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Mono- and di-cationic hydrido boron compounds \ddagger

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Brønsted acid HNTf₂ (Tf = SO₂CF₃) mediated dehydrogenative hydride abstraction from (L¹)BH₃ (**3**) and (L²)BH₃ (**4**) (L¹ = IPrCH₂ = 1,3-(2,6-di-isopropylphenyl)imidazol-2-methylidene (**1**); L² = SIPrCH₂ = 1,3-(2,6-di-isopropylphenyl)imidazolidin-2-methylidene (**2**)) affords thermally stable hydride bridged mono-cationic hydrido boron compounds [(L¹)BH₂]₂(μ-H)(NTf₂) (**5**) and [(L²)BH₂]₂(μ-H)(NTf₂) (**6**). Furthermore, hydride abstraction yields di-cationic hydrido boron compounds [(L¹)BH]₂(μ-H)₂(NTf₂)₂ (**7**) and [(L²)BH]₂(μ-H)₂(NTf₂)₂ (**8**). Unique cationic boron compounds with CH₂BH₂(μ-H)BH₂CH₂ (**5** and **6**) and CH₂BH(μ-H)₂BHCH₂ (**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.

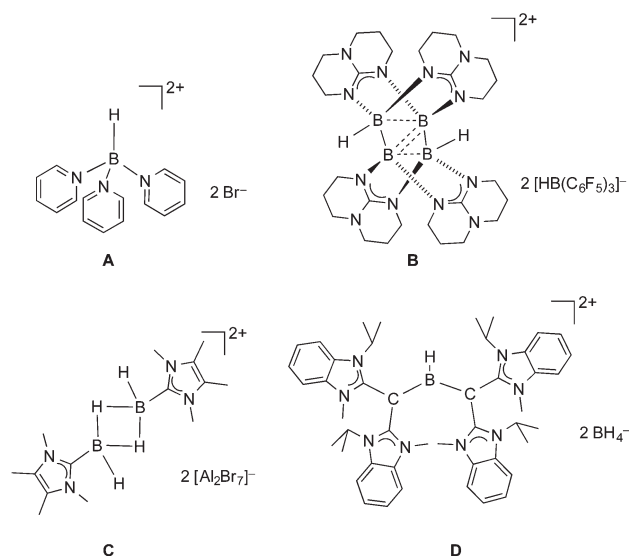
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Introduction

Investigation of thermally stable exotic main group compounds with elusive chemical and electronic properties has been a subject of considerable research interest.¹ Boron compounds play an important role in organic synthesis and materials science.² The search for new boron compounds with unique bonding motifs and electronic structures has been a major focus in molecular main group chemistry.³ A variety of mono-cationic boron compounds such as borinium [R₂B]⁺, borenium [(L)R₂B]⁺, and boronium [(L)₂R₂B]⁺ species (L = a neutral ligand) have been isolated and characterized.^{2c,4} Recent studies have demonstrated a remarkable activity of borenium compounds in Lewis acid catalysis as well as in the functionalization of small molecules.^{2c,5} 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}



Scheme 1 Di-cationic hydrido boron compounds A–D.

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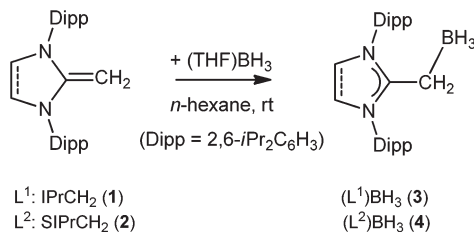
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† This paper is dedicated to Professor Manfred Scheer on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: Crystallographic data and computational details. CCDC 1401734 (**4**), 1060035 (**5**), 1060034 (**8**) and 1060033 (**9**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02237a

Cowley *et al.* reported the first hydrido boron di-cation (**A**) stabilized by a pyridine ligand (Scheme 1).^{6f} A direct B–B coupling reaction of a mono-cationic species to afford a di-cationic boron compound (**B**) stabilized by a cyclic guanidine ligand has been recently described by Himmel and co-workers.^{4c} Singlet carbenes have been recognized as most suitable candidates for taming highly reactive main group species.^{3n,7} Therefore, boryl radicals,^{3r,8} borenium ions,^{4e,5a,d,6b,9} boryl anions,^{2e,3i,q,s,10} borylenes,^{3e,o,7b,11} diborene,^{3g,12} and di-boryne^{3k} compounds have been successfully isolated by using





Scheme 2 Synthesis of NHO–borane compounds **3** and **4**.

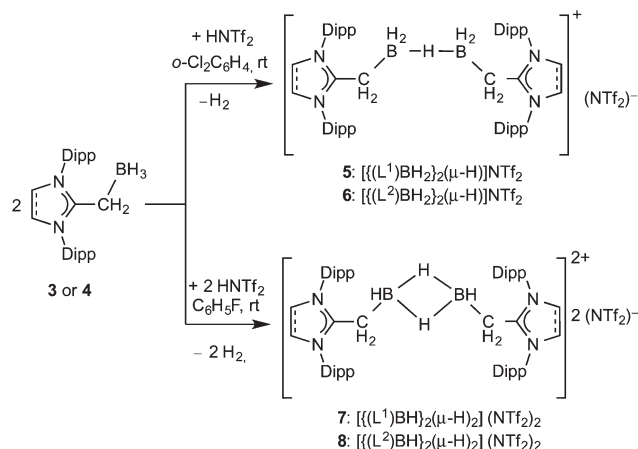
N-heterocyclic carbenes (NHCs). Curran *et al.* employed an NHC and isolated a hydride-bridged boron di-cation (C).^{6b} A carbodicarbene stabilized hydrido boron di-cation (D) has been reported very recently by Ong and co-workers.^{6a}

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.^{3n,13} 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.¹⁴ N-Heterocyclic olefins (NHOs) and their borane adducts were already known as early as in 1993,¹⁵ interest in this class of ligands incited us very recently.¹⁶ NHOs (**1** and **2**, Scheme 2) are strong nucleophiles but rather weak electron donors (Lewis bases) than NHCs.¹⁷ Therefore, NHOs readily react with a NHC-stabilized dichlorosilylene (IPr)SiCl₂ to furnish silyl-functionalized NHOs and liberate free IPr (IPr = 1,3-(2,6-di-isopropylphenyl)imidazol-2-ylidene).¹⁸ Similarly, K₂C₈ reduction of (NHO)BRX₂ (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.^{14b} Herein, we report on a very facile route to NHO-stabilized mono- and dicationic hydrido boron compounds featuring [CH₂BH₂(μ-H)-BH₂CH₂] and [CH₂BH(μ-H)₂BHCH₂] bonding motifs. Synthesis, characterization, reactivity, structure, and computational analysis of these compounds are presented.

Results and discussion

The reaction of an NHO (L¹ or L²) with (THF)BH₃ quantitatively yields (L¹)BH₃ (**3**) and (L²)BH₃ (**4**) as white solids (L¹ = IPrCH₂ (**1**) and L² = SIPrCH₂ (**2**); IPrCH₂ = 1,3-(2,6-di-isopropylphenyl)imidazol-2-methylidene and SIPrCH₂ = 1,3-(2,6-di-isopropylphenyl)imidazol-2-methylidene) (Scheme 2). Treatment of compounds **3** and **4** with 0.5 eq. of bis(trifluoromethane)sulfonimide (HNTf₂) readily affords mono-cationic hydrido boron compounds [(L¹)BH₂]₂(μ-H)](NTf₂) (**5**) and [(L²)BH₂]₂(μ-H)](NTf₂) (**6**) in a high yield (Scheme 3).

Compounds **3–6** have been characterized by ¹H, ¹¹B and ¹³C NMR as well as IR spectroscopic studies. The exocyclic methylene (CH₂) 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 ¹H NMR spectrum at δ 1.60 and δ 1.41 ppm, respectively. Each of compounds **5** (δ –15.4) and **6** (δ –16.4) exhibits a broad ¹¹B NMR signal, which is shifted towards downfield (ca. 14 ppm) when compared with the respective starting compound **3** (δ –29.9) or **4** (δ –29.5). Moreover, the ¹¹B NMR chemical shift, each for **5** and **6**, is ca. 10 ppm downfield compared to NHC-analogues.^{6b} This may be due to the lower basicity of L¹ and L² ligands than that of NHCs. Nevertheless, compounds **5** and **6** are stable both in solution (CH₂Cl₂, CHCl₃, C₆H₅F, and 1,2-Cl₂C₆H₄) and solid phases at room temperature under an inert gas (Ar or N₂) 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 solid-state 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(sp²)–C(sp³) 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.¹⁹

In order to shed light into the electronic structures, we carried out DFT calculations (M06-2X/def2-SVP)²⁰ 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†) very similar geometries for the H₂B–H–BH₂ 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 analysis²¹ (Table 1) the boron fragment B₂H₅ is negatively charged by –0.23 e and –0.20 e for **5** and **6**,



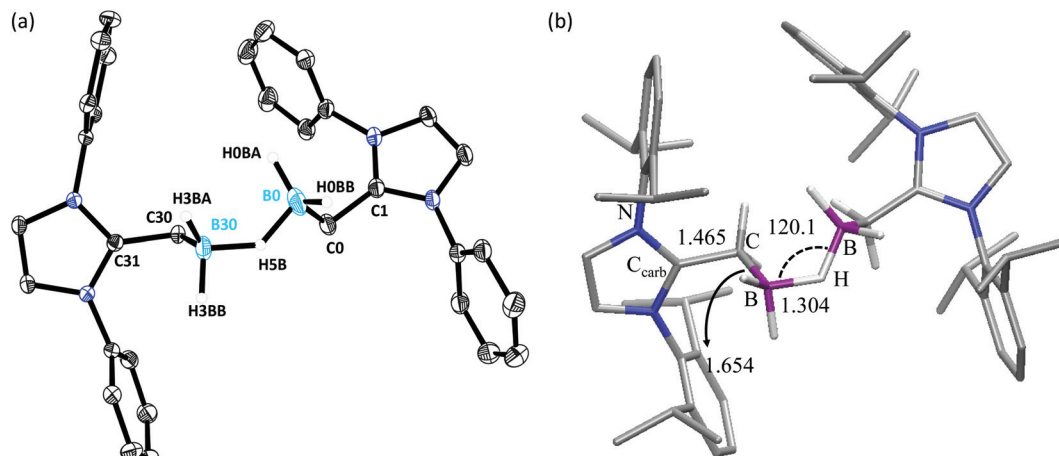


Fig. 1 (a) Molecular structure of compound 5. Hydrogen atoms except those on the $\text{H}_2\text{B}-\text{H}-\text{BH}_2$ moiety, isopropyl groups, and the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50% probability level. Boron bound hydrogen atoms were refined 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–HOBA 1.12(2) [1.211], B0–HOBB 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(B)	Q(μH)	Q(C)	Q(C_{carb})	Q(N)	WBO(B– μH)	WBO(C–B)	WBO(B–B)	WBO(C– C_{carb})
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)²² analysis reveals the presence of a $3c-2e$ bond (Tables S2 and S3[†]) B– μH –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 σ -bonds which are polarized toward the carbon end ($\sim 70\%$ at C).

The reaction of 3 and 4 with HNTf_2 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_2Cl_2 and 1,2- $\text{Cl}_2\text{C}_6\text{H}_4$ but are freely dissolved in acetonitrile. The ^{11}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_2BH_2 core features two $3c-2e$ bonds with the B \cdots B distance of 1.755 Å. This is actually similar to B \cdots B distances in cationic $(\text{NHC})\text{BH}_2$ ^{6b} as well as in neutral RBH_2 dimers.²³ Similarly, the B \cdots B distance in 8 is consistent with that of the parent B_2H_6 determined by electron diffraction (1.77 Å)²⁴ or X-ray methods (1.78–1.79 Å).²⁵

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 pre-

dicted B–H bond lengths are longer than the experimental values, which is a feature commonly observed between solid-state and theoretical structures which refer to isolated molecules.²⁶ The experimentally observed B–B distances are well represented by DFT calculations. The short B \cdots 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 di-cations. In this case, NBO calculations revealed the occurrence of two B–H–B $3c-2e$ bonds in the $\text{HB}(\mu\text{-H})_2\text{BH}$ moiety where 43% is located at the H bridges and $\sim 28\%$ at each boron atom (Tables S4 and S5[†]). The NHO ligands have a C–B σ -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 model²⁷ which has successfully been used to explain the structure of boron compounds^{3m,28} and to predict new boron molecules with unusual bonding situations.^{3k,3o,29} Compounds 5–8 may be formally considered as complexes where a charged central



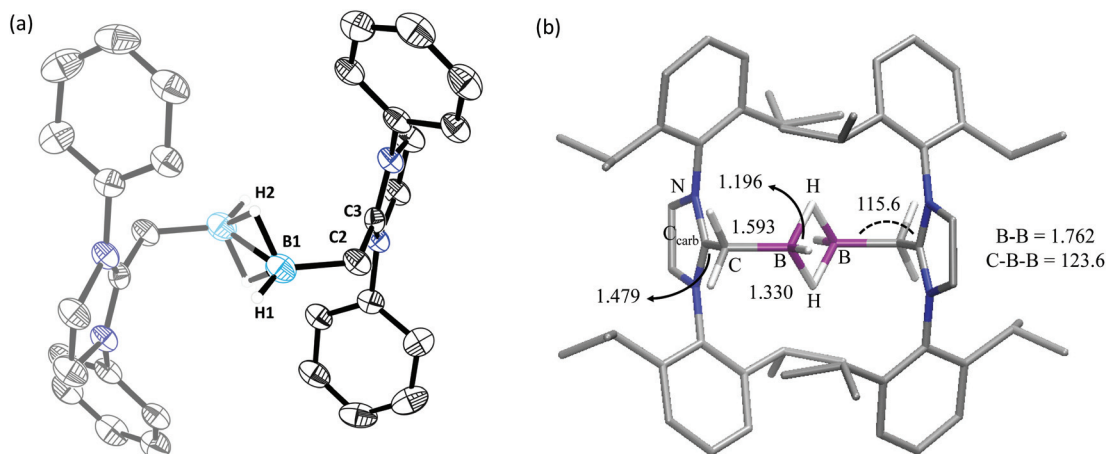
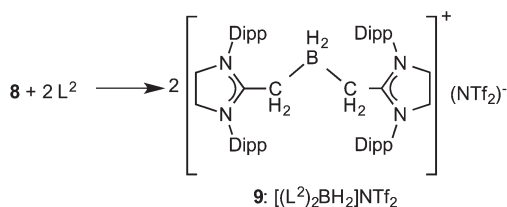


Fig. 2 (a) Molecular structure of compound **8**. Hydrogen atoms except those on the HBH₂BH moiety, isopropyl groups, and the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50% probability level. Boron bound hydrogen atoms were refined without restraints. Selected 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 L² to boronium ion **9**.

boron fragment (B₂H₅⁺ in the mono-cations and B₂H₄²⁺ in the di-cations) serves as an acceptor and the NHOs serve as donors, NHO → B₂H_n^q ← 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 BH₂⁺ fragment in the cations (L → BH₂ ← L)^{+,3m}

Treatment of **8** with two equivalents of the NHO (L²) leads to the clean formation of a boronium compound [(L²)₂BH₂]⁺[NTf₂]⁻ (**9**) (Scheme 4). The ¹¹B NMR spectrum of **9** shows a broad signal at δ –23.8 ppm. While hydrogen atoms of the BH₂ group could not be located, the ¹H NMR spectrum of compound **9** exhibits a remarkably up-field signal (δ 0.34 ppm) for methylene (CH₂BH₂) protons, which has been confirmed by a ¹H–¹³C-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 CH₂BH₂CH₂ 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 ν(B–H) stretching vibrations from 2230 to 2463 cm⁻¹. IR absorption bands in the 1561–1594 cm⁻¹ region may be assigned for the bridging ν(B–H) vibrations.³⁰

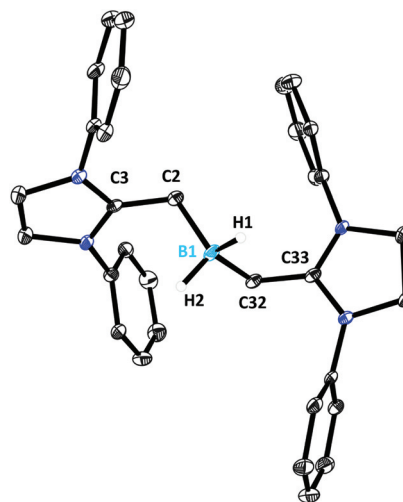


Fig. 3 Molecular structure of compound **9**. Hydrogen atoms except those on the BH₂ moiety, isopropyl groups as well as the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50% probability level. Boron bound hydrogen atoms were refined without restraints. Selected 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. CD₂Cl₂, CH₂Cl₂, *o*-Cl₂C₆H₄ and *o*-Cl₂C₆H₄ (over CaH₂), C₆D₆ 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). ^1H , ^{11}B and ^{13}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. $(\text{THF})\text{BH}_3$ (Aldrich) and HNTf_2 (Aldrich) were used without further purification. SIPrCH_2 (L^1) (1) and IPrCH_2 (L^2) (2) were prepared by adopting the reported methods.^{14b,31}

Synthesis and characterization of compounds 3–9

$(\text{L}^1)\text{BH}_3$ (3). A 1 M THF solution of $(\text{THF})\text{BH}_3$ (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]⁺, 416.33 [M]⁺. Elemental analysis for $\text{C}_{28}\text{H}_{41}\text{N}_2\text{B}$ (416): C 80.75, H 9.92, N 6.73; found C 80.44, H 9.85, N 6.68. IR (cm^{-1}): 2960, 2871, 2322, 2258, 2230, 1560. ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ 1.16 (d, 12H, $J = 6.8$ Hz, HCMe_2); 1.36 (d, 12H, $J = 6.8$ Hz, HCMe_2); 1.60 (br, 2H, CCH₂); 2.70 (sept, 4H, $J = 6.8$ Hz, HCMe_2); 6.98 (s, 2H, NCH); 7.36 (d, 4H, $J = 7.9$ Hz, $m\text{-C}_6\text{H}_3$); 7.56 (t, 2H, $J = 7.7$ Hz, $p\text{-C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , 25 °C): δ 16.55 (CCH₂); 22.97, 26.02 (HCMe_2); 29.49 (HCMe_2); 121.55 (NCH); 125.13 ($m\text{-C}_6\text{H}_3$); 131.50, 131.98 ($p\text{-C}_6\text{H}_3$, $o\text{-C}_6\text{H}_3$); 146.66 (*ipso*- C_6H_3); 165.41 (CCH₂) ppm. $\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2 , 25 °C): δ –29.89 ppm. ^{11}B NMR (160 MHz, CD_2Cl_2 , 25 °C): δ –29.89 (q, $J_{\text{B-H}} = 85.43$ Hz) ppm.

Synthesis of $(\text{L}^2)\text{BH}_3$ (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 $(\text{THF})\text{BH}_3$ (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 $\text{C}_{28}\text{H}_{43}\text{N}_2\text{B}$ (418): C 80.36, H 10.36, N 6.69; found C 79.98, H 9.96, N 6.67. IR (cm^{-1}): 2924, 2854, 2347, 2273, 2239, 1531. ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ 1.29 (d, 12H, $J = 6.9$ Hz, HCMe_2); 1.34 (br, 2H, CCH₂); 1.41 (d, 12H, $J = 6.7$ Hz, HCMe_2); 3.22 (sept, 4H, $J = 6.8$ Hz, HCMe_2); 4.07 (s, 4H, NCH₂); 7.32 (d, 4H, $J = 7.5$ Hz, $m\text{-C}_6\text{H}_3$); 7.46 (t, 2H, $J = 7.7$ Hz, $p\text{-C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , 25 °C): δ 18.46 (CCH₂); 23.72, 26.37 (HCMe_2); 29.39 (HCMe_2); 51.71 (NCH₂); 125.39 ($m\text{-C}_6\text{H}_3$); 130.56, 132.60 ($p\text{-C}_6\text{H}_3$, $o\text{-C}_6\text{H}_3$); 147.60 (*ipso*- C_6H_3); 183.07 (CCH₂) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2 , 25 °C): δ –29.51 ppm. ^{11}B NMR (160 MHz, CD_2Cl_2 , 25 °C): δ –29.51 (q, $J_{\text{B-H}} = 88.28$ Hz) ppm.

$\{[(\text{L}^1)\text{BH}_2]_2(\mu_2\text{-H})\}\text{NTf}_2$ (5). To a 50 mL Schlenk flask containing 3 (0.50 g, 1.2 mmol) and HNTf_2 (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_2). 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*]⁺ (M* = cationic unit). Elemental analysis for $\text{C}_{58}\text{H}_{81}\text{N}_5\text{B}_2\text{F}_6\text{O}_4\text{S}_2$ (1112): C 62.64, H 7.34, N 6.30; found C 62.33, H 7.21, N 6.18. IR (cm^{-1}): 2924, 2854, 2463, 2412, 2067, 1565. ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ 1.13 (*pseudo*-t, 24H, HCMe_2); 1.53 (br, 2H, CCH₂); 2.31 (sept, 4H, $J = 6.8$ Hz, HCMe_2); 7.08 (s, 2H, NCH); 7.29 (d, 4H, $J = 7.8$ Hz, $m\text{-C}_6\text{H}_3$); 7.55 (t, 2H, $J = 7.8$ Hz, $p\text{-C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , 25 °C): δ 15.08 (CCH₂); 22.86, 25.78 (HCMe_2); 29.47 (HCMe_2); 122.91 (NCH); 125.27 ($m\text{-C}_6\text{H}_3$); 130.84, 132.13 ($p\text{-C}_6\text{H}_3$, $o\text{-C}_6\text{H}_3$); 146.03 (*ipso*- C_6H_3); 158.67 (CCH₂) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2 , 25 °C): δ –15.43 ppm. ^{19}F (282 MHz, CD_2Cl_2 , 25 °C) = δ –79.52 ppm.

$\{[(\text{L}^2)\text{BH}_2]_2(\mu_2\text{-H})\}\text{NTf}_2$ (6). Compound 6 was prepared by adopting a similar method as discussed for compound 5 using 4 (0.26 g, 0.62 mmol) and HNTf_2 (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* = cationic unit). Elemental analysis for $\text{C}_{58}\text{H}_{85}\text{N}_5\text{B}_2\text{F}_6\text{O}_4\text{S}_2$ (1116): C 62.42, H 7.68, N 6.28; found C 61.77, H 7.51, N 6.16. IR (cm^{-1}): 2932, 2844, 2459, 2420, 2053, 1560. ^1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ 1.17 (d, 12H, $J = 6.8$ Hz, HCMe_2); 1.20 (br, 2H, CCH₂); 1.24 (d, 12H, $J = 6.8$ Hz, HCMe_2); 2.84 (sept, 4H, $J = 6.8$ Hz, HCMe_2); 4.05 (s, 4H, NCH₂); 7.23 (d, 4H, $J = 7.8$ Hz, $m\text{-C}_6\text{H}_3$); 7.41 (t, 2H, $J = 7.7$ Hz, $p\text{-C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , 25 °C): δ 16.56 (CCH₂); 23.63, 26.22 (HCMe_2); 29.39 (HCMe_2); 52.08 (NCH₂); 125.57, 126.30 ($m\text{-C}_6\text{H}_3$); 131.34, 131.27, 132.52 ($p\text{-C}_6\text{H}_3$, $o\text{-C}_6\text{H}_3$); 147.88, 147.12 (*ipso*- C_6H_3); 178.33 (CCH₂) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2 , 25 °C): δ –16.38 ppm. ^{19}F (282 MHz, CD_2Cl_2 , 25 °C) = δ –79.53 ppm.

$\{[(\text{L}^1)\text{BH}_2]_2\}\text{NTf}_2$ (7). To a 50 mL Schlenk flask containing 3 (0.66 g, 1.57 mmol) and HNTf_2 (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 $\text{C}_{60}\text{H}_{80}\text{N}_6\text{B}_2\text{F}_{12}\text{O}_8\text{S}_4$ (1391): C 51.80, H 5.80, N 6.04; found C 51.10, H 5.62, N 5.75. IR (cm^{-1}): 2920, 2854, 2723, 2600, 2369, 1589, 1561. ^1H NMR (300 MHz, CD_3CN , 25 °C): δ 1.20 (d, 12H, $J = 6.8$ Hz, HCMe_2); 1.33 (d, 12H, $J = 6.8$ Hz, HCMe_2); 1.78 (br, 2H, CCH₂); 2.44 (sept, 4H, $J = 6.8$ Hz, HCMe_2); 7.50 (d, 4H, $J = 7.9$ Hz, $m\text{-C}_6\text{H}_3$); 7.53 (s, 2H, NCH); 7.65 (t, 2H, $J = 7.3$ Hz, $p\text{-C}_6\text{H}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN , 25 °C): δ 15.49 (CCH₂); 22.71, 25.54 (HCMe_2); 29.95 (HCMe_2); 125.87 (NCH); 126.30 ($m\text{-C}_6\text{H}_3$); 131.33, 132.81 ($p\text{-C}_6\text{H}_3$, $o\text{-C}_6\text{H}_3$); 146.78 (*ipso*- C_6H_3); 157.03 (CCH₂) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CD_3CN , 25 °C): δ –19.89 ppm. ^{19}F (282 MHz, CD_3CN , 25 °C) = δ –80.16 ppm.

$\{[(\text{L}^2)\text{BH}_2]_2\}\text{NTf}_2$ (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*]⁺ (M* = cationic unit). Elemental analysis



for $C_{60}H_{84}N_6B_2F_{12}O_8S_4$ (1395): C 51.65, H 6.07, N 6.02; found C 51.22, H 5.85, N 5.95. IR (cm^{-1}): 2924, 2836, 2724, 2584, 2365, 1594, 1564. 1H NMR (300 MHz, CD_3CN , 25 °C): δ 1.31 (d, 12H, $J = 6.8$ Hz, HCM_{e2}); 1.36 (d, 12H, $J = 6.8$ Hz, HCM_{e2}); 1.44 (br, 2H, CCH_2); 3.06 (sept, 4H, $J = 6.8$ Hz, HCM_{e2}); 4.21 (s, 4H, NCH_2); 7.41 (d, 4H, $J = 7.8$ Hz, $m-C_6H_3$); 7.52 (t, 2H, $J = 7.7$ Hz, $p-C_6H_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN , 25 °C): δ 16.82 (CCH_2); 23.54, 26.24 (HCM_{e2}); 29.70 (HCM_{e2}); 52.65 (NCH_2); 126.19, 126.59 ($m-C_6H_3$); 131.33, 131.94, 132.61 ($p-C_6H_3$, $o-C_6H_3$); 147.41, 147.88 ($ipso-C_6H_3$); 177.31 (CCH_2) ppm. $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2 , 25 °C): δ -19.78 ppm. ^{19}F (282 MHz, CD_3CN , 25 °C) = δ -80.13 ppm.

$\{[(L^2)BH_2]\}(NTf_2)_2$ (9). To a 50 mL fluorobenzene solution of 8 (2.50 g, 1.79 mmol) was added L^2 (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]⁺ (M* = cationic unit). Elemental analysis for $C_{58}H_{82}N_5BF_6O_4S_2$ (1102): C 63.20, H 7.50, N 6.35; found C 63.01, H 7.31, N 6.19. IR (cm^{-1}): 2922, 2853, 2724, 2586, 1711, 1595, 1566. 1H NMR (300 MHz, CD_2Cl_2 , 25 °C): δ 0.35 (br, 2H, CCH_2); 0.98 (d, 12H, $J = 6.7$ Hz, HCM_{e2}); 1.15 (d, 12H, $J = 6.8$ Hz, HCM_{e2}); 2.76 (sept, 4H, $J = 6.8$ Hz, HCM_{e2}); 3.96

(s, 4H, NCH_2); 7.14 (d, 4H, $J = 7.9$ Hz, $m-C_6H_3$); 7.34 (t, 2H, $J = 7.7$ Hz, $p-C_6H_3$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2 , 25 °C): δ 22.53 (CCH_2); 23.46, 26.56 (HCM_{e2}); 29.49 (HCM_{e2}); 51.58 (NCH_2); 125.62 ($m-C_6H_3$); 131.06, 131.74 ($p-C_6H_3$, $o-C_6H_3$); 147.30 ($ipso-C_6H_3$); 181.15 (CCH_2) ppm. $^{11}B\{^1H\}$ NMR (96 MHz, CD_2Cl_2 , 25 °C): δ -24.03 ppm. ^{19}F (282 MHz, CD_2Cl_2 , 25 °C) = δ -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_α 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_α radiation) with INCOATEC Quazar mirror optics. The data were integrated with SAINT³³ and a multi-scan absorption correction with SADABS³⁴ was applied. The structure solution was performed with SHELXT³⁵ and structure refinement was performed with SHELXL,³⁶ 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

Compound	4	5	8	9
CCDC number	1401734	1060035	1060034	1060033
Empirical formula	$C_{28}H_{43}BN_2$	$C_{58}H_{81}B_2F_6N_5O_4S_2$	$C_{60.66}H_{85.32}B_2Cl_{1.32}F_{12}N_6O_8S_4$	$C_{67}H_{89.50}BF_{7.50}N_5O_4S_2$
Formula weight [$g\ mol^{-1}$]	418.45	1112.01	1451.24	1246.36
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Wavelength [\AA]	0.71073	0.56086	0.56086	0.56086
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions [\AA]	$a = 11.624(2)$ $b = 15.921(3)$ $c = 14.028(2)$	$a = 10.754(2)$ $b = 16.407(2)$ $c = 18.510(2)$	$a = 12.306(2)$ $b = 12.691(2)$ $c = 13.389(2)$	$a = 13.061(3)$ $b = 15.613(4)$ $c = 16.727(4)$
α [$^\circ$]	90	83.78(2)	95.14(2)	96.88(2)
β [$^\circ$]	99.23(2)	73.47(2)	101.53(2)	101.45(2)
γ [$^\circ$]	90	83.41(2)	118.07(2)	98.29(2)
Volume [\AA^3]	2562.5(8)	3100.4(4)	1766.6(6)	3269.2(14)
Z	4	2	1	2
Absorption coefficient [mm^{-1}]	0.062	0.085	0.146	0.088
$F(000)$	920	1184	760	1326
Crystal size [mm^3]	0.100 \times 0.100 \times 0.100	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 [$^\circ$]	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_{int}	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 [$I > 2\sigma(I)$]	$R_1 = 0.0446$, $wR_2 = 0.1078$	$R_1 = 0.0383$, $wR_2 = 0.0901$	$R_1 = 0.0745$, $wR_2 = 0.2054$	$R_1 = 0.0544$, $wR_2 = 0.1442$
R indices (all data)	$R_1 = 0.0631$, $wR_2 = 0.1167$	$R_1 = 0.0550$, $wR_2 = 0.0999$	$R_1 = 0.0956$, $wR_2 = 0.2259$	$R_1 = 0.0737$, $wR_2 = 0.1589$
Largest diff. peak and hole ($e\ \text{\AA}^{-3}$)	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^{20a} combined with the def2-SVP basis set.^{20b} Stationary points were located with the Berny algorithm³⁸ using redundant coordinates. Analytical Hessians were computed to determinate the nature of the stationary points.³⁹ All geometry optimizations were performed using the Gaussian 09 suite of programs.⁴⁰ The NBO^{21,22,41} analyses have been carried out with the GENNBO 5.9⁴² program at the M06-2X/def2-TZVPP level of theory.

Conclusions

In conclusion, mono-cationic $[\{(\text{L}^1)\text{BH}_2\}_2(\mu\text{-H})](\text{NTf}_2)$ (5) and $[\{(\text{L}^2)\text{BH}_2\}_2(\mu\text{-H})](\text{NTf}_2)$ (6) and di-cationic $[\{(\text{L}^1)\text{BH}\}_2(\mu\text{-H})_2](\text{NTf}_2)_2$ (7) and $[\{(\text{L}^2)\text{BH}\}_2(\mu\text{-H})_2](\text{NTf}_2)_2$ (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 $\text{CH}_2\text{BH}_2(\mu\text{-H})\text{-BH}_2\text{CH}_2$ (5 and 6) and $\text{CH}_2\text{BH}(\mu\text{-H})_2\text{BHCH}_2$ (7 and 8) scaffolds have been analysed using experimental and theoretical methods. The NHO ligand forms a C–B σ -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 $\text{HB}(\mu\text{-H})_2\text{BH}$ 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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