 (t, 2H, CH<sub>2</sub>), 6.86 ppm (s, 2H, CH), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.45–171.97, 120.04, 118.92 50.26, 35.74, 23.40, 10.93 ppm; IR (KBr):  $\tilde{\nu}$  = 3125, 2965, 2877, 2295, 1572, 1474, 1412, 1384, 1251, 1221, 1127, 864, 728, 636, 577 cm<sup>-1</sup>; HRMS (ESI): *m/z*: calcd for C<sub>7</sub>H<sub>14</sub>BN<sub>2</sub>: 137.1250 [*M*]<sup>+</sup>; found: 137.1246; elemental analysis calcd for C<sub>7</sub>H<sub>15</sub>BN<sub>2</sub>: C 60.92, H 10.95, N 20.30; found: C 60.75, H 11.03, N, 20.19.

## Synthesis of compound 4

As a general procedure, 26.6 g (100 mmol) 1-methy-3-butyl imidazolium iodide and 4.68 g (120 mmol) sodium borohydride was stirred for 18 h at 125 °C to afford the crude product, which was purified by column chromatography (20% EtOAc/hexane) to afford 4 as a colorless liquid. Yield: 65%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.70–1.31 (m, 6H, CH<sub>3</sub>, BH<sub>3</sub>), 1.37 (m, 2H, CH<sub>2</sub>), 1.76 (m, 2H, CH<sub>2</sub>), 3.73 (s, 2H, CH<sub>3</sub>), 4.10 (d, 2H, CH<sub>2</sub>), 6.81 ppm (d, 2H, CH); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 120.01, 118.81, 48.55, 35.81, 32.19, 19.68,

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13.66 ppm; IR (KBr):  $\tilde{\nu}$  = 3164, 3125, 2958, 2934, 2871, 2339, 2281, 1572, 1474, 1412, 1238, 1180, 1126, 864, 728, 636, 575 cm<sup>-1</sup>; HRMS (ESI): *m/z*: calcd for C<sub>8</sub>H<sub>16</sub>BN<sub>2</sub>: 151.1407 [*M*]<sup>+</sup>; found: 151.1401; elemental analysis calcd (%) for C<sub>8</sub>H<sub>17</sub>BN<sub>2</sub>: C 60.92, H 10.95, N 20.30; found: C 60.75, H 11.03, N 20.19.

#### Synthesis of compound 5

As a general procedure, 25.0 g (100 mmol) 1-methy-3-allyl imidazolium iodide and 4.68 g (120 mmol) sodium borohydride was stirred for 18 h at 125 °C to afford the crude product, which was purified by column chromatography (20% EtOAc/hexane) to afford **5** as a colorless liquid. Yield: 60%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.71– 1.35 (m, 3H, BH<sub>3</sub>), 3.75 (s, 3H, CH<sub>3</sub>), 4.74 (d, 2H, CH<sub>2</sub>), 5.27 (dd, 2H, CH<sub>2</sub>), 5.93 (m, 1H, CH), 6.86 ppm (d, 2H, CH), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.85–172.39, 132.42, 120.36, 118.97, 118.63, 50.98, 35.89 ppm; IR (KBr):  $\tilde{\nu}$  = 3166, 3129, 2946, 2340, 2281, 1646, 1572, 1472, 1411, 1253, 1216, 1122, 994, 862, 729, 634, 606 cm<sup>-1</sup>; HRMS (ESI): *m/z*: calcd for C<sub>7</sub>H<sub>12</sub>BN<sub>2</sub>: 135.1094 [*M*]<sup>+</sup>; found: 135.1094; elemental analysis calcd (%) for C<sub>7</sub>H<sub>13</sub>BN<sub>2</sub>: C 61.82, H 9.63, N 20.60; found: C 61.75, H 9.71, N 20.45.

#### Synthesis of compound 6

As a general procedure, 25.2 g (100 mmol) 1, 3-diethyl imidazolium iodide and 4.68 g (120 mmol) sodium borohydride was stirred for 18 h at 125 °C to afford the crude product, which was purified by column chromatography (20% EtOAc/hexane) to afford **6** as a white solid. M.p. 41 °C; yield: 67%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.72-1.41$  (m, 9H, CH<sub>3</sub>, BH<sub>3</sub>), 4.16 (q, 4H, CH<sub>2</sub>), 6.87 ppm (s, 2H, CH), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 170.14-171.16$ , 118.35, 43.55, 15.42 ppm; IR (KBr):  $\ddot{\nu} = 3126$ , 2975, 2931, 2307, 1568, 1472, 1432, 1378, 1349, 1266, 1206, 1120, 1044, 803, 761, 740, 649 cm<sup>-1</sup>; HRMS (ESI): *m/z*: calcd for C<sub>7</sub>H<sub>14</sub>BN<sub>2</sub>:: 137.1250 [*M*]<sup>+</sup>; found: 137.1246; elemental analysis calcd (%) for C<sub>7</sub>H<sub>15</sub>BN<sub>2</sub>: C 60.92, H 10.95, N 20.30; found: C 60.75, H 11.03, N 20.19.

#### Instrumentation and analysis methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker 400 AVANCE spectrometer (400 and 101 MHz, respectively) with internal standard (<sup>1</sup>H NMR: CDCl<sub>3</sub> at  $\delta$ =7.28 ppm; <sup>13</sup>C NMR: CDCl<sub>3</sub> at  $\delta$ =77.16 ppm). IR spectra were performed on Perkin–Elmer Spectrum Two IR Spectrometers. HRMS were performed on Shimadzu LCMS-IT-TOF mass spectrometer using electrospray ionization (ESI). Elemental analysis was performed on Flash EA-1112 elemental analyzer. Thermal property measurements were performed on TGA/DSC1 and DSC3 Mettler Toledo calorimeter equipped with auto cool accessory. Densities were measured on a Micromeritics Accupyc II 1340 gas pycnometer at 25 °C. Viscosity measurements were performed on a Brookfield Rheometer DV3T at 25 °C. Ignition photographs of NHC-borane compounds with the oxidizer of 100% HNO<sub>3</sub> were recorded on an Olympus i-speed 3.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 11472251, 11572258), China Postdoctoral Science Foundation (2015M570796), Development Foundation of CAEP (No. 2015B0302056, 2014B0302039), and the Talent Startup Foundation of ICM (ST2014006). **Keywords:** boranes · green chemistry · hydrazines hypergolicity · propellants

- J. P. Agrawal in *High Energy Materials: Propellants, Explosives and Pyrotechnics* (Ed.: J. P. Agrawal), Wiley-VCH, Weinheim, Germany, 2010, Chapter 4.
- [2] S. Schneider, T. Hawkins, Y. Ahmed, S. Deplazes, J. Mills in *lonic Liquids: Science and Applications, Vol. 1117* (Eds.: A. E. Visser, N. J. Bridges, R. D. Rogers), ACS Symposium Series, American Chemical Society, Washington, DC, **2012**, Chapter 1.
- [3] F. K. Kamal, B. Yann, B. Rachid, K. Charles in Applications of lonic Liquids in Science and Technology (Ed.: S. Handy), Intech, 2011, Chapter 21.
- [4] I. Frank, A. Hammerl, T. M. Klapötke, C. Nonnenberg, Prop. Explos. Pyrotech. 2005, 30, 44–52.
- [5] C. B. Jones, R. Haiges, T. Schroer, K. O. Christe, Angew. Chem. Int. Ed. 2006, 45, 4981–4984; Angew. Chem. 2006, 118, 5103–5106.
- [6] Q. H. Zhang, J. M. Shreeve, Chem. Rev. 2014, 114, 10527-10574.
- [7] Q. H. Zhang, J. M. Shreeve, Chem. Eur. J. 2013, 19, 15446-15451.
- [8] E. Sebastiao, C. Cook, A. Hu, M. Murugesu, J. Mater. Chem. A 2014, 2, 8153–8173.
- [9] J. J. Tian, Q.-H. Zhang, Chin. J. Energy Mater. 2014, 22, 580.
- [10] Y. Q. Zhang, H. X. Gao, Y. H. Joo, J. M. Shreeve, Angew. Chem. Int. Ed. 2011, 50, 9554–9562; Angew. Chem. 2011, 123, 9726–9734.
- [11] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. Int. Ed. 2006, 45, 3584–3601; Angew. Chem. 2006, 118, 3664–3682.
- [12] a) S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau, G. Drake, *Energy Fuels* 2008, *22*, 2871–2872; b) T. Litzinger, S. lyer, *Energy Fuels* 2011, *25*, 72–76; c) K. Chingin, R. H. Perry, S. D. Chambreau, G. L. Vaghjiani, R. N. Zare, *Angew. Chem. Int. Ed.* 2011, *50*, 8634–8637; *Angew. Chem.* 2011, *123*, 8793–8796; d) H. X. Gao, Y. H. Joo, B. Twamley, Z. Q. Zhuo, J. M. Shreeve, *Angew. Chem. Int. Ed.* 2009, *48*, 2792–2795; *Angew. Chem.* 2009, *121*, 2830–2833.
- [13] L. He, G. H. Tao, D. M. Parrish, J. M. Shreeve, Chem. Eur. J. 2010, 16, 5736-5743.
- [14] Y. Q. Zhang, J. M. Shreeve, Angew. Chem. Int. Ed. 2011, 50, 935–937; Angew. Chem. 2011, 123, 965–967.
- [15] a) Q. H. Zhang, P. Yin, J. H. Zhang, J. M. Shreeve, *Chem. Eur. J.* 2014, *20*, 6909–6914; b) W. Q. Zhang, X. J. Qi, S. Huang, J. S. Li, Q. H. Zhang, *J. Mater. Chem. A* 2015, *3*, 20664–20672; c) S. Huang, X. J. Qi, W. Q. Zhang, T. L. Liu, Q. H. Zhang, *Chem. Asian J.* 2015, *10*, 2725–2732.
- [16] a) S. Q. Li, H. X. Gao, J. M. Shreeve, Angew. Chem. Int. Ed. 2014, 53, 2969–2972; Angew. Chem. 2014, 126, 3013–3016; b) D. Chand, J. H. Zhang, J. M. Shreeve, Chem. Eur. J. 2015, 21, 13297–13301.
- [17] T. L. Liu, Q. J. Qi, S. Huang, L. H. Jiang, J. L. Li, C. L. Tang, Q. H. Zhang, Chem. Commun. 2016, 52, 2031 – 2034.
- [18] S. Schneider, T. Hawkins, Y. Ahmed, M. Rosander, L. Hudgens, J. Mills, Angew. Chem. Int. Ed. 2011, 50, 5886–5888; Angew. Chem. 2011, 123, 6008–6010.
- [19] F. Dielmann, O. Back, M. H. Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* 2012, 337, 1526–1528.
- [20] D. Mendoza-Espinosa, B. Donnadieu, G. Bertrand, J. Am. Chem. Soc. 2010, 132, 7264–7265.
- [21] M. Y. Abraham, Y. Z. Wang, Y. M. Xie, P. R. Wei, H. F. Schaefer, P. V. Schleyer, G. H. Robinson, *Chem. Eur. J.* **2010**, *16*, 432–435.
- [22] J. Campos, L. S. Sharninghausen, R. H. Crabtree, D. Balcells, Angew. Chem. Int. Ed. 2014, 53, 12808–12811; Angew. Chem. 2014, 126, 13022– 13025.
- [23] J. C. Walton, M. M. Brahmi, L. Fensterbank, E. Lacote, M. Malacria, Q. L. Chu, S. H. Ueng, A. Solovyev, D. P. Curran, J. Am. Chem. Soc. 2010, 132, 2350–2358.
- [24] S. Gardner, T. Kawamoto, D. P. Curran, J. Org. Chem. 2015, 80, 9794– 9797.
- [25] M. Toure, O. Chuzel, J. L. Parain, J. Am. Chem. Soc. 2012, 134, 17892– 17895.
- [26] P. Bissinger, H. Braunschweig, T. Kupfer, Organometallics 2010, 29, 3987–3990.
- [27] F. L. Hirshfeld, Theor. Chim. Acta 1977, 44, 129-138.

6

[28] T. Köddermann, C. Wertz, A. Heintz, R. Ludwig, Angew. Chem. Int. Ed. 2006, 45, 3697–3702; Angew. Chem. 2006, 118, 3780–3785.

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- [29] M. H. Ghatee, A. R. Zolghadr, J. Phys. Chem. C 2013, 117, 2066-2077.
- [30] Gaussian 09, Revision D. 01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian. Inc., Wallingford CT, 2009.
- [31] R. G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, **1989**.
- [32] J. H. Zhang, J. M. Shreeve, J. Am. Chem. Soc. 2014, 136, 4437-4445.
- [33] G. Sutton, O. Bilbarz, Rocket Propulsion Elements, 7th ed., John Wiley& Sons, Hoboken, New Jersey, 2001.
- [34] S. Sato, A. Matsuo, T. Endo, J. Kasahara, J. Propul. Power 2006, 22, 64– 70.
- [35] S. Gordon, B. J. McBride, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications, I: Analysis. NASA Reference Publication 1311, **1994**.
- [36] B. J. McBride, S. Gordon, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications, II: User manual and program description. NASA Reference Publication 1311, 1996.

Received: March 21, 2016 Published online on ■■ ■, 0000



# **FULL PAPER**



S. Huang, X. Qi, T. Liu, K. Wang, W. Zhang, J. Li, Q. Zhang\*

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Towards Safer Rocket Fuels: Hypergolic Imidazolylidene-Borane Compounds as Replacements for Hydrazine Derivatives



**Making a bang!** Imidazolylidene-borane compounds with a zwitterionic structure exhibited fast spontaneous combustion on contact with 100% HNO<sub>3</sub> (see picture). Among these hypergolic liquids, compound **5** has potential application as safer hypergolic fuels in liquid bipropellant formulations.

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