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ARTICLE

Mono- and Di-Cationic Hydrido Boron Compounds† ‡

Rajendra S. Ghadwal,* [a, b] Christian J. Schürmann,[b] Diego M. Andrada[c] and Gernot Frenking[c]

Brønsted acid HNTf$_2$ (Tf = SO$_2$CF$_3$) mediated dehydrogenative hydride abstraction from (L^1)BH$_3$ (**3**) and (L^2)BH$_3$ (**4**) (L^1 = IPrCH$_2$ = 1,3-(2,6-di-isopropylphenyl)imidazol-2-methylidene (**1**); L^2 = SIPrCH$_2$ = 1,3-(2,6-di-isopropylphenyl)imidazolidin-2-meth-ylidiene (**2**)) affords thermally stable hydride bridged mono-cationic hydrido boron compounds [{(L^1)BH$_2$}$_2$(μ-H)](NTf$_2$) (**5**) and [{(L^2)BH$_2$}$_2$(μ-H)](NTf$_2$) (**6**). Further hydride abstraction yields di-cationic hydrido boron compounds [{(L^1)BH}$_2$(μ-H)$_2$](NTf$_2$)$_2$ (**7**) and [{(L^2)BH}$_2$(μ-H)$_2$](NTf$_2$)$_2$ (**8**). Unique cationic boron compounds with CH$_2$BH$_2$(μ-H)BH$_2$CH$_2$ (**5** and **6**) and CH$_2$BH(μ-H)$_2$BHCH$_2$ (**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.

Introduction

Investigation of thermally stable exotic main group compounds with elusive chemical and electronic properties has been a subject of considerable research interests.[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 [R$_2$B]$^+$, borenium [(L)R$_2$B]$^+$, and boronium [(L)$_2$R$_2$B]$^+$ species (L = a neutral ligand) have been isolated and characterized.[2c, 4] Recent advances 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]

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 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, 5d, 6b, 9] boryl anions,[2e, 3i, 3q, 3s, 10] borylenes,[3e, 3o, 7b, 11] diborene[3g, 12] and diboryne[3k] compounds have been successfully isolated using 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]
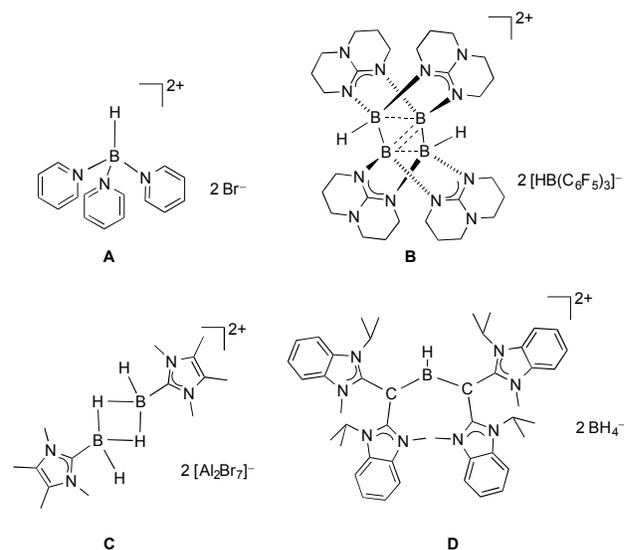
Scheme 1 Di-cationic hydrido boron compounds **A**-**D**.

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

a. Institut für Anorganische Chemie, Universität Bielefeld, Universitätstrasse 25, 33615 Bielefeld, Germany.
E-mail: rghadwal@uni-bielefeld.de.
b. Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany
c. Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße, 35032 Marburg, Germany.

interested in new class of carbon-donor ligands.[14] N-Heterocyclic olefins (NHOs) and their borane adducts were already known as early as in 1993,[15] interests in this class of ligands incited 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 dichloro-silylene (IPr)SiCl$_2$ to furnish silyl-functionalized NHOs and liberate free IPr (IPr = 1,3-(2,6-di-isopropylphenyl)imidazol-2-ylidene).[18] Similarly, KC$_8$ reduction of (NHO)BRX$_2$ (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 di-cationic hydrido boron compounds featuring [CH$_2$BH$_2$(μ-H)BH$_2$CH$_2$] and [CH$_2$BH(μ-H)$_2$BHCH$_2$] bonding motifs. Synthesis, characterization, reactivity, structure, and computational analysis of these compounds are presented.

Results and Discussion

Reaction of an NHO (L^1 or L^2) with (THF)BH$_3$ quantitatively yields (L^1)BH$_3$ (**3**) and (L^2)BH$_3$ (**4**) as white solids (L^1 = IPrCH$_2$ (**1**) and L^2 = SIPrCH$_2$ (**2**); IPrCH$_2$ = 1,3-(2,6-di-isopropylphenyl)-imidazol-2-methylidene and SIPrCH$_2$ = 1,3-(2,6-di-isopropyl-phenyl)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)BH$_2$}$_2$(μ-H)](NTf$_2$) (**5**) and [{(L^2)BH$_2$}$_2$(μ-H)](NTf$_2$) (**6**) in a high yield (Scheme 3).

L^1: IPrCH$_2$ (**1**)   (L^1)BH$_3$ (**3**)
L^2: SIPrCH$_2$ (**2**)   (L^2)BH$_3$ (**4**)
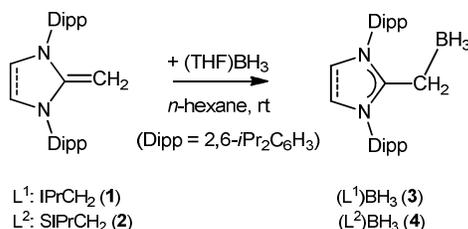
Scheme 2 Synthesis of NHO-borane compounds **3** and **4**.

Compounds **3**-**6** have been characterized by ^{1}H, ^{11}B and ^{13}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 the ^{1}H 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 ^{11}B 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 ^{11}B 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 L^1 and L^2 ligands than that of NHCs. Nevertheless, compounds **5** and **6** are stable both in solution (CH$_2$Cl$_2$, CHCl$_3$, C$_6$H$_5$F, and 1,2-Cl$_2$C$_6$H$_4$) and solid phases at room temperature under an inert gas (Ar or N$_2$) atmosphere.
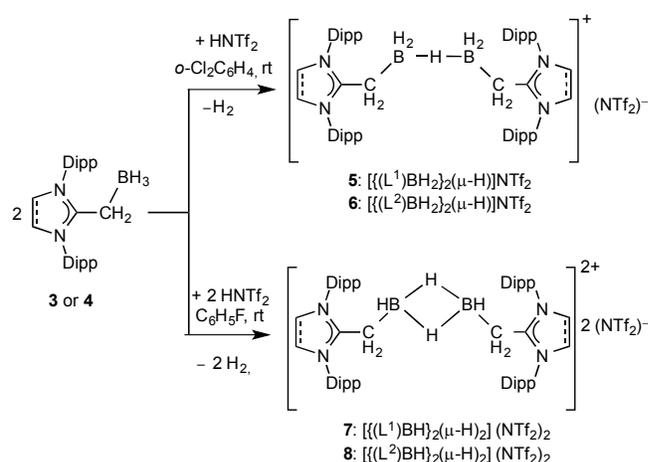
Scheme 3 Synthesis of mono- and di-cationic hydrido boron compounds **5**-**8**.

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(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.[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 H$_2$B–H–BH$_2$ moiety. Compound **6** represents slightly longer B–μH bond length and more acute C$_{(carbene)}$–C–B angles than in **5**. Based on the natural population analysis[21] (Table 1) the boron fragment B$_2$H$_5$ is negatively charged by –0.23 e and –0.20 e for **5** and **6**, 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 (~ 70 % at C).

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

(a)

(b)
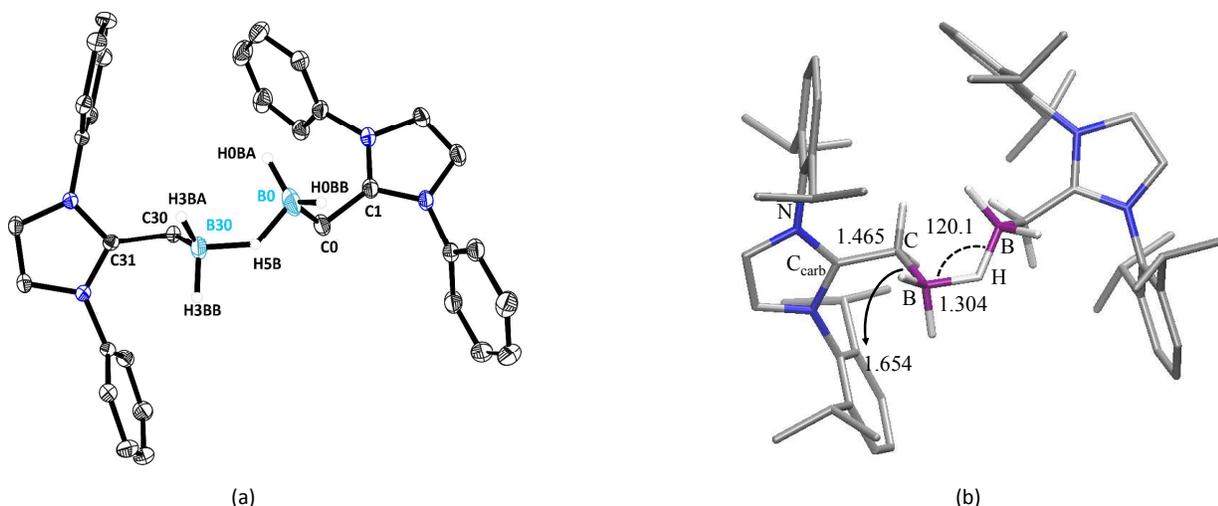
Fig. 1 (a) Molecular structure of compound **5**. Hydrogen atoms except on the $H_2B–H–BH_2$ moiety, isopropyl groups, and the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50 % probability level. Boron bound hydrogen atoms were refined without restraints. Selected experimental and theoretical [M06-2X/def2-SVP] bond lengths [Å] and 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**.

soluble in CH_2Cl_2 and $1,2\text{-}Cl_2C_6H_4$ 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 the figure 2. The BH_2BH_2 core features two 3c-2e bonds with the B···B distance of 1.755 Å. This is actually similar to B···B distances in a cationic $(NHC)BH_2$[6b] as well as in neutral RBH_2 dimers.[23] Similarly, the B···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 predicted 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 the 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 di-cations. In this case, NBO calculations revealed the occurrence of two B–H–B 3c-2e bonds in the $HB(\mu\text{-}H)_2BH$ moiety where 43 % is located at the H bridges and ~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 model[27] 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

Table 1 NPA charges and Wiberg Bond Order values at the M06-2X/def2- TZVPP of compounds **5-9**.

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

(a)

(b)
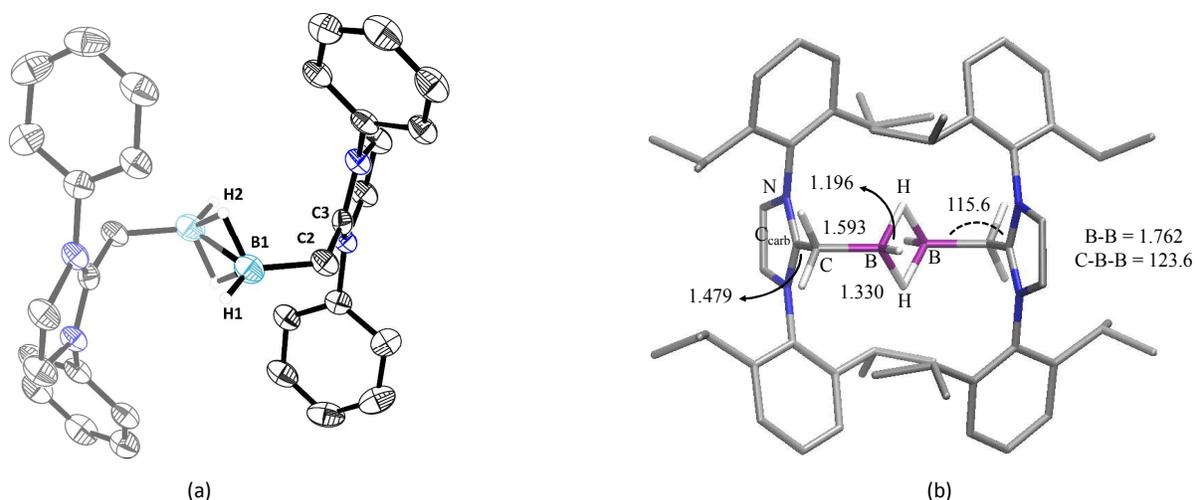
Fig. 2 (a) Molecular structure of compound **8**. Hydrogen atoms except on the HBHHBH moiety, isopropyl groups, and the anionic part have been omitted for clarity. Thermal ellipsoids are represented at the 50 % probability level. Boron bound hydrogen atoms were refined without restraints. Selected experimental and theoretical [M06-2X/def2-SVP] bond lengths [Å] and 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**.

where a charged central 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 the 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 $(L \rightarrow BH_2 \leftarrow L)^+$.[3m]

Treatment of **8** with two equivalent of the NHO (L^2) leads to the clean formation of a boronium compound $[(L^2)_2BH_2][NTf_2]$ (**9**) (Scheme 4). The ^{11}B NMR spectrum of **9** shows a broad signal at δ − 23.8 ppm. While hydrogen atoms of the BH_2 group could not be located, the ^{1}H NMR spectrum of compound **9** exhibits a remarkably up-field signal (δ 0.34 ppm) for methylene (CH_2BH_2) protons, which has been confirmed by a [1]H-^{13}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 $CH_2BH_2CH_2$ moiety with the C–B–C angle of 109.22°. 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 v(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 v(B–H) vibrations.[30]

Fig. 3 Molecular structure of compound **9**. Hydrogen atoms except on the BH_2 moiety, methyl moieties 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 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].

9: $[(L^2)_2BH_2]NTf_2$

Scheme 4 Reaction of **8** with L^2 to boronium ion **9**.

Experimental

All synthesis 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 dry argon atmosphere prior to use. All other solvents were dried and purified by 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. (THF)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 reported methods.[14b, 31]

Synthesis and characterization of compounds 3-9

(L^1)BH$_3$ (3): A 1M 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 4h. 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$_2$Cl$_2$/*n*-hexane (1:1) solution. Mp.: 201 °C. MS (ESI, m/z [M]): 415.33 [M–H]$^+$, 416.33 [M]$^+$. Elemental analysis for C$_{28}$H$_{41}$N$_2$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$_2$Cl$_2$, 25 °C): δ 1.16 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 1.36 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 1.60 (br, 2H, CC*H*$_2$); 2.70 (sept, 4H, *J* = 6.8 Hz, *H*CMe$_2$); 6.98 (s, 2H, NC*H*); 7.36 (d, 4H, *J* = 7.9 Hz, *m*-C$_6$*H*$_3$); 7.56 (t, 2H, *J* = 7.7 Hz *p*-C$_6$*H*$_3$). $^{13}C{^1H}$ NMR (75 MHz, CD$_2$Cl$_2$, 25 °C): δ 16.55 (C*C*H$_2$); 22.97, 26.02 (HC*Me*$_2$); 29.49 (*H*CMe$_2$); 121.55 (NCH) 125.13 (*m*-C$_6$H$_3$); 131.50 131.98 (*p*-C$_6$H$_3$, *o*-C$_6$H$_3$); 146.66 (*ipso*-C$_6$H$_3$); 165.41 (*C*CH$_2$) ppm. B{^1H}NMR (96 MHz, CD$_2$Cl$_2$, 25 °C): δ – 29.89 ppm. ^{11}B NMR (160 MHz, CD$_2$Cl$_2$, 25 °C): δ – 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$_3$ (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 C$_{28}$H$_{43}$N$_2$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$_2$Cl$_2$, 25 °C): δ 1.29 (d, 12H, *J* = 6.9 Hz, HC*Me*$_2$); 1.34 (br, 2H, CC*H*$_2$); 1.41 (d, 12H, *J* = 6.7 Hz, HC*Me*$_2$); 3.22 (sept, 4H, *J* = 6.8 Hz, *H*CMe$_2$); 4.07 (s, 4H, NC*H*$_2$); 7.32 (d, 4H, *J* = 7.5 Hz, *m*-C$_6$*H*$_3$); 7.46 (t, 2H, *J* = 7.7 Hz *p*-C$_6$*H*$_3$). $^{13}C{^1H}$ NMR (75 MHz, CD$_2$Cl$_2$, 25 °C): δ 18.46 (C*C*H$_2$); 23.72, 26.37 (HC*Me*$_2$); 29.39 (*H*CMe$_2$); 51.71 (NCH$_2$); 125.39 (*m*-C$_6$H$_3$); 130.56, 132.60 (*p*-C$_6$H$_3$, *o*-C$_6$H$_3$); 147.60 (*ipso*-C$_6$H$_3$); 183.07 (*C*CH$_2$) ppm. $^{11}B{^1H}$ NMR (96 MHz, CD$_2$Cl$_2$, 25 °C): δ – 29.51 ppm. ^{11}B NMR (160 MHz, CD$_2$Cl$_2$, 25 °C): δ – 29.51 (q, *J*$_{B-H}$ = 88.28 Hz) ppm.

[{(L^1)BH$_2$}$_2$(μ$_2$-H)]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. Effervesces indicated the formation of a gas (apparently H$_2$). Further stirring at room temperature for 2h afforded 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 get 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 C$_{58}$H$_{81}$N$_5$B$_2$F$_6$O$_4$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$_2$Cl$_2$, 25 °C): δ 1.13 (*pseudo*-t, 24H, HC*Me*$_2$); 1.53 (br, 2H, CC*H*$_2$); 2.31 (sept, 4H, *J* = 6.8 Hz, *H*CMe$_2$); 7.08 (s, 2H, NC*H*); 7.29 (d, 4H, *J* = 7.8 Hz, *m*-C$_6$*H*$_3$); 7.55 (t, 2H, *J* = 7.8 Hz, *p*-C$_6$*H*$_3$). $^{13}C{^1H}$ NMR (75 MHz, CD$_2$Cl$_2$, 25 °C): δ 15.08 (C*C*H$_2$); 22.86, 25.78 (HC*Me*$_2$); 29.47 (*H*CMe$_2$); 122.91 (NCH); 125.27 (*m*-C$_6$H$_3$); 130.84 132.13 (*p*-C$_6$H$_3$, *o*-C$_6$H$_3$); 146.03 (*ipso*-C$_6$H$_3$); 158.67 (*C*CH$_2$) ppm. $^{11}B{^1H}$ NMR (96 MHz, CD$_2$Cl$_2$, 25 °C): δ – 15.43 ppm. ^{19}F (282 MHz, CD$_2$Cl$_2$, 25 °C) = δ – 79.52 ppm.

[{(L^2)BH$_2$}$_2$(μ$_2$-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 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 C$_{58}$H$_{85}$N$_5$B$_2$F$_6$O$_4$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$_2$Cl$_2$, 25 °C): δ 1.17 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 1.20 (br, 2H, CC*H*$_2$); 1.24 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 2.84 (sept, 4H, *J* = 6.8 Hz, *H*CMe$_2$); 4.05 (s, 4H, NC*H*$_2$); 7.23 (d, 4H, *J* = 7.8 Hz, *m*-C$_6$*H*$_3$); 7.41 (t, 2H, *J* = 7.7 Hz *p*-C$_6$*H*$_3$). $^{13}C{^1H}$ NMR (75 MHz, CD$_2$Cl$_2$, 25 °C): δ 16.56 (C*C*H$_2$); 23.63, 26.22 (HC*Me*$_2$); 29.39 (*H*CMe$_2$); 52.08 (NCH$_2$); 125.57, 126.30 (*m*-C$_6$H$_3$); 131.34, 131.27, 132.52 (*p*-C$_6$H$_3$, *o*-C$_6$H$_3$); 147.88, 147.12 (*ipso*-C$_6$H$_3$); 178.33 (*C*CH$_2$) ppm. $^{11}B{^1H}$ NMR (96 MHz, CD$_2$Cl$_2$, 25 °C): δ – 16.38 ppm. ^{19}F (282 MHz, CD$_2$Cl$_2$, 25 °C) = δ – 79.53 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$_2$ (0.44 g, 1.57 mmol) was added 20 mL of fluorobenzene at room temperature. Further stirring at room temperature for 4h afforded 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$_{60}$H$_{80}$N$_6$B$_2$F$_{12}$O$_8$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$_3$CN, 25 °C): δ 1.20 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 1.33 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 1.78 (br, 2H, CC*H*$_2$); 2.44 (sept, 4H, *J* = 6.8 Hz, *H*CMe$_2$); 7.50 (d, 4H, *J* = 7.9 Hz, *m*-C$_6$*H*$_3$); 7.53 (s, 2H, NC*H*); 7.65 (t, 2H, *J* = 7.3 Hz *p*-C$_6$*H*$_3$). $^{13}C{^1H}$ NMR (75 MHz, CD$_3$CN, 25 °C): δ 15.49 (C*C*H$_2$); 22.71, 25.54 (HC*Me*$_2$); 29.95 (*H*CMe$_2$); 125.87 (NCH); 126.30 (*m*-C$_6$H$_3$); 131.33 132.81 (*p*-C$_6$H$_3$, *o*-C$_6$H$_3$); 146.78 (*ipso*-C$_6$H$_3$); 157.03 (*C*CH$_2$) ppm. $^{11}B{^1H}$ NMR (160 MHz, CD$_3$CN, 25 °C): δ – 19.89 ppm. ^{19}F (282 MHz, CD$_3$CN, 25 °C) = δ – 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*]$^+$ (M* = cationic unit). Elemental analysis for C$_{60}$H$_{84}$N$_6$B$_2$F$_{12}$O$_8$S$_4$ (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$_3$CN, 25 °C): δ 1.31 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 1.36 (d, 12H, *J* = 6.8 Hz, HC*Me*$_2$); 1.44 (br, 2H, CC*H*$_2$); 3.06 (sept, 4H, *J* = 6.8 Hz, *H*CMe$_2$); 4.21 (s, 4H, NC*H*$_2$); 7.41 (d, 4H, *J* = 7.8 Hz, *m*-C$_6$*H*$_3$); 7.52 (t, 2H, *J* = 7.7 Hz *p*-C$_6$*H*$_3$). $^{13}C{^1H}$ NMR (75 MHz, CD$_3$CN, 25 °C): δ 16.82 (C*C*H$_2$); 23.54, 26.24 (HC*Me*$_2$); 29.70 (*H*CMe$_2$); 52.65 (NCH$_2$); 126.19, 126.59 (*m*-C$_6$H$_3$); 131.33, 131.94, 132.61 (*p*-C$_6$H$_3$, *o*-C$_6$H$_3$); 147.41, 147.88 (*ipso*-C$_6$H$_3$); 177.31 (*C*CH$_2$) ppm. $^{11}B{^1H}$ NMR (96 MHz, CD$_2$Cl$_2$, 25 °C): δ – 19.78ppm. ^{19}F (282 MHz, CD$_3$CN,, 25 °C) = δ – 80.13 ppm.

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[{(L^2)$_2$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 4h. Removal of the volatiles under vacuum afforded 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 ºC for two days to yield colorless crystalline solid of compound **9** (2.70 g, 68%). Mp.: 273 ºC. MS (ESI, m/z [M]): 821.67, 822.67, 820.67 [M*]$^+$ (M* = cationic unit). Elemental analysis for C$_{58}$H$_{82}$N$_5$BF$_6$O$_4$S$_2$ (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. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 ºC): δ 0.35 (br, 2H, CCH_2); 0.98 (d, 12H, J = 6.7 Hz, HCMe_2); 1.15 (d, 12H, J = 6.8 Hz, HCMe_2); 2.76 (sept, 4H, J = 6.8 Hz, HCMe$_2$); 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{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$, 25 ºC): δ 22.53 (CCH$_2$); 23.46, 26.56 (HCMe_2); 29.49 (HCMe$_2$); 51.58 (NCH$_2$); 125.62 (m-C$_6$H$_3$); 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{^{1}H} NMR (96 MHz, CD$_2$Cl$_2$, 25 ºC): δ – 24.03 ppm. ^{19}F (282 MHz, CD$_2$Cl$_2$, 25 ºC) = 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 with 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

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Table 2 Crystallographic and structure refinement data for 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]	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, $P\,2_1/c$	Triclinic, P-1	Triclinic, P-1	Triclinic, P-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)
α [°]	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^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 x 0.100 x 0.100	0.195 x 0.194 x 0.104	0.317 x 0.301 x 0.110	0.180 x 0.153 x 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	23574 / 6095	238549 / 15500	52767 / 6769	161683 / 11676
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	15500 / 513 / 768	6769 / 1636 / 863	11676 / 111 / 808
Goodness-of-fit on F^2	1.039	1.024	1.044	1.044
Final R indices [I>2sigma(I)]	$R1$ = 0.0446, $wR2$ = 0.1078	$R1$ = 0.0383, $wR2$ = 0.0901	$R1$ = 0.0745, $wR2$ = 0.2054	$R1$ = 0.0544, $wR2$ = 0.1442
R indices (all data)	$R1$ = 0.0631, $wR2$ = 0.1167	$R1$ = 0.0550, $wR2$ = 0.0999	$R1$ = 0.0956, $wR2$ = 0.2259	$R1$ = 0.0737, $wR2$ = 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

(Mo K_α radiation) with INCOATEC Quazar mirror optics. The data were integrated with SAINT[33] and a multi-scan absorption correction with SADABS[34] was applied. The structure solution was performed with SHELXT[35] and structure refinement was performed with SHELXL,[36] using the graphical user interface SHELXLE.[37] All non-hydrogen atoms were 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 through difference Fourier analysis and the positions were refined.

Computational details

The geometries of the 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 algorithm[38] 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 5.9[42] program at the M06-2X/def2-TZVPP level of theory.

Conclusions

In conclusion, mono-cationic [{(L¹)BH₂}₂(μ-H)](NTf₂) (**5**) and [{(L²)BH₂}₂(μ-H)](NTf₂) (**6**) and di-cationic [{(L¹)BH}₂(μ-H)₂](NTf₂)₂ (**7**) and [{(L²)BH}₂(μ-H)₂](NTf₂)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 CH₂BH₂(μ-H)BH₂CH₂ (**5** and **6**) and CH₂BH(μ-H)₂BHCH₂ (**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 for **5** and **6**. 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.

Acknowledgements

Notes and references

Crystallographic data of compounds **4**, **5**, **8** and **9** have been deposited with the Cambridge Crystallographic Centre. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

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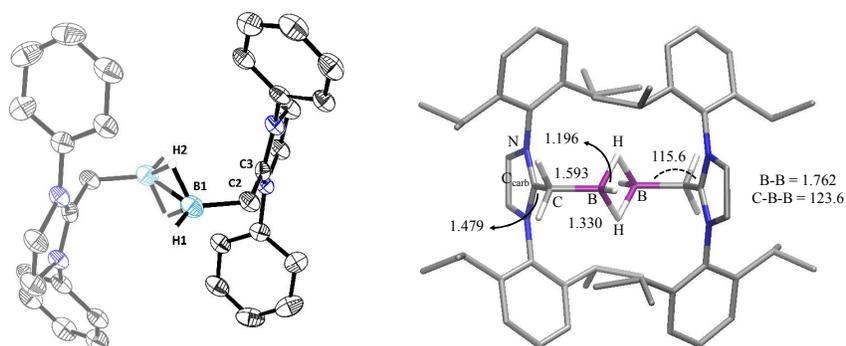
Stable mono- and di-cationic hydrido boron compounds featuring $CH_2BH_2(\mu\text{-}H)BH_2CH_2$ and $CH_2BH(\mu\text{-}H)_2BHCH_2$ cores are readily accessible by dehydrogenative hydride abstractions. NBO calculations revealed the occurrence of two B–H–B 3c-2e bonds in the $HB(\mu\text{-}H)_2BH$ moiety of di-cations (**7** and **8**) , where 43 % is located at the H bridges and ~28 % at each boron atom.