

# Mass spectrometric evidence for collisionally induced removal of H<sub>2</sub> from monoanions of <sup>10</sup>B *nido*-carborane derivatives investigated by electrospray ionization quadrupole linear ion trap and Fourier transform ion cyclotron resonance mass spectrometry

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Some newly synthesized <sup>10</sup>B *nido*-carborane derivatives, i.e., 7,8-dicarba-*nido*-undecaborane monoanions ([7-Me-8-R-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup>K<sup>+</sup>, R = H, butyl, hexyl, octyl and decyl), have been fully characterised and examined by electrospray ionization and Fourier transform ion cyclotron resonance mass spectrometry with liquid chromatographic separation (LC/ESI-FTICR-MS). These boron-containing compounds exhibit abundant molecular ions ([M]<sup>-</sup>) at *m/z* 140.22631 [C<sub>3</sub><sup>10</sup>B<sub>9</sub>H<sub>14</sub>]<sup>-</sup>, *m/z* 196.28883 [C<sub>7</sub><sup>10</sup>B<sub>9</sub>H<sub>22</sub>]<sup>-</sup>, *m/z* 224.32032 [C<sub>9</sub><sup>10</sup>B<sub>9</sub>H<sub>26</sub>]<sup>-</sup>, *m/z* 252.35133 [C<sub>11</sub><sup>10</sup>B<sub>9</sub>H<sub>30</sub>]<sup>-</sup> and *m/z* 280.38354 [C<sub>13</sub><sup>10</sup>B<sub>9</sub>H<sub>34</sub>]<sup>-</sup> at the normal tube lens voltage setting of -90 V, which was an instrumental parameter value selected in the tuning operation. Additional [M-*n*H<sub>2</sub>]<sup>-</sup> (*n* = 1–4) ions were observed in the mass spectra when higher tube lens voltages were applied, i.e., -140 V. High-resolution FTICR-MS data revealed the accurate masses of fragment ions, bearing either an even or an odd number of electrons. Collision-induced dissociation of the [M-*n*H<sub>2</sub>]<sup>-</sup> ions (*n* = 0–4) in the quadrupole linear ion trap (LTQ) analyzer confirmed the loss of hydrogen molecules from the molecular ions. It is suggested that the loss of H<sub>2</sub> molecules from the alkyl chain is a consequence of the stabilization effect of the *nido*-carborane charged polyhedral skeleton. Copyright © 2009 John Wiley & Sons, Ltd.

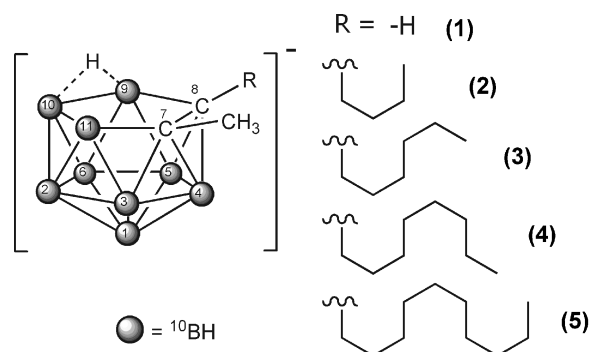
Safe, efficient and compact hydrogen storage is a major challenge in order to realize hydrogen-powered transport.<sup>1</sup> Currently, the storage of hydrogen in the absorbed form is considered as the most appropriate way to solve this problem, albeit a medium capable of absorbing and releasing large quantities of hydrogen easily and reliably is still being actively sought. Previous work on hydrogen-storage compounds has focused mainly on carbon nanotubes and hydrogen clathrate-hydrate compounds.<sup>2</sup> However, these materials only work in fuel cells at low temperatures (e.g., 20 K) or high pressures.<sup>3</sup> The traditional hydrides (i.e., NaAlH<sub>4</sub>, Na<sub>3</sub>AlH<sub>6</sub>, NaBH<sub>4</sub>, MgH<sub>2</sub>, etc.) have excellent H-volume storage capacity, good and tuneable kinetics and reversibility, but poor H-storage by weight.<sup>4</sup> Porous carbon and hybrid materials have the capability of high mass storage capacity but, since adsorption is of molecular hydrogen, they can only work at cryogenic conditions. The light metal alloys have the required mass density, but poor kinetics and high

absorption temperatures/pressures. The complex hydrides undergo chemical reactions while desorbing/adsorbing, thus restricting kinetics and reversibility.<sup>4</sup>

Recently, several boron-containing compounds have proven to be of potential interest for applications in the field of hydrogen storage.<sup>5</sup> To the best of our knowledge, however, there have been few studies concerning the possible application of carboranes as dihydrogen-storage molecules. Carboranes are cage-shaped molecules in which boron and carbon form the polyhedral skeleton. These cages possess quite high boron content, and display extraordinary thermal, kinetic and photochemical stabilities relative to other boron clusters.<sup>6</sup> As such, they have been attracting considerable interest as effective drugs in anticancer boron neutron capture therapy (BNCT).<sup>7</sup> The source of boron in the new BNCT sensitizers is usually the neutral *o*-carborane (*o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) or the anionic *nido*-carborane ([*o*-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup>) species. These cages are said to have relative high boron content and to display extraordinary thermal, kinetic and photochemical stabilities relative to other boron clusters.<sup>8,9</sup>

As part of our continuing interest in polycarboranyl-azaporphyrins (PCPzs), which are a family of boron-containing complexes with high potential as BNCT agents, we synthesized some <sup>10</sup>B-7,8-dicarba-*nido*-undecaborane

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**Figure 1.** Ball-and-stick representation of the synthesized  $^{10}\text{B}$  *nido*-carborane derivatives with the following formulae  $[\text{C}_x\text{B}_9\text{H}_{2x+8}]^-$  ( $x=3, 7, 9, 11$  and  $13$ ): 7-methyl-7,8-*nido*-undecaborane (1), 7-methyl-8-*n*-butyl-7,8-*nido*-undecaborane (2), 7-methyl-8-*n*-hexyl-7,8-*nido*-undecaborane (3), 7-methyl-8-*n*-octyl-7,8-*nido*-undecaborane (4), 7-methyl-8-*n*-decyl-7,8-*nido*-undecaborane (5).

potassium salt derivatives (see Fig. 1) taken as building blocks of nanosized water-soluble PCPZs.<sup>10–12</sup> The choice of using B-10-enriched compounds is primarily related to the fact that  $^{10}\text{B}$  is the active boron isotope in BNCT. Such *nido*-carborane derivatives were investigated by combining high-performance liquid chromatographic (HPLC) separations with Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), which is unmatched in mass resolution as well as accurate mass measurement capability.<sup>13,14</sup>

Mass spectrometry is a very effective means of identifying carboranes and some examples have been reported in which electrospray ionization (ESI) and matrix-assisted laser desorption/ionization are used to investigate boron-containing compounds.<sup>7,15–18</sup> Herein we report the LC/ESI-MS characterization of several  $^{10}\text{B}$ -7,8-dicarba-*nido*-undecaborane potassium salt monoanion derivatives, prepared from the corresponding *closo*-dicarbadodecaboranes. In the course of this study we observed ions which seem to indicate the repeated elimination of  $\text{H}_2$  molecules, presumably from the alkyl chain, when a relatively high tube lens voltage was applied. Confirmation of the eliminations was provided by accurate mass measurements. It is thus proposed that *nido*-carborane alkyl derivatives may have a potential as chemical precursors of molecular hydrogen-storage media.<sup>19</sup>

## EXPERIMENTAL

### Chemicals

The  $^{10}\text{B}$ -enriched compounds 7-methyl-7,8-*nido*-undecaborane (1), 7-methyl-8-*n*-butyl-7,8-*nido*-undecaborane (2), 7-methyl-8-*n*-hexyl-7,8-*nido*-undecaborane (3), 7-methyl-8-*n*-octyl-7,8-*nido*-undecaborane (4) and 7-methyl-8-*n*-decyl-7,8-*nido*-undecaborane (5) were synthesized using the procedure reported in the Supporting Information (S1).  $^{10}\text{B}$ -enriched 1-methyl-*o*-carborane (purity > 98%) was purchased from Katchem spol. s.r.o. (Prague, Czech Republic). Decanoic acid, hexanoic acid, analytical grade methanol and ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) were purchased from Sigma-Aldrich (Buchs, Switzerland). Stock solution of 1, 2, 3, 4, 5, decanoic acid and hexanoic acid were prepared by

dissolving the substances in methanol at an approximate concentration of 1 mg/mL and stored at  $-20^\circ\text{C}$ . Standard solutions for LC/MS analyses were prepared by diluting the stock solution with  $\text{MeOH}/\text{H}_2\text{O}$  with 0.1%  $\text{NH}_4\text{HCO}_3$  (w/v) (70:30, v/v). Pure nitrogen (99.996%) was delivered to the LC/MS system as the sheath gas. The ion trap pressure was maintained with helium (99.999%) which was used for trapping ions and for their collisional activation.

### LC separation conditions and PDA ESI-LTQ-FTICR-MS instrumentation

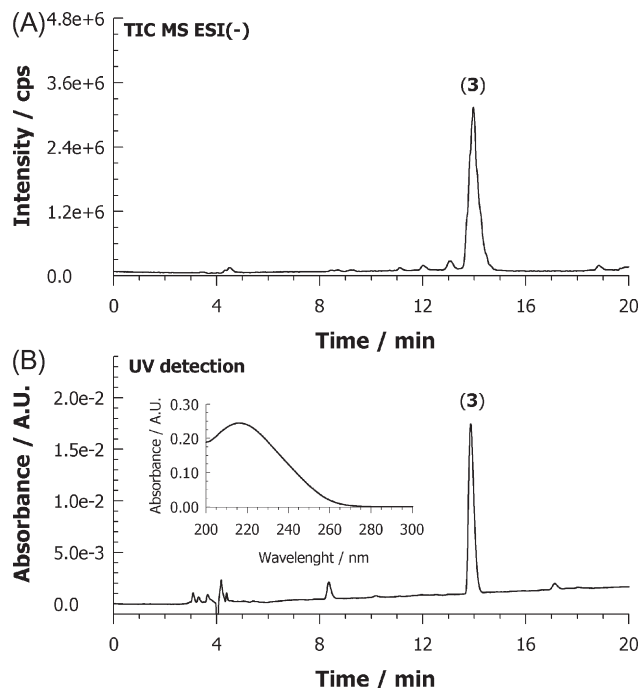
All experiments were performed using a Surveyor LC system coupled to a Surveyor photo-detector array (PDA) and a hybrid linear quadrupole ion trap (LTQ) coupled with a 7-T FTICR mass spectrometer (all the instrumentation was supplied by Thermo Fisher Scientific Inc., Bremen, Germany). A Discovery C18 stationary phase (Supelco Inc., Bellefonte, PA, USA) with a guard column (20 mm  $\times$  2.1 mm) of the same packing material (Supelco Inc.) was used for separation. The column dimensions were 4.6 mm  $\times$  250 mm with an average particle size of 5  $\mu\text{m}$  and pore size of 180  $\text{\AA}$ . A 20  $\mu\text{L}$  loop was used for injections. Pure water supplied by a Milli-Q RG unit (Millipore, Bedford, MA, USA) with the addition of 0.1% (w/v) ammonium bicarbonate was used as eluent A, and  $\text{MeOH}$  as eluent B. The LC pump was operated at a flow rate of 0.80 mL/min and the elution gradient was as follows: 0 to 2 min, 70% B; 2 to 30 min, solvent B increased linearly to 95%; and 50 to 60 min at 100% B. The system was re-equilibrated at 30% A for 5 min before the next injection. Separations were performed at ambient temperature of  $21 \pm 2^\circ\text{C}$  with an eluent splitting 3:1 after the analytical column to allow 200  $\mu\text{L}/\text{min}$  to enter the ESI source. The PDA detector scanned the range 200–400 nm in steps of 1 nm and a sample rate of 5 Hz. The mass spectrometric conditions were optimized by direct infusion of standard solutions of compounds 1, 2, 3, 4 and 5 at ca. 1 mg/L in 30:70 v/v of A/B mobile phase into the ionization source using a carrier solution composed of 70:30 (v/v) of  $\text{MeOH}/\text{H}_2\text{O}$  + 0.1%  $\text{NH}_4\text{HCO}_3$ . The instrument was tuned to facilitate the ionization process and achieve the highest sensitivity. The negative ion mode for ESI-FTICR-MS and ESI-linear ion trap (LIT)-MS/MS analysis was selected and the electrospray voltage, heated capillary temperature and voltage, tube lens voltage, sheath gas flow rate and auxiliary gas flow rate were varied to maximize the ion transmission. The spray voltage was set at  $-3.9\text{ kV}$ , the temperature of the ion transfer tube was set at  $250^\circ\text{C}$ , the applied capillary voltage was set at  $-38\text{ V}$ , and the tube lens voltage was set at  $-90\text{ V}$ . The sheath gas ( $\text{N}_2$ ) flow rate used was 40 a.u. (arbitrary units) and the auxiliary gas flow rate was set to zero (a.u.). Full scan experiments were performed in the ICR cell in the range  $m/z$  50–350; tandem mass spectrometry (MS/MS) experiments were carried out in the linear ion trap (LTQ) using collision-induced dissociation (CID) and applying a relative collision energy of 45%. Mass spectra were acquired as profile data at a resolution of 200 000 (full width at half maxima (FWHM)) at  $m/z$  400. The automatic gain control (AGC) ion population target in full scan MS was 30 000 for LTQ-MS and 5 000 000 for FTICR-MS and the ion population target for  $\text{MS}^n$  was set to 10 000 for LTQ-MS. The maximum ion injection time was 10 ms for LTQ-MS and 200 ms for

FTICR-MS. The LTQ and FTICR mass spectrometers were calibrated according to the manufacturer's instructions both in positive and negative ion detection mode using a solution of caffeine (gives a protonated molecule at  $m/z$  195), tetrapeptide Met-Arg-Phe-Ala (MRFA) ( $m/z$  524), sodium dodecyl sulfate (gives anion at  $m/z$  265) and sodium taurocholate ( $m/z$  514). Data acquisition and analysis were accomplished using Xcalibur software package (version 2.0 SR1, Thermo Fisher Scientific Inc.). The chromatographic raw data were imported, elaborated and plotted by SigmaPlot 10.0 (Systat Software, Inc., London, UK).

## RESULTS AND DISCUSSION

### LC/ESI-FTICR-MS of the 7-methyl-8-hexyl-7,8-dicarba-*nido*-undecaborane monoanion

Synthetic and characterization details concerning all the  $^{10}\text{B}$  *nido*-undecaborane potassium salts and their neutral precursor *closo*-dodecaboranes are reported in the Supporting Information. According to X-ray studies on a number of monoanionic *nido*-carboranes,<sup>20,21</sup> the 7-methyl-8-hexyl-7,8-dicarba-*nido*-undecaborane anion (**3**) can be thought of as a carborane cage open on the top, characterized by a surface of *exo* B–H bonds directed radially outward from the delta-hedral cluster and by a BHB (*endo*) bridging hydrogen atom (Fig. 1). The water solubility of the anion is guaranteed by using  $\text{K}^+$  as counterion. To ascertain the purity of each prepared *nido*-carborane anion, a combined LC/ESI-FTICR-MS method was used. The LC separation was accomplished in less than 16 min using a reversed-phase  $\text{C}_{18}$  column and a mobile phase composed of buffered  $\text{NH}_4\text{HCO}_3$  (0.1% w/v) at pH 6.9 and a gradient methanol elution. A typical chromatogram of **3** is shown in Fig. 2(A), where a single peak

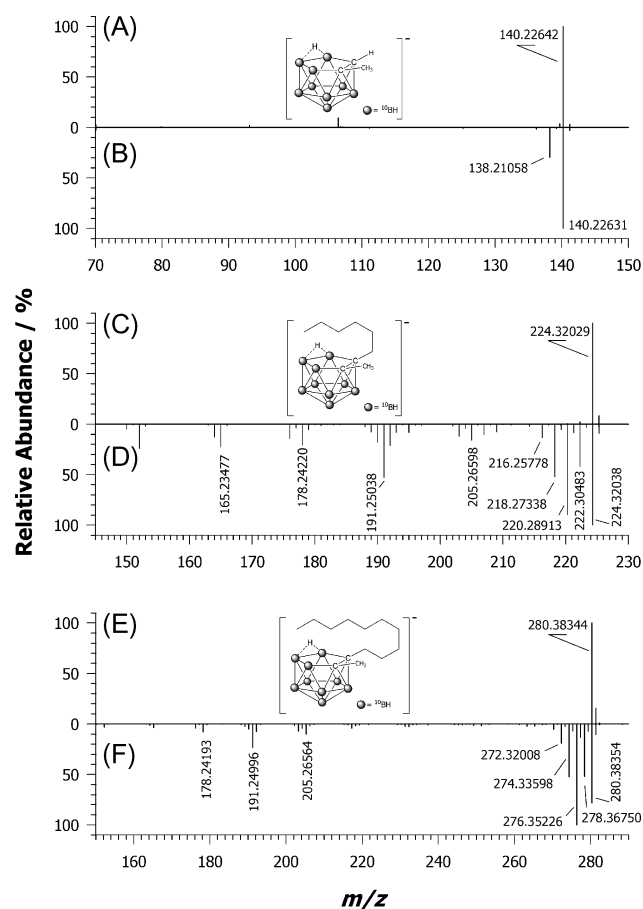


**Figure 2.** (A) LC/ESI-FTICR-MS total ion current chromatogram of the [7-methyl-8-*n*-hexyl-7,8-*nido*- $\text{C}_2\text{B}_9\text{H}_{11}$ ] $^-$  monoanion. (B) LC-PDA recorded at  $\lambda_{\text{max}} = 216$  nm as shown in the inset (background subtracted).

at 14.1 min was observed. The same separation was also recorded by using a PDA detector and the corresponding profile acquired at a wavelength of 216 nm is illustrated in Fig. 2(B). Similar chromatographic behavior was observed for all the derivatives analyzed (data not shown).

### Effects of the tube lens voltage on the $^{10}\text{B}$ *nido*-carborane derivatives and accurate mass analysis

The most important parameters that affect the signal quality during ESI-MS operation are the ESI capillary voltage, ion transfer capillary temperature, capillary tube lens voltage, offset voltage, and gases and solution flow rates. As reported in the Experimental section, the mass spectrometric conditions were optimized automatically. The high-resolution mass spectra of derivatives **1**, **3** and **5** obtained in the negative ion mode at a tube lens setting of  $-90$  V are shown in Figs. 3(A), 3(C) and 3(E), respectively. As expected, all the ions are singly charged. Taking compound **3** as an example, there is a singly charged ion at  $m/z$  224.32029, to which we attributed the formula  $[\text{C}_9\text{B}_9\text{H}_{26}]^-$ , and is hereafter



**Figure 3.** Negative ion ESI high-resolution mass spectrum acquired upon LC/ESI-FTICR-MS of *nido*-carborane monoanions **1**, **3** and **5**. The top spectra (A, C and E) are those recorded at a tube lens voltage of  $-90$  V using standard tuning procedures, while the bottom spectra (B, D and F) were obtained at  $-140$  V. Labels are placed at the most abundant ions. The data was acquired on a hybrid linear ion trap cyclotron resonance mass spectrometer.

**Table 1.** Nominal mass values, experimental and calculated accurate masses, relative signal intensities, suggested product ions with the corresponding formulae and mass accuracy as evaluated by LC/ESI-FTICR-MS of 7-methyl-8-*n*-hexyl-7,8-*nido*-undecaborane monoanion (**3**)<sup>a</sup>

Nominal <i>m/z</i> value <sup>b</sup>	Measured <i>m/z</i> value <sup>c</sup>	Relative int. (%) <sup>d</sup>	Ion assignment	Chemical formula	Even/odd electron ions <sup>e</sup>	Calculated <i>m/z</i> value	Accuracy (ppm) <sup>f</sup>
224.3	224.32038	52	[M] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>9</sub> H <sub>26</sub> ] <sup>-</sup>	EE <sup>-</sup>	224.32043	-0.22
222.3	222.30483	47	[M-H <sub>2</sub> ] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>9</sub> H <sub>24</sub> ] <sup>-</sup>	EE <sup>-</sup>	222.30478	0.22
220.3	220.28913	100	[M-2H <sub>2</sub> ] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>9</sub> H <sub>22</sub> ] <sup>-</sup>	EE <sup>-</sup>	220.28913	0.00
218.3	218.27338	88	[M-3H <sub>2</sub> ] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>9</sub> H <sub>20</sub> ] <sup>-</sup>	EE <sup>-</sup>	218.27348	-0.46
216.3	216.25778	28	[M-4H <sub>2</sub> ] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>9</sub> H <sub>18</sub> ] <sup>-</sup>	EE <sup>-</sup>	216.25783	-0.23
209.3	209.26871	8	[M-H <sub>2</sub> -BH <sub>3</sub> ] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>8</sub> H <sub>21</sub> ] <sup>-</sup>	EE <sup>-</sup>	209.26837	1.62
207.3	207.25301	10	[M-2H <sub>2</sub> -BH <sub>3</sub> ] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>8</sub> H <sub>19</sub> ] <sup>-</sup>	EE <sup>-</sup>	207.25272	1.40
205.3	205.26598	15	[M-2H <sub>2</sub> -CH <sub>3</sub> ] <sup>-</sup>	[C <sub>8</sub> <sup>10</sup> B <sub>9</sub> H <sub>19</sub> ] <sup>-</sup>	OE <sup>-</sup>	205.26621	-1.12
203.3	203.25035	12	[M-3H <sub>2</sub> -CH <sub>3</sub> ] <sup>-</sup>	[C <sub>8</sub> <sup>10</sup> B <sub>9</sub> H <sub>17</sub> ] <sup>-</sup>	OE <sup>-</sup>	203.25056	-1.03
195.3	195.25298	8.4	[M-H <sub>2</sub> -BH <sub>2</sub> CH <sub>3</sub> ] <sup>-</sup>	[C <sub>8</sub> <sup>10</sup> B <sub>8</sub> H <sub>19</sub> ] <sup>-</sup>	EE <sup>-</sup>	195.25272	1.33
193.2	193.23742	8.4	[M-2H <sub>2</sub> -BH <sub>2</sub> CH <sub>3</sub> ] <sup>-</sup>	[C <sub>8</sub> <sup>10</sup> B <sub>8</sub> H <sub>17</sub> ] <sup>-</sup>	EE <sup>-</sup>	193.23707	1.81
192.3	192.25789	21	[M-H <sub>2</sub> -C <sub>2</sub> H <sub>6</sub> ] <sup>-</sup>	[C <sub>9</sub> <sup>10</sup> B <sub>9</sub> H <sub>18</sub> ] <sup>-</sup>	EE <sup>-</sup>	192.25783	0.31
191.3	191.25038	62	[M-2H <sub>2</sub> -C <sub>2</sub> H <sub>5</sub> ] <sup>-</sup>	[C <sub>7</sub> <sup>10</sup> B <sub>9</sub> H <sub>17</sub> ] <sup>-</sup>	OE <sup>-</sup>	191.25056	-0.94
190.2	190.24232	18	[M-2H <sub>2</sub> -C <sub>2</sub> H <sub>6</sub> ] <sup>-</sup>	[C <sub>7</sub> <sup>10</sup> B <sub>9</sub> H <sub>16</sub> ] <sup>-</sup>	EE <sup>-</sup>	190.24218	0.74
189.2	189.23466	8	[M-3H <sub>2</sub> -C <sub>2</sub> H <sub>5</sub> ] <sup>-</sup>	[C <sub>7</sub> <sup>10</sup> B <sub>9</sub> H <sub>15</sub> ] <sup>-</sup>	OE <sup>-</sup>	189.23491	-1.32
188.2	188.22692	2.5	[M-3H <sub>2</sub> -C <sub>2</sub> H <sub>6</sub> ] <sup>-</sup>	[C <sub>7</sub> <sup>10</sup> B <sub>9</sub> H <sub>14</sub> ] <sup>-</sup>	EE <sup>-</sup>	188.22653	2.07
179.2	179.25036	5.9	[M-H <sub>2</sub> -C <sub>3</sub> H <sub>7</sub> ] <sup>-</sup>	[C <sub>6</sub> <sup>10</sup> B <sub>9</sub> H <sub>17</sub> ] <sup>-</sup>	OE <sup>-</sup>	179.25056	-1.12
178.2	178.24220	20	[M-H <sub>2</sub> -C <sub>3</sub> H <sub>8</sub> ] <sup>-</sup>	[C <sub>6</sub> <sup>10</sup> B <sub>9</sub> H <sub>16</sub> ] <sup>-</sup>	EE <sup>-</sup>	178.24218	0.11
177.2	177.23478	3.8	[M-2H <sub>2</sub> -C <sub>3</sub> H <sub>7</sub> ] <sup>-</sup>	[C <sub>6</sub> <sup>10</sup> B <sub>9</sub> H <sub>15</sub> ] <sup>-</sup>	OE <sup>-</sup>	177.23491	-0.73
176.2	176.22658	14	[M-2H <sub>2</sub> -C <sub>3</sub> H <sub>8</sub> ] <sup>-</sup>	[C <sub>6</sub> <sup>10</sup> B <sub>9</sub> H <sub>14</sub> ] <sup>-</sup>	EE <sup>-</sup>	176.22653	0.28
165.2	165.23477	23	[M-H <sub>2</sub> -C <sub>4</sub> H <sub>9</sub> ] <sup>-</sup>	[C <sub>5</sub> <sup>10</sup> B <sub>9</sub> H <sub>15</sub> ] <sup>-</sup>	OE <sup>-</sup>	165.23491	-0.85
164.2	164.22663	13	[M-H <sub>2</sub> -C <sub>4</sub> H <sub>10</sub> ] <sup>-</sup>	[C <sub>5</sub> <sup>10</sup> B <sub>9</sub> H <sub>14</sub> ] <sup>-</sup>	EE <sup>-</sup>	164.22653	0.61
152.2	152.22643	24	[M-H <sub>2</sub> -C <sub>5</sub> H <sub>12</sub> ] <sup>-</sup>	[C <sub>4</sub> <sup>10</sup> B <sub>9</sub> H <sub>14</sub> ] <sup>-</sup>	EE <sup>-</sup>	152.22653	-0.66
150.2	150.21100	5.2	[M-2H <sub>2</sub> -C <sub>5</sub> H <sub>12</sub> ] <sup>-</sup>	[C <sub>4</sub> <sup>10</sup> B <sub>9</sub> H <sub>12</sub> ] <sup>-</sup>	EE <sup>-</sup>	150.21088	0.80
139.2	139.19030	2	[M-H <sub>2</sub> -BH <sub>2</sub> C <sub>5</sub> H <sub>11</sub> ] <sup>-</sup>	[C <sub>4</sub> <sup>10</sup> B <sub>8</sub> H <sub>11</sub> ] <sup>-</sup>	EE <sup>-</sup>	139.19012	1.29
138.2	138.21098	5.7	[M-C <sub>6</sub> H <sub>14</sub> ] <sup>-</sup>	[C <sub>3</sub> <sup>10</sup> B <sub>9</sub> H <sub>12</sub> ] <sup>-</sup>	EE <sup>-</sup>	138.21088	0.72

<sup>a</sup> See Fig. 3(D).<sup>b</sup> Nominal mass of the *nido*-carborane MS ions.<sup>c</sup> Experimental value of *nido*-carborane ions.<sup>d</sup> Relative intensity in the mass spectra.<sup>e</sup> Even or odd electron species.<sup>f</sup> Mass accuracy in parts per million (ppm) with external calibration.

denoted as [M]<sup>-</sup>. As the theoretical mass of the [C<sub>9</sub><sup>10</sup>B<sub>9</sub>H<sub>26</sub>]<sup>-</sup> anion is 224.32043, an excellent accuracy of -0.6 ppm ( $\Delta m = -0.00014$  *m/z* units) was obtained. Usually, changes in the tube lens voltage affect the ion transmittance through the intermediate vacuum region of the ESI interface employed. Interestingly, the degree of fragmentation can be influenced by the tube lens voltage; in fact, as reported by Catinella *et al.*,<sup>22</sup> the possibility of fragmentation outside the ion trap cannot be ruled out due to the quite long transfer path between the entrance capillary and the ion trap. In such a path some solvent molecules are present that would be highly effective in the activation and subsequent decomposition processes. We thus examined the mass spectrometric behavior of <sup>10</sup>B *nido*-carboranes **1–5** as a function of the tube lens voltage. The tube lens voltage can be varied to a certain extent without making the mass spectrum bad owing to poor focusing conditions. Negative ion ESI mass spectra of **1**, **3** and **5** at a tube lens setting of -140 V are shown in Figs. 3(B), 3(D) and 3(F), respectively. As can be seen, a slight change in this instrumental parameter leads to ions additional to the even-electron (EE) molecular ion [M]<sup>-</sup>. Again considering the data of compound **3** at *m/z* 224.32038, four ions were observed at *m/z* 222.30483, 220.28913, 218.27338 and 216.25778 which

correspond to [M-H<sub>2</sub>]<sup>-</sup>, [M-2H<sub>2</sub>]<sup>-</sup>, [M-3H<sub>2</sub>]<sup>-</sup> and [M-4H<sub>2</sub>]<sup>-</sup> species (see Table 1). The mass spectrum seemed to indicate the sequential loss of molecular hydrogen (2.01565 Da) in the gas phase from the *nido*-carborane species, by the effects of the relatively high voltage of the tube lens. This hydrogen removal was also reported by Slepukhina *et al.* while studying the protonated form of the [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> ion.<sup>23</sup>

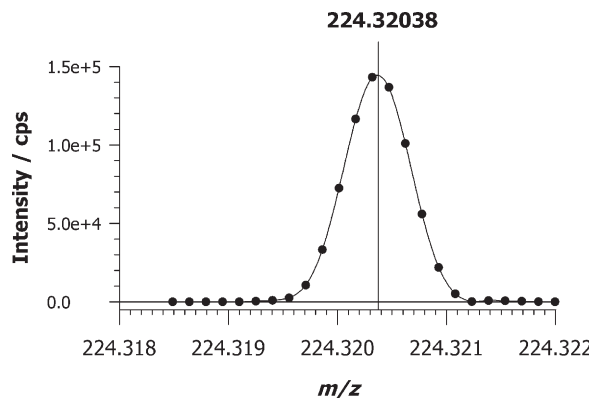
In the mass spectra obtained at a high voltage setting of the tube lens (Figs. 3(D) and 3(F)), additional ions appear that result from significant fragmentation. The various ions formed in the mass spectra of **3** are summarized in Table 1, where the accurate mass data for the ions (measured *m/z* values) and their relative signal intensities are listed. In the same table are also given the assignment for each ion in the mass spectrum, the corresponding ion formula along with the even/odd electron parity and finally the evaluated mass accuracy. We achieved average absolute mass deviations of 0.23 ppm (standard deviation 0.99 ppm) and maximum deviations of less than 2.1 ppm. The result of the current ESI-MS analysis demonstrates the occurrence of odd-electron (OE) species, whereas ESI, which is initiated by a charge site, normally generates mostly EE fragment ions.<sup>24</sup> OE dissociations, which involve homolytic bond cleavages

and the formation of radical product ions, are much less common for CID under ESI and atmospheric pressure chemical ionization (APCI) conditions.<sup>25</sup> Examples of OE product ions being formed in CID have occasionally been reported for compounds such as aromatic sulfonamides,<sup>26</sup> conjugated oximes,<sup>27</sup> flavonoid *O*-glycosides,<sup>28,29</sup> and aromatic ethers.<sup>30</sup> In the mass spectrum of **3** (see Table 1) some ions do occur at odd-numbered *m/z* values and these OE species are presumably formed by elimination of neutral radicals such as CH<sub>3</sub><sup>•</sup>, C<sub>2</sub>H<sub>5</sub><sup>•</sup>, C<sub>3</sub>H<sub>7</sub><sup>•</sup> and C<sub>4</sub>H<sub>9</sub><sup>•</sup>. This loss of neutral radicals results mainly from simple C–C bond fission, thus suggesting cleavage of the alkyl chain. Some of these OE ions (e.g., *m/z* 191.25038 and 165.23477) were observed at relatively high signal intensity. Another unusual feature was the repeated loss of both dihydrogen and borane molecules from [M]<sup>−</sup> to give [M–H<sub>2</sub>–BH<sub>3</sub>]<sup>−</sup> (C<sub>9</sub><sup>10</sup>B<sub>8</sub>H<sub>21</sub>) and [M–2H<sub>2</sub>–BH<sub>3</sub>]<sup>−</sup> (C<sub>9</sub><sup>10</sup>B<sub>8</sub>H<sub>19</sub>) ions at *m/z* 209.26871 and 207.25301, respectively.

All <sup>10</sup>B *nido*-carborane compounds **1–5** were analyzed by LC/ESI-FTICR-MS in negative ion mode and the data are listed in Table 2. The selected mass spectra were examined at the apex of each chromatographic peak. The theoretical masses of the <sup>10</sup>B *nido*-carborane derivatives were calculated and compared: the mass accuracies were always lower than −1.5 ppm using external calibration regardless of the measured ion signal intensity. Under these experimental conditions, the measurements are more than sufficient for unambiguous identification of the chemical formulae. In Fig. 4 the high-resolution FTICR mass spectrum of the monoisotopic ion of **3** is illustrated, as an example, revealing excellent peak shape with a resolving power ( $R_{\text{FWHM}}$ ) greater than 300 000.

### MS evidence of H<sub>2</sub> removal from <sup>10</sup>B *nido*-carborane derivatives

To investigate whether the hydrogen loss originated from the polyhedral skeleton or from the alkyl moiety, the analysis of the mass spectrometric behavior of <sup>10</sup>B-7,8-dicarba-*nido*-undecaborane potassium salt derivatives with different alkyl chain lengths was crucial. As the tube lens voltage was increased from −90 to −140 V the appearance of ions indicative of hydrogen loss was seen in all the mass spectra of **1–5**. In detail, for **1** the loss of a single H<sub>2</sub> molecule was observed, for **2** three H<sub>2</sub> molecules and for **3**, **4** and **5** a maximum of four hydrogen molecules could be lost. Hence,



**Figure 4.** The evaluated resolving power ( $R_{\text{FWHM}} = m/\text{FWHM}$ ) of compound **3** at *m/z* 224.32038 was greater than  $3 \times 10^5$ . A 7-T ICR-MS instrument was employed.

increasing the alkyl chain length leads to an increased loss of hydrogen molecules, till a constant level of four H<sub>2</sub> molecules is reached for the six-carbon chain derivative and this remains constant as the alkyl chain length is increased further. It is important to mention that the interpretation of these results was significantly facilitated by the use of <sup>10</sup>B-enriched compounds as they provide high-quality ESI mass spectra, in which the intact anion was the dominant ion in the mass spectrum.

To ascertain the role of the polyhedral skeleton on this release of hydrogen, the same experiments were performed on the cognate compounds, i.e., decanoic acid and hexanoic acid, compounds having a polar head group and a nonpolar tail region, similar to the molecules under study (see Fig. S2 in Supporting Information). The mass spectra acquired at −90 V and −140 V tube lens voltage for the two fatty acids were undistinguishable, i.e., no hydrogen loss nor any fragmentation was observed when the tube lens voltage was increased. Such an observation confirms that hydrogen loss from the alkyl chain under soft ionization conditions is energetically likely only in the presence of a charged moiety having an energetically stabilizing effect, such as the *nido*-carborane cage. Further investigation is needed to understand the extent of this phenomenon.

Furthermore, to explain all the observed product ion profiles of the molecular ions of *nido*-carborane derivatives, i.e.,

**Table 2.** Accurate mass measurements and elemental formulae of <sup>10</sup>B *nido*-carborane monoanions examined by high-resolution ESI-FTICR-MS<sup>a</sup>

<sup>10</sup> B <i>nido</i> -carborane monoanions		Elemental formula	Calculated mass of [M] <sup>−</sup> ( <i>m/z</i> )	Measured <i>m/z</i> value <sup>b</sup>	mmu <sup>c</sup>	Accuracy (ppm) <sup>d</sup>
7-methyl-7,8- <i>nido</i> -undecaborane	<b>1</b>	[C <sub>3</sub> <sup>10</sup> B <sub>9</sub> H <sub>14</sub> ] <sup>−</sup>	140.22653	140.22631	−0.22	−1.57
7-methyl-8- <i>n</i> -butyl-7,8- <i>nido</i> -undecaborane	<b>2</b>	[C <sub>7</sub> <sup>10</sup> B <sub>9</sub> H <sub>22</sub> ] <sup>−</sup>	196.28913	196.28883	−0.30	−1.53
7-methyl-8- <i>n</i> -hexyl-7,8- <i>nido</i> -undecaborane	<b>3</b>	[C <sub>9</sub> <sup>10</sup> B <sub>9</sub> H <sub>26</sub> ] <sup>−</sup>	224.32043	224.32038	−0.05	−0.22
7-methyl-8- <i>n</i> -octyl-7,8- <i>nido</i> -undecaborane	<b>4</b>	[C <sub>11</sub> <sup>10</sup> B <sub>9</sub> H <sub>30</sub> ] <sup>−</sup>	252.35173	252.35133	−0.40	−1.59
7-methyl-8- <i>n</i> -decyl-7,8- <i>nido</i> -undecaborane	<b>5</b>	[C <sub>13</sub> <sup>10</sup> B <sub>9</sub> H <sub>34</sub> ] <sup>−</sup>	280.38303	280.38354	0.51	1.82

<sup>a</sup> See experimental conditions described in Fig. 2.

<sup>b</sup> Experimental value of monoanions acquired at −140 V tube lens voltage (i.e., high setting).

<sup>c</sup> Mass error in millimass units.

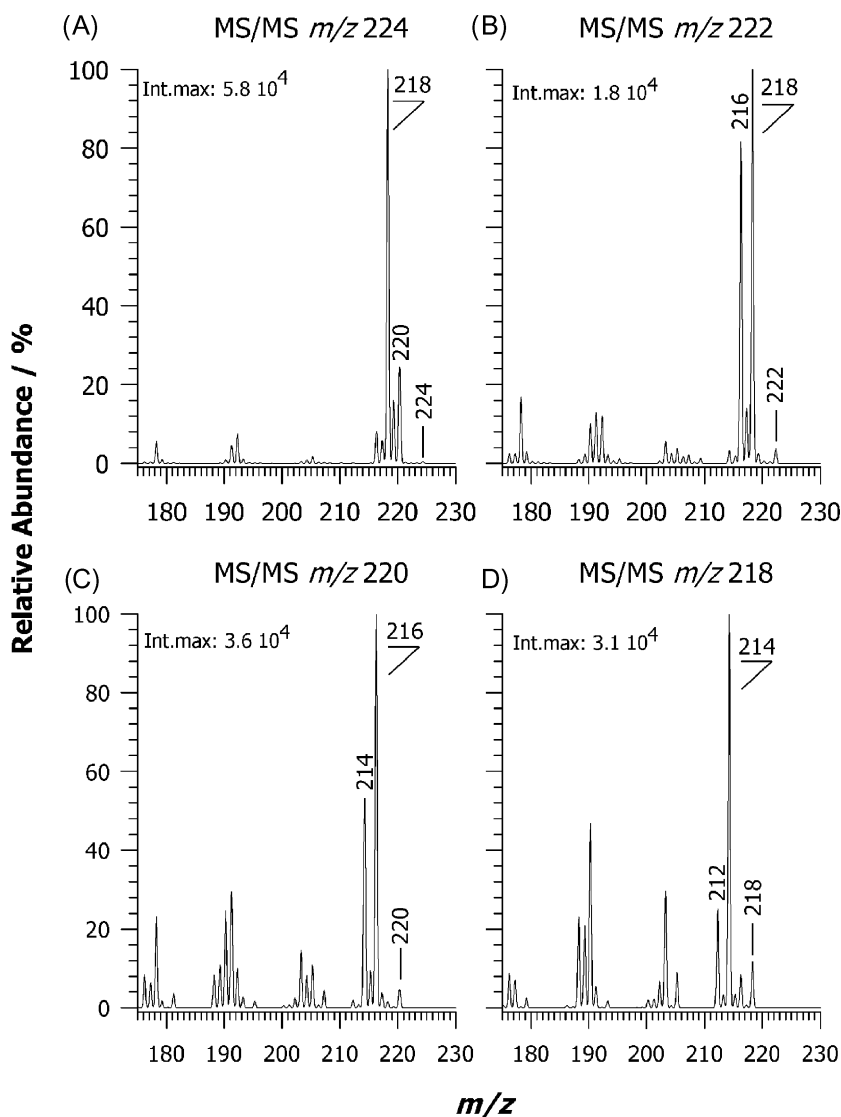
<sup>d</sup> Accuracy expressed in terms of parts per million (ppm), ppm =  $10^6 \Delta m/m$ , where  $\Delta m$  is the difference between the observed and calculated mass.

the formation of ions involving loss of hydrogen, the 'charge-remote fragmentation' (CRF) mechanism cannot be evoked.<sup>31</sup> Indeed, the CRF mechanism is typically suggested for fragmentation reactions under high-energy (i.e., keV)<sup>32</sup> collisional activation in closed-shell ions such as fatty acid carboxylate anions. Multiple dehydrogenation was observed only in previous mass spectrometric studies performed to investigate gas-phase ion/molecule reactions of *o*-carborane (12) (*o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) neutrals and cations.<sup>33</sup>

### MS/MS of <sup>10</sup>B *nido*-carborane derivatives

When an ion with a high translational energy undergoes an inelastic collision with a neutral, part of the translational energy is converted into internal energy of the ion, leading to subsequent decomposition. CID has been described as a two-step phenomenon of excitation (activation) by collision where a fraction of an ion's kinetic energy is transferred into internal modes and this is followed by subsequent dissociation of the excited ion.<sup>34</sup> In an LTQ, the precursor

ions are isolated and accelerated by 'on-resonance' excitation causing collisions to occur and product ions are detected by subsequent ejection from the trap. MS/MS experiments using the LTQ analyzer were performed to obtain further information on the fragmentation behavior of the *nido*-carborane derivatives. As an example, the results obtained for compound **3** are shown in Fig. 5. Collisions between the precursor [M]<sup>-</sup> ion at *m/z* 224 (see Fig. 5(A)) and the neutral target gas are accompanied by an increase in internal energy, which induces decomposition. Two common product ions, [M-2H<sub>2</sub>]<sup>-</sup> and [M-3H<sub>2</sub>]<sup>-</sup>, were yielded by elimination of H<sub>2</sub> molecules and formation of [M-4]<sup>-</sup> and [M-6]<sup>-</sup> ions at *m/z* 220 and 218, respectively. As expected, the *m/z* 220 and 218 ions do not only stem from applying a relatively high tube lens voltage, but can also be formed under conventional CID conditions. The same experiments were performed on the precursor ions at *m/z* 222 ([M-H<sub>2</sub>]<sup>-</sup>), 220 ([M-2H<sub>2</sub>]<sup>-</sup>) and 218 ([M-3H<sub>2</sub>]<sup>-</sup>) obtained in the ESI process (see Figs. 5(B), 5(C) and 5(D)), and yet again the molecular hydrogen loss was



**Figure 5.** Negative-ion ESI-MS/MS product ion spectra of precursor ions at *m/z* 224 (A), 222 (B), 220 (C), and 218 (D), which correspond to [M]<sup>-</sup>, [M-H<sub>2</sub>]<sup>-</sup>, [M-2H<sub>2</sub>]<sup>-</sup> and [M-3H<sub>2</sub>]<sup>-</sup>, respectively. The ions of each spectrum are normalized to the most abundant ion. The CID experiments were carried out on a LTQ mass spectrometer.

corroborated. A similar mass spectrometric behavior was confirmed for compounds **1**, **2**, **4** and **5** (data not shown).

CID-MS experiments were performed on both deprotonated fatty acids, decanoic and hexanoic; mass spectra were acquired at 30% collision energy (a.u.). The major ions in the product ion spectrum of both acids comprised the [M-H]<sup>-</sup> precursor ions along with those formed by the loss of water and carbon dioxide from the carboxylic group (see Fig. S3 in Supporting Information). Interestingly, no product ions indicative of hydrogen loss from these compounds were observed. Increasing the collision energy produced progressively less signal intensity for all the ions in agreement with previously published results.<sup>35</sup>

These findings are an additional proof for the stabilizing effect of *nido*-dicarborane skeletons on the release of H<sub>2</sub> molecules from the alkyl chains. Although the actual initiation site on the carbon chain still remains to be identified, the current results suggest that the -CH<sub>2</sub>- moieties close to the *nido*-dicarborane skeleton are the most possible candidates. Therefore, the stabilization effect of *nido*-dicarborane skeletons either along with a relatively high voltage setting of the tube lens or the collisional effects of the target gas in the quadrupole linear trap triggers a process of H<sub>2</sub> release. Owing to such a capability these compounds are likely to provide an effective alternative as molecular hydrogen-storage molecules.<sup>36,37</sup>

## CONCLUSIONS

We have shown that *nido*-carboranes can be easily analyzed by negative ion electrospray ionization mass spectrometry. The outstanding feature of the mass spectrometric results is the repeated elimination of one up to four hydrogen molecules per *nido*-carborane unit, and this brings an excellent opportunity to exploit these alkyl derivatives for the safe storage of molecular hydrogen. In order to clarify the structural and electronic factors governing the multiple release of dihydrogen by *nido*-carborane-based clusters, experimental and theoretical studies will be performed in our laboratories on the design, synthesis, and characterization of new boron-containing polyhedral systems.

## SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

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