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# Mono- and di-cationic hydrido boron compounds †‡

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Brønsted acid HNTf<sub>2</sub> (Tf = SO<sub>2</sub>CF<sub>3</sub>) mediated dehydrogenative hydride abstraction from (L<sup>1</sup>)BH<sub>3</sub> (**3**) and (L<sup>2</sup>)BH<sub>3</sub> (**4**) (L<sup>1</sup> = IPrCH<sub>2</sub> = 1,3-(2,6-di-isopropylphenyl)imidazol-2-methylidene (**1**); L<sup>2</sup> = SIPrCH<sub>2</sub> = 1,3-(2,6-di-isopropylphenyl)imidazol-2-methylidene (**1**); L<sup>2</sup> = SIPrCH<sub>2</sub> = 1,3-(2,6-di-isopropylphenyl)imidazolidin-2-methylidiene (**2**)) affords thermally stable hydride bridged monocationic hydrido boron compounds [{(L<sup>1</sup>)BH<sub>2</sub>}<sub>2</sub>( $\mu$ -H)](NTf<sub>2</sub>) (**5**) and [{(L<sup>2</sup>)BH<sub>2</sub>}<sub>2</sub>( $\mu$ -H)](NTf<sub>2</sub>) (**6**). Furthermore, hydride abstraction yields di-cationic hydrido boron compounds [{(L<sup>1</sup>)BH}<sub>2</sub>( $\mu$ -H)<sub>2</sub>](NTf<sub>2</sub>)<sub>2</sub> (**7**) and [{(L<sup>2</sup>)-BH}<sub>2</sub>( $\mu$ -H)<sub>2</sub>](NTf<sub>2</sub>)<sub>2</sub> (**8**). Unique cationic boron compounds with CH<sub>2</sub>BH<sub>2</sub>( $\mu$ -H)BH<sub>2</sub>CH<sub>2</sub> (**5** and **6**) and CH<sub>2</sub>BH( $\mu$ -H)<sub>2</sub>BHCH<sub>2</sub> (**7** and **8**) moieties feature a 3c-2e bond and have been fully characterized. Interesting electronic and structural features of compounds **5–8** are analysed using spectroscopic, crystallographic, and computational methods.

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# Introduction

Investigation of thermally stable exotic main group compounds with elusive chemical and electronic properties has been a subject of considerable research interest.<sup>1</sup> Boron compounds play an important role in organic synthesis and materials science.<sup>2</sup> The search for new boron compounds with unique bonding motifs and electronic structures has been a major focus in molecular main group chemistry.<sup>3</sup> A variety of mono-cationic boron compounds such as borinium  $[R_2B]^+$ , borenium  $[(L)R_2B]^+$ , and boronium  $[(L)_2R_2B]^+$  species (L = a)neutral ligand) have been isolated and characterized.<sup>2c,4</sup> Recent studies have demonstrated a remarkable activity of borenium compounds in Lewis acid catalysis as well as in the functionalization of small molecules.<sup>2c,5</sup> Interestingly, so far only a few di-cationic boron compounds, in particular with a hydride ligand, have been isolated and adequately characterized (Scheme 1).4c,6

<sup>b</sup>Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany Cowley et al. reported the first hydrido boron di-cation (A)

stabilized by a pyridine ligand (Scheme 1).<sup>6f</sup> A direct B-B coup-

ling reaction of a mono-cationic species to afford a di-cationic

boron compound (B) stabilized by a cyclic guanidine ligand







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<sup>†</sup>This paper is dedicated to Professor Manfred Scheer on the occasion of his 60th birthday.

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Scheme 2 Synthesis of NHO-borane compounds 3 and 4.

N-heterocyclic carbenes (NHCs). Curran *et al.* employed an NHC and isolated a hydride-bridged boron di-cation (C).<sup>6b</sup> A carbodicarbene stabilized hydrido boron di-cation (D) has been reported very recently by Ong and co-workers.<sup>6a</sup>

While the flanking substituents at the imidazole nitrogen atoms of an NHC are well endowed to encapsulate a reactive species to be stabilized, but they may prevent its accessibility for further reactions.<sup>3n,13</sup> Moreover, NHC-coordinated main group species sometimes do not exhibit the expected reactivity owing to the diminished electrophilicity. This is due to the strong NHC-element interaction. To circumvent this situation and to expand the scope of reactive main group species to functionalize organic substrates, we became interested in the new class of carbon-donor ligands.<sup>14</sup> N-Heterocyclic olefins (NHOs) and their borane adducts were already known as early as in 1993,<sup>15</sup> interest in this class of ligands incited us very recently.<sup>16</sup> NHOs (1 and 2, Scheme 2) are strong nucleophiles but rather weak electron donors (Lewis bases) than NHCs.<sup>17</sup> Therefore, NHOs readily react with a NHC-stabilized dichlorosilvlene (IPr)SiCl<sub>2</sub> to furnish silvl-functionalized NHOs and liberate free IPr (IPr = 1,3-(2,6-di-isopropylphenyl)imidazol-2ylidene).<sup>18</sup> Similarly, KC<sub>8</sub> reduction of (NHO)BRX<sub>2</sub> (R = I or Ph; X = Cl or I) compounds led to the insertion of a borylene into a C-N bond to yield boryl-functionalized NHOs.<sup>14b</sup> Herein, we report on a very facile route to NHO-stabilized mono- and dicationic hydrido boron compounds featuring [CH<sub>2</sub>BH<sub>2</sub>(µ-H)- $BH_2CH_2$ ] and  $[CH_2BH(\mu-H)_2BHCH_2]$  bonding motifs. Synthesis, characterization, reactivity, structure, and computational analysis of these compounds are presented.

### Results and discussion

The reaction of an NHO  $(L^1 \text{ or } L^2)$  with  $(\text{THF})\text{BH}_3$  quantitatively yields  $(L^1)\text{BH}_3$  (3) and  $(L^2)\text{BH}_3$  (4) as white solids  $(L^1 = \text{IPrCH}_2 (1) \text{ and } L^2 = \text{SIPrCH}_2 (2)$ ;  $\text{IPrCH}_2 = 1,3$ -(2,6-di-isopropylphenyl)-imidazol-2-methylidene and  $\text{SIPrCH}_2 = 1,3$ -(2,6-di-isopropylphenyl)imidazolidin-2-methylidiene) (Scheme 2). Treatment of compounds 3 and 4 with 0.5 eq. of bis(trifluoromethane)sulfonimide (HNTf\_2) readily affords mono-cationic hydrido boron compounds  $[\{(L^1)\text{BH}_2\}_2(\mu-\text{H})](\text{NTf}_2)$  (5) and  $[\{(L^2)\text{BH}_2\}_2(\mu-\text{H})](\text{NTf}_2)$  (6) in a high yield (Scheme 3).

Compounds 3–6 have been characterized by <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR as well as IR spectroscopic studies. The exocyclic methylene ( $CH_2$ ) group each in 3 and 4 appears as a broad signal in





Scheme 3 Synthesis of mono- and di-cationic hydrido boron compounds 5-8.

the <sup>1</sup>H NMR spectrum at  $\delta$  1.60 and  $\delta$  1.41 ppm, respectively. Each of compounds 5 ( $\delta$  -15.4) and 6 ( $\delta$  -16.4) exhibits a broad <sup>11</sup>B NMR signal, which is shifted towards downfield (*ca.* 14 ppm) when compared with the respective starting compound 3 ( $\delta$  -29.9) or 4 ( $\delta$  -29.5). Moreover, the <sup>11</sup>B NMR chemical shift, each for 5 and 6, is *ca.* 10 ppm downfield compared to NHC-analogues.<sup>6b</sup> This may be due to the lower basicity of L<sup>1</sup> and L<sup>2</sup> ligands than that of NHCs. Nevertheless, compounds 5 and 6 are stable both in solution (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>F, and 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) and solid phases at room temperature under an inert gas (Ar or N<sub>2</sub>) atmosphere.

Suitable single crystals for X-ray diffraction study were obtained by a slow diffusion of n-hexane into a saturated dichloromethane solution of 5 at room temperature. The solidstate structure of 5 revealed the formation of a hydride bridged mono-cationic boron compound (Fig. 1). The B-(µ-H)-B bond is apparently derived from a 3c-2e (three-center-two-electrons) interaction. The C(0)-B(0) bond length of 1.630 Å in 5 is slightly shorter than that of 4 (1.68 Å). The C(0)-C(1) bond lengths of 4 (1.452 Å) and 5 (1.467) are comparable with  $C(sp^2)$ – $C(sp^3)$  single bond distances. All hydrogen atoms near the boron atom were located on difference Fourier maps and refined isotropically as independent atoms. Due to experimental restrictions, all B-H distances are underestimated. The electron density of hydrogen is always shifted towards the bonding partner and due to the lack of core electrons, a shortened B-H bond length is obtained in the IAM refinement.<sup>19</sup>

In order to shed light into the electronic structures, we carried out DFT calculations (M06-2X/def2-SVP)<sup>20</sup> for **5** and **6**. The optimized bond lengths and angles of **5** are in good agreement with the experimental values (Fig. 1). A comparison of the calculated structures of **5** and **6** indicates (Fig. S2 in the ESI<sup>+</sup><sub>+</sub>) very similar geometries for the H<sub>2</sub>B–H–BH<sub>2</sub> moiety. Compound **6** presents a slightly longer B–µH bond length and more acute  $C_{(carbene)}$ –C–B angles than those in **5**. Based on the natural population analysis<sup>21</sup> (Table 1) the boron fragment B<sub>2</sub>H<sub>5</sub> is negatively charged by –0.23 e and –0.20 e for **5** and **6**,



Fig. 1 (a) Molecular structure of compound 5. Hydrogen atoms except those on the  $H_2B-H-BH_2$  moiety, isopropyl groups, and the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50% probability level. Boron bound hydrogen atoms were refined without restraints. Selected experimental and theoretical [M06-2X/def2-SVP] bond lengths [Å] and the bond angle [°]: B0-C0 1.630(2) [1.654], B0-H5B 1.260(11) [1.304], B0-H0BA 1.12(2) [1.211], B0-H0BB 1.09(2) [1.212], C0-C1 1.467(2) [1.465], B30-C30 1.633(2) [1.647], B30-H5B 1.27(2) [1.313], B30-H3BA 1.10(2) [1.213], B30-H3BB 1.10(12) [1.217], C30-C31 1.468(2) [1.468], C1-C0-B0 111.1(2) [109.3], C31-C30-B30 110.2(1) [107.7]. (b) Optimized structure (M06-2X/def2-SVP) of compound 5.

Table 1 NPA charges (Q) and Wiberg Bond Order (WBO) values of compounds 5-9 at M06-2X/def2-TZVPP

Compound	$Q(\mathbf{B})$	$Q(\mu H)$	$Q(\mathbf{C})$	$Q(C_{carb})$	$Q(\mathbf{N})$	WBO(B-µH)	WBO(C-B)	WBO(B-B)	WBO(C-C <sub>carb</sub> )
5	-0.10	+0.05	-0.73	+0.57	-0.35	0.49	0.83	0.29	1.08
6	-0.10	+0.03	-0.75	+0.69	-0.42	0.50	0.81	0.29	1.10
7	+0.11	+0.13	-0.78	+0.53	-0.33	0.46	0.91	0.64	1.05
8	+0.11	+0.13	-0.80	+0.66	-0.39	0.46	0.90	0.65	1.05
9	-0.08	—	-0.74	+0.69	-0.42	—	0.78	—	1.11

respectively. Additionally, natural bond orbital (NBO)<sup>22</sup> analysis reveals the presence of a 3c-2e bond (Tables S2 and S3<sup>‡</sup>) B- $\mu$ H-B where 47% is at the H atom and roughly 26% on each of the boron atoms. NBO results also point out that the ligands bind boron by C-B  $\sigma$ -bonds which are polarized toward the carbon end (~70% at C).

The reaction of **3** and **4** with HNTf<sub>2</sub> in a 1:1 molar ratio cleanly yields di-cationic hydrido boron compounds **7** and **8** (Scheme 3) as white solids. Compounds **7** and **8** are rather poorly soluble in CH<sub>2</sub>Cl<sub>2</sub> and 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub> but are freely dissolved in acetonitrile. The <sup>11</sup>B NMR spectrum of each of **7** (-19.89) and **8** (-19.78) exhibits a broad resonance, which is *ca.* 10 ppm downfield compared to that of **3** and **4**. The molecular structure of **8** is shown in Fig. 2. The BH<sub>2</sub>BH<sub>2</sub> core features two 3c-2e bonds with the B…B distance of 1.755 Å. This is actually similar to B…B distances in cationic (NHC)BH<sub>2</sub><sup>6b</sup> as well as in neutral RBH<sub>2</sub> dimers.<sup>23</sup> Similarly, the B…B distance in **8** is consistent with that of the parent B<sub>2</sub>H<sub>6</sub> determined by electron diffraction (1.77 Å)<sup>24</sup> or X-ray methods (1.78–1.79 Å).<sup>25</sup>

The exact location of the B–H hydrogen is uncertain due to the experimental restrictions. Nevertheless, DFT(M06-2X/def2-SVP) optimized structures present a reasonable agreement with the experimental structure (Fig. 2). The theoretically predicted B-H bond lengths are longer than the experimental values, which is a feature commonly observed between solidstate and theoretical structures which refer to isolated molecules.<sup>26</sup> The experimentally observed B-B distances are well represented by DFT calculations. The short B...B distances possibly indicate a weak bond. In fact, the B-B Wiberg Bond Indices (WBO in Table 1) are 0.64 au and 0.65 au for compounds 7 and 8, respectively. The increase in the bond order comes from the significantly shorter B-B distances in the dications. In this case, NBO calculations revealed the occurrence of two B-H-B 3c-2e bonds in the HB(µ-H)2BH moiety where 43% is located at the H bridges and ~28% at each boron atom (Tables S4 and S5<sup>‡</sup>). The NHO ligands have a C–B  $\sigma$ -bond where the polarization towards carbon is slightly lower (65% for 7 and 8) than that in 5 and 6. The calculated charge distribution for the latter di-cationic species suggests that a positive charge of roughly +1.5 e resides at the NHO ligands. The somewhat counter intuitive charge at the boron atom can be rationalized in terms of the donor-acceptor bonding model<sup>27</sup> which has successfully been used to explain the structure of boron compounds<sup>3m,28</sup> and to predict new boron molecules with unusual bonding situations.3k,30,29 Compounds 5-8 may be formally considered as complexes where a charged central



**Fig. 2** (a) Molecular structure of compound **8**. Hydrogen atoms except those on the HBHHBH moiety, isopropyl groups, and the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50% probability level. Boron bound hydrogen atoms were refined without restraints. Selected experimental and theoretical [M06-2X/def2-SVP] bond lengths [Å] and the bond angle [°]: B1–C2 1.601(4) [1.593], B1–B1#1 1.755(7) [1.762], B1–H1 1.07(3)) [1.196], B1–H2 1.28(3) [1.330], C2–C3 1.488(3) [1.479], C2–B1–B1#1 123.6(3) [123.5], C3–C2–B1 118.6(2) [115.7]. (b) Optimized structure (M06-2X/def2-SVP) of compound **8**.



Scheme 4 Reaction of 8 with L<sup>2</sup> to boronium ion 9.

boron fragment ( $B_2H_5^+$  in the mono-cations and  $B_2H_4^{2+}$  in the di-cations) serves as an acceptor and the NHOs serve as donors, NHO  $\rightarrow B_2H_n^{\ q} \leftarrow$  NHO. The strong charge donation leads to negative charges at boron in the cations 5 and 6 and to rather small positive charges in the di-cations 7 and 8. A negative partial charge was previously found at the  $BH_2^+$  fragment in the cations (L  $\rightarrow BH_2 \leftarrow L_1^{+}$ .<sup>3m</sup>

Treatment of 8 with two equivalents of the NHO (L<sup>2</sup>) leads to the clean formation of a boronium compound  $[(L^2)_2BH_2]$ - $[NTf_2]$  (9) (Scheme 4). The <sup>11</sup>B NMR spectrum of 9 shows a broad signal at  $\delta$  –23.8 ppm. While hydrogen atoms of the BH<sub>2</sub> group could not be located, the <sup>1</sup>H NMR spectrum of compound 9 exhibits a remarkably up-field signal ( $\delta$  0.34 ppm) for methylene ( $CH_2BH_2$ ) protons, which has been confirmed by a <sup>1</sup>H-<sup>13</sup>C-HSQC (heteronuclear single quantum coherence) experiment. Colourless crystals of 9 were obtained from a solution of dichloromethane/*n*-hexane (4 : 1) at room temperature. The molecular structure of 9 features a CH<sub>2</sub>BH<sub>2</sub>CH<sub>2</sub> moiety with the C-B-C angle of 109.22° (Fig. 3). The C-B bond distance of 1.69 Å is comparable to that of 8.

Compounds **3–9** exhibit characteristic absorption bands for the terminal  $\nu$ (B–H) stretching vibrations from 2230 to 2463 cm<sup>-1</sup>. IR absorption bands in the 1561–1594 cm<sup>-1</sup> region may be assigned for the bridging  $\nu$ (B–H) vibrations.<sup>30</sup>



**Fig. 3** Molecular structure of compound **9**. Hydrogen atoms except those on the BH<sub>2</sub> moiety, isopropyl groups as well as the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50% probability level. Boron bound hydrogen atoms were refined without restraints. Selected experimental and theoretical [M06-2X/def2-SVP] bond lengths [Å] and the bond angle [°]: B1–C2 1.689(3) [1.693], B1–C32 1.690(3) [1.694], B1–H1 1.12(2) [1.226], B1–H2 1.12(2) [1.226], C2–C3 1.456(3) [1.455], C32–C33 1.459(3) [1.455], C2–B1–C32 109.2(2) [109.2], C3–C2–B1 111.9(2) [107.8], C33–C32–B1 110.5(2) [107.6].

## Experimental

All syntheses and manipulations were carried out under an inert atmosphere of dry argon or nitrogen gas using Schlenk line techniques and a glove box.  $CD_2Cl_2$ ,  $CH_2Cl_2$ ,  $o-Cl_2C_6D_4$  and  $o-Cl_2C_6H_4$  (over  $CaH_2$ ),  $C_6D_6$  and THF (over K-benzophenone ketyl) were dried and distilled under a dry argon atmosphere prior to use. All other solvents were dried and purified

by using a MBRAUN solvent purification system (MB SPS 800). <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance III 300 or a Bruker Avance DRX 500 spectrometer. ESI mass spectra were recorded with a Bruker micrOTOF or a Bruker maXis spectrometer. Melting points were measured with a Büchi Melting Point B-540 apparatus. Elemental analyses were performed at the Institute for Inorganic Chemistry, Universität Göttingen. (THF)BH<sub>3</sub> (Aldrich) and HNTf<sub>2</sub> (Aldrich) were used without further purification. SIPrCH<sub>2</sub> (L<sup>1</sup>) (1) and IPrCH<sub>2</sub> (L<sup>2</sup>) (2) were prepared by adopting the reported methods.<sup>14b,31</sup>

#### Synthesis and characterization of compounds 3-9

 $(L^1)BH_3$  (3). A 1 M THF solution of  $(THF)BH_3$  (3.6 mL, 3.60 mmol) was added to an *n*-hexane solution of  $L^{1}$  (1) (1.44 g, 3.57 mmol) at room (25 °C) temperature. The resulting white slurry was stirred for 4 h. Filtration through a glass frit afforded a white solid, which was washed with 20 mL n-hexane and dried under vacuum to yield 3 (1.34 g, 90%). Colorless crystals of 2 were grown from a 20 mL  $CH_2Cl_2/n$ -hexane (1:1) solution. Mp.: 201 °C. MS (ESI, m/z [M]): 415.33 [M - H]<sup>+</sup>, 416.33  $[M]^+$ . Elemental analysis for C<sub>28</sub>H<sub>41</sub>N<sub>2</sub>B (416): C 80.75, H 9.92, N 6.73; found C 80.44, H 9.85, N 6.68. IR (cm<sup>-1</sup>): 2960, 2871, 2322, 2258, 2230, 1560. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  1.16 (d, 12H, J = 6.8 Hz, HCMe<sub>2</sub>); 1.36 (d, 12H, J =6.8 Hz, HCMe<sub>2</sub>); 1.60 (br, 2H, CCH<sub>2</sub>); 2.70 (sept, 4H, J = 6.8 Hz,  $HCMe_2$ ; 6.98 (s, 2H, NCH); 7.36 (d, 4H, I = 7.9 Hz,  $m-C_6H_3$ ); 7.56 (t, 2H, J = 7.7 Hz, p-C<sub>6</sub> $H_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 16.55 (CCH<sub>2</sub>); 22.97, 26.02 (HCMe<sub>2</sub>); 29.49 (HCMe<sub>2</sub>); 121.55 (NCH); 125.13  $(m-C_6H_3)$ ; 131.50, 131.98  $(p-C_6H_3)$ ;  $o-C_6H_3$ ; 146.66 (*ipso-C*<sub>6</sub>H<sub>3</sub>); 165.41 (*C*CH<sub>2</sub>) ppm. B{<sup>1</sup>H}NMR (96 MHz,  $CD_2Cl_2$ , 25 °C):  $\delta$  –29.89 ppm. <sup>11</sup>B NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  –29.89 (q,  $J_{B-H}$  = 85.43 Hz) ppm.

Synthesis of  $(L^2)BH_3$  (4). Compound 4 was prepared by adopting a similar method as described for 3 using  $L^2$  (2) (1.37 g, 3.38 mmol) and (THF)BH<sub>3</sub> (3.4 mL, 3.4 mmol) as colorless crystals (1.20 g, 84%). Mp.: 202 °C. MS (ESI, m/z [M]): 417.34  $[M - H]^+$ , 418.34  $[M]^+$ . Elemental analysis for C<sub>28</sub>H<sub>43</sub>N<sub>2</sub>B (418): C 80.36, H 10.36, N 6.69; found C 79.98, H 9.96, N 6.67. IR (cm<sup>-1</sup>): 2924, 2854, 2347, 2273, 2239, 1531. <sup>1</sup>H NMR (300 MHz,  $CD_2Cl_2$ , 25 °C):  $\delta$  1.29 (d, 12H, J = 6.9 Hz, HCMe<sub>2</sub>); 1.34 (br, 2H, CCH<sub>2</sub>); 1.41 (d, 12H, J = 6.7 Hz, HCMe<sub>2</sub>); 3.22 (sept, 4H, J = 6.8 Hz,  $HCMe_2$ ); 4.07 (s, 4H,  $NCH_2$ ); 7.32 (d, 4H, J = 7.5 Hz, m-C<sub>6</sub> $H_3$ ); 7.46 (t, 2H, J = 7.7 Hz, p-C<sub>6</sub> $H_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 18.46 (CCH<sub>2</sub>); 23.72, 26.37  $(HCMe_2)$ ; 29.39  $(HCMe_2)$ ; 51.71  $(NCH_2)$ ; 125.39  $(m-C_6H_3)$ ; 130.56, 132.60 (*p*-C<sub>6</sub>H<sub>3</sub>, *o*-C<sub>6</sub>H<sub>3</sub>); 147.60 (*ipso*-C<sub>6</sub>H<sub>3</sub>); 183.07 (CCH<sub>2</sub>) ppm.  $^{11}B{^1H}$  NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ –29.51 ppm. <sup>11</sup>B NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ –29.51  $(q, J_{B-H} = 88.28 \text{ Hz}) \text{ ppm.}$ 

 $[{(L^1)BH_2}_2(\mu_2-H)]NTf_2$  (5). To a 50 mL Schlenk flask containing 3 (0.50 g, 1.2 mmol) and HNTf<sub>2</sub> (0.17 g, 0.6 mmol) was added 10 mL of *o*-dichlorobenzene at room temperature. Effervescence indicated the formation of a gas (apparently H<sub>2</sub>). Further stirring at room temperature for 2 h afforded a colorless clear solution, which was combined with 20 mL of *n*-hexane. A white residue was separated out, which was washed with 5 mL of *n*-hexane and dried under vacuum to obtain compound 5 as a white solid (0.40 g, 60%). Mp.: 210 °C. MS (ESI, *m*/*z* [M]): 831.66 [M\*]<sup>+</sup> (M\* = cationic unit). Elemental analysis for C<sub>58</sub>H<sub>81</sub>N<sub>5</sub>B<sub>2</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub> (1112): C 62.64, H 7.34, N 6.30; found C 62.33, H 7.21, N 6.18. IR (cm<sup>-1</sup>): 2924, 2854, 2463, 2412, 2067, 1565. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 1.13 (*pseudo*-t, 24H, HC*Me*<sub>2</sub>); 1.53 (br, 2H, CC*H*<sub>2</sub>); 2.31 (sept, 4H, *J* = 6.8 Hz, *H*CMe<sub>2</sub>); 7.08 (s, 2H, NC*H*); 7.29 (d, 4H, *J* = 7.8 Hz, *m*-C<sub>6</sub>H<sub>3</sub>); 7.55 (t, 2H, *J* = 7.8 Hz, *p*-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 15.08 (CCH<sub>2</sub>); 22.86, 25.78 (HC*Me*<sub>2</sub>); 29.47 (HCMe<sub>2</sub>); 122.91 (NCH); 125.27 (*m*-C<sub>6</sub>H<sub>3</sub>); 130.84, 132.13 (*p*-C<sub>6</sub>H<sub>3</sub>, *o*-C<sub>6</sub>H<sub>3</sub>); 146.03 (*ipso*-C<sub>6</sub>H<sub>3</sub>); 158.67 (CCH<sub>2</sub>) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ -15.43 ppm. <sup>19</sup>F (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) = δ -79.52 ppm.

 $[{(L<sup>2</sup>)BH<sub>2</sub>}_2(\mu_2-H)]NTf_2$  (6). Compound 6 was prepared by adopting a similar method as discussed for compound 5 using 4 (0.26 g, 0.62 mmol) and HNTf2 (0.08 g, 0.31 mmol) as a white solid (0.19 g, 55%). Mp.: 211 °C. MS (ESI, m/z [M]): 835.70  $[M^*]^+$  (M<sup>\*</sup> = cationic unit). Elemental analysis for C<sub>58</sub>H<sub>85</sub>N<sub>5</sub>B<sub>2</sub>F<sub>6</sub>O<sub>4</sub>S<sub>2</sub> (1116): C 62.42, H 7.68, N 6.28; found C 61.77, H 7.51, N 6.16. IR (cm<sup>-1</sup>): 2932, 2844, 2459, 2420, 2053, 1560. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 1.17 (d, 12H, J = 6.8 Hz, HCMe<sub>2</sub>); 1.20 (br, 2H, CCH<sub>2</sub>); 1.24 (d, 12H, J =6.8 Hz, HCMe<sub>2</sub>); 2.84 (sept, 4H, J = 6.8 Hz, HCMe<sub>2</sub>); 4.05 (s, 4H, NCH<sub>2</sub>); 7.23 (d, 4H, J = 7.8 Hz, m-C<sub>6</sub>H<sub>3</sub>); 7.41 (t, 2H, J = 7.7 Hz, *p*-C<sub>6</sub> $H_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  16.56 (CCH<sub>2</sub>); 23.63, 26.22 (HCMe<sub>2</sub>); 29.39 (HCMe<sub>2</sub>); 52.08 (NCH<sub>2</sub>); 125.57, 126.30  $(m-C_6H_3)$ ; 131.34, 131.27, 132.52  $(p-C_6H_3)$ o-C<sub>6</sub>H<sub>3</sub>); 147.88, 147.12 (*ipso-C*<sub>6</sub>H<sub>3</sub>); 178.33 (CCH<sub>2</sub>) ppm. <sup>11</sup>B  ${}^{1}H$  NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  -16.38 ppm.  ${}^{19}F$  $(282 \text{ MHz}, \text{CD}_2\text{Cl}_2, 25 \text{ °C}) = \delta - 79.53 \text{ ppm}.$ 

 $[{(L^1)BH_2}_2](NTf_2)_2$  (7). To a 50 mL Schlenk flask containing 3 (0.66 g, 1.57 mmol) and HNTf<sub>2</sub> (0.44 g, 1.57 mmol) was added 20 mL of fluorobenzene at room temperature. Further stirring at room temperature for 4 h afforded a white suspension, which was combined with 10 mL of n-hexane. A white solid was separated out, which was washed with 5 mL of n-hexane and dried under vacuum to obtain compound 7 (0.82 g, 74%). Mp.: 202 °C. Elemental analysis for C<sub>60</sub>H<sub>80</sub>N<sub>6</sub>B<sub>2</sub>F<sub>12</sub>O<sub>8</sub>S<sub>4</sub> (1391): C 51.80, H 5.80, N 6.04; found C 51.10, H 5.62, N 5.75. IR (cm<sup>-1</sup>): 2920, 2854, 2723, 2600, 2369, 1589, 1561. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 25 °C): δ 1.20 (d, 12H, J = 6.8 Hz, HCMe<sub>2</sub>); 1.33 (d, 12H, J = 6.8 Hz, HCMe<sub>2</sub>); 1.78 (br, 2H, CCH<sub>2</sub>); 2.44 (sept, 4H, J = 6.8 Hz, HCMe<sub>2</sub>); 7.50 (d, 4H, J = 7.9 Hz, m-C<sub>6</sub> $H_3$ ); 7.53 (s, 2H, NCH); 7.65 (t, 2H, J = 7.3 Hz,  $p-C_6H_3$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  15.49 (CCH<sub>2</sub>); 22.71, 25.54 (HCMe<sub>2</sub>); 29.95 (HCMe<sub>2</sub>); 125.87 (NCH); 126.30  $(m-C_6H_3)$ ; 131.33, 132.81  $(p-C_6H_3, o-C_6H_3)$ ; 146.78  $(ipso-C_6H_3)$ ; 157.03 (CCH<sub>2</sub>) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$ -19.89 ppm. <sup>19</sup>F (282 MHz, CD<sub>3</sub>CN, 25 °C) =  $\delta$  -80.16 ppm.

 $[{(L^2)BH_2}_2](NTf_2)_2$  (8). Under similar experimental conditions as described for 7, treatment of 4 (0.27 g, 0.64 mmol) with HNTf\_2 (0.18 g, 0.64 mmol) afforded compound 8 as a white solid (0.39 g, 86%). Mp.: 197 °C. MS (ESI, *m*/*z* [M]): 834.68, 833.68 [M\*]<sup>+</sup> (M\* = cationic unit). Elemental analysis

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for C<sub>60</sub>H<sub>84</sub>N<sub>6</sub>B<sub>2</sub>F<sub>12</sub>O<sub>8</sub>S<sub>4</sub> (1395): C 51.65, H 6.07, N 6.02; found C 51.22, H 5.85, N 5.95. IR (cm<sup>-1</sup>): 2924, 2836, 2724, 2584, 2365, 1594, 1564. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  1.31 (d, 12H, *J* = 6.8 Hz, HC*Me*<sub>2</sub>); 1.36 (d, 12H, *J* = 6.8 Hz, HC*Me*<sub>2</sub>); 1.44 (br, 2H, CC*H*<sub>2</sub>); 3.06 (sept, 4H, *J* = 6.8 Hz, *H*CMe<sub>2</sub>); 4.21 (s, 4H, NC*H*<sub>2</sub>); 7.41 (d, 4H, *J* = 7.8 Hz, *m*-C<sub>6</sub>*H*<sub>3</sub>); 7.52 (t, 2H, *J* = 7.7 Hz, *p*-C<sub>6</sub>*H*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  16.82 (CC*H*<sub>2</sub>); 23.54, 26.24 (HC*Me*<sub>2</sub>); 29.70 (HCMe<sub>2</sub>); 52.65 (NCH<sub>2</sub>); 126.19, 126.59 (*m*-C<sub>6</sub>H<sub>3</sub>); 131.33, 131.94, 132.61 (*p*-C<sub>6</sub>H<sub>3</sub>, *o*-C<sub>6</sub>H<sub>3</sub>); 147.41, 147.88 (*ipso*-C<sub>6</sub>H<sub>3</sub>); 177.31 (CCH<sub>2</sub>) ppm. <sup>11</sup>B {<sup>1</sup>H} NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  -19.78 ppm. <sup>19</sup>F (282 MHz, CD<sub>3</sub>CN, 25 °C) =  $\delta$  -80.13 ppm.

[{(L<sup>2</sup>)<sub>2</sub>BH<sub>2</sub>}](NTf<sub>2</sub>)<sub>2</sub> (9). To a 50 mL fluorobenzene solution of 8 (2.50 g, 1.79 mmol) was added L<sup>2</sup> (1.45 g, 3.58 mmol) at room temperature and stirred for 4 h. Removal of the volatiles under vacuum afforded an off-white solid. The residue was dissolved in 20 mL of dichloromethane and 10 mL of *n*-hexane was added. The resulting solution was stored at 3 °C for two days to yield a colorless crystalline solid of compound 9 (2.70 g, 68%). Mp.: 273 °C. MS (ESI, *m*/*z* [M]): 821.67, 822.67, 820.67 [M\*]<sup>+</sup> (M\* = cationic unit). Elemental analysis for C<sub>58</sub>H<sub>82</sub>N<sub>5</sub>BF<sub>6</sub>O<sub>4</sub>S<sub>2</sub> (1102): C 63.20, H 7.50, N 6.35; found C 63.01, H 7.31, N 6.19. IR (cm<sup>-1</sup>): 2922, 2853, 2724, 2586, 1711, 1595, 1566. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 0.35 (br, 2H, CCH<sub>2</sub>); 0.98 (d, 12H, *J* = 6.7 Hz, HCMe<sub>2</sub>); 1.15 (d, 12H, *J* = 6.8 Hz, HCMe<sub>2</sub>); 2.76 (sept, 4H, *J* = 6.8 Hz, *H*CMe<sub>2</sub>); 3.96 (s, 4H, NCH<sub>2</sub>); 7.14 (d, 4H, J = 7.9 Hz, m-C<sub>6</sub>H<sub>3</sub>); 7.34 (t, 2H, J = 7.7 Hz, p-C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  22.53 (CCH<sub>2</sub>); 23.46, 26.56 (HCMe<sub>2</sub>); 29.49 (HCMe<sub>2</sub>); 51.58 (NCH<sub>2</sub>); 125.62 (m-C<sub>6</sub>H<sub>3</sub>); 131.06, 131.74 (p-C<sub>6</sub>H<sub>3</sub>, o-C<sub>6</sub>H<sub>3</sub>); 147.30 (*ipso*-C<sub>6</sub>H<sub>3</sub>); 181.15 (CCH<sub>2</sub>) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  -24.03 ppm. <sup>19</sup>F (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) =  $\delta$  -79.55 ppm.

#### Crystallographic details

Suitable single crystals were selected from the mother liquor under Schlenk conditions and covered with perfluorinated polyether oil on a microscope slide, which was cooled under a nitrogen gas flow using the X-Temp2 device.32 The diffraction data of compounds 5, 8 and 9 were collected at 100 K on a Bruker D8 three circle diffractometer, equipped with a SMART APEX II CCD detector and an INCOATEC microfocus source (Ag  $K_{\alpha}$  radiation) with INCOATEC Quazar mirror optics (Table 2). The diffraction data of compound 4 were collected at 100 K on a Bruker D8 three-circle diffractometer, equipped with a SMART APEX II CCD detector and an INCOATEC microfocus source (Mo  $K_{\alpha}$  radiation) with INCOATEC Quazar mirror optics. The data were integrated with SAINT<sup>33</sup> and a multi-scan absorption correction with SADABS<sup>34</sup> was applied. The structure solution was performed with SHELXT<sup>35</sup> and structure refinement was performed with SHELXL,<sup>36</sup> using the graphical user interface SHELXLE.37 All non-hydrogen atoms were

Table 2	Crystallographic and	structure refinement data	of compounds 4, 5, 8 and 9
	Crystattographic and	structure remiteriterit data	

Compound	4	5	8	9
CCDC number	1401734	1060035	1060034	1060033
Empirical formula	$C_{28}H_{43}BN_2$	$C_{58}H_{81}B_2F_6N_5O_4S_2$	C <sub>60.66</sub> H <sub>85.32</sub> B <sub>2</sub> Cl <sub>1.32</sub> F <sub>12</sub> N <sub>6</sub> O <sub>8</sub> S <sub>4</sub>	C <sub>67</sub> H <sub>89,50</sub> BF <sub>7,50</sub> N <sub>5</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight [g mol <sup>-1</sup> ]	418.45	1112.01	1451.24	1246.36
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.56086	0.56086	0.56086
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, P1	Triclinic, <i>P</i> 1	Triclinic, <i>P</i> 1
Unit cell dimensions [Å]	a = 11.624(2)	a = 10.754(2)	a = 12.306(2)	a = 13.061(3)
	b = 15.921(3)	b = 16.407(2)	b = 12.691(2)	b = 15.613(4)
	c = 14.028(2)	c = 18.510(2)	c = 13.389(2)	c = 16.727(4)
$\alpha$ [°]	90	83.78(2)	95.14(2)	96.88(2)
β[°]	99.23(2)	73.47(2)	101.53(2)	101.45(2)
γ [°]	90	83.41(2)	118.07(2)	98.29(2)
Volume [Å <sup>3</sup> ]	2562.5(8)	3100.4(4)	1766.6(6)	3269.2(14)
Z	4	2	1	2
Absorption coefficient [mm <sup>-1</sup> ]	0.062	0.085	0.146	0.088
F(000)	920	1184	760	1326
Crystal size [mm <sup>3</sup> ]	$0.100\times0.100\times0.100$	$0.195 \times 0.194 \times 0.104$	$0.317 \times 0.301 \times 0.110$	$0.180 \times 0.153 \times 0.079$
Theta range for data collection [°]	1.775 to 27.887	1.289 to 22.073	2.508 to 20.125	1.739 to 19.601
Reflections collected/unique	23 574/6095	238 549/15 500	52 767/6769	161 683/11 676
R <sub>int</sub>	0.0369	0.0605	0.0554	0.0810
Completeness	99.9	100.0	99.8	99.6
Max. and min. transmission	0.7456 and 0.7110	0.7447 and 0.7196	0.4251 and 0.3948	0.7444 and 0.6314
Data/restraints/parameters	6095/3/300	15 500/513/768	6769/1636/863	11 676/111/808
Goodness-of-fit on $F^2$	1.039	1.024	1.044	1.044
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0446,$	$R_1 = 0.0383,$	$R_1 = 0.0745,$	$R_1 = 0.0544,$
	$wR_2 = 0.1078$	$wR_2 = 0.0901$	$wR_2 = 0.2054$	$wR_2 = 0.1442$
R indices (all data)	$R_1 = 0.0631,$	$R_1 = 0.0550,$	$R_1 = 0.0956,$	$R_1 = 0.0737,$
	$wR_2 = 0.1167$	$wR_2 = 0.0999$	$wR_2 = 0.2259$	$wR_2 = 0.1589$
Largest diff. peak and hole $(e A^{-3})$	0.280 and -0.214	0.334 and -0.440	0.785 and -0.449	0.746 and -0.565

refined with anisotropic displacement parameters. All hydrogen atoms, except those bound to boron atoms, were assigned to ideal positions and refined using a riding model with  $U_{iso}$ constrained to 1.2 (1.5) times the  $U_{eq}$  value of the parent carbon atom. The positions of boron bound hydrogen atoms were found by difference Fourier analysis and the positions were refined.

#### **Computational details**

The geometries of compounds **5–9** have been optimized using the functional M06-2X<sup>20a</sup> combined with the def2-SVP basis set.<sup>20b</sup> Stationary points were located with the Berny algorithm<sup>38</sup> using redundant coordinates. Analytical Hessians were computed to determinate the nature of the stationary points.<sup>39</sup> All geometry optimizations were performed using the Gaussian 09 suite of programs.<sup>40</sup> The NBO<sup>21,22,41</sup> analyses have been carried out with the GENNBO 5.9<sup>42</sup> program at the M06-2X/ def2-TZVPP level of theory.

## Conclusions

In conclusion, mono-cationic  $[\{(L^1)BH_2\}_2(\mu-H)](NTf_2)$  (5) and  $[\{(L^2)BH_2\}_2(\mu-H)](NTf_2)$  (6) and di-cationic  $[\{(L^1)BH\}_2(\mu-H)_2](NTf_2)_2$  (7) and  $[\{(L^2)BH\}_2(\mu-H)_2](NTf_2)_2$  (8) hydrido boron compounds are readily accessible by a hydride abstraction reaction of 3 and 4 with a commercially available Brønsted acid. Structure and bonding of these compounds featuring  $CH_2BH_2(\mu-H)$ -BH<sub>2</sub>CH<sub>2</sub> (5 and 6) and  $CH_2BH(\mu-H)_2BHCH_2$  (7 and 8) scaffolds have been analysed using experimental and theoretical methods. The NHO ligand forms a C–B  $\sigma$ -bond, where the polarization towards carbon is slightly lower (65% for 7 and 8) than that for 5 and 6. NBO calculations revealed the occurrence of two B–H–B 3c–2e bonds in the HB( $\mu$ -H)<sub>2</sub>BH moiety where 43% is located at the H bridges and ~28% at each boron atom.

Crystallographic data of compounds 4, 5, 8 and 9 have been deposited with the Cambridge Crystallographic Data Centre.

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