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Synthesis and Characterization of a New Guanidine–Borane Complex and a Dinuclear Boron(II) Hydride with Bridging Guanidinate Ligands

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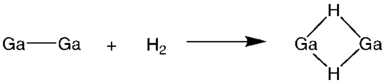
We report the synthesis and structural characterization of the new monomeric borane complex $H_3B{\cdot}hppH$ (hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine), which represents the first example of a structurally characterized 1:1 complex between hppH and a group 13 element hydride. Significant intramolecular and, in the crystalline phase, intermolecular H···H contacts are established in this complex. It is shown that the complex can be used as a precursor to new dinuclear boron(II) compounds featuring a B–B single bond. Thus H_2 elimination followed by dimerization of $H_3B{\cdot}hppH$ leads to $[(hpp)BH]_2$ with two bridging hpp units. The structural details derived from X-ray diffraction measurements are reported.

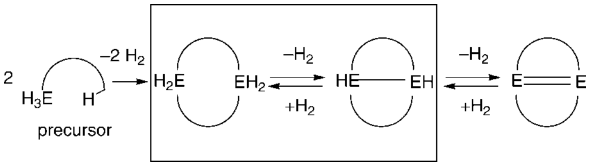
Introduction

In Linus Pauling's concept of electronegativity, the dissociation energy of a compound A–B is comparable to half of the sum of the dissociation energies of A_2 and B_2, if A and B have similar electronegativities. This implies that reactions of the type $E\text{–}E + H_2 \rightarrow 2EH$ (where E represents any element in the periodic table) should be associated with a small reaction enthalpy at standard conditions if the electronegativity of E is close to that of H. If the reaction barrier can be controlled to remain low, the chances of reversibility of such a reaction under mild conditions are increased, and E–E might be regarded as a molecular hydrogen storage material. An inspection of the periodic table shows that the (Pauling) electronegativities of main-group elements E such as B (2.0), P (2.1), As (2.0), Sb (1.9), Bi (1.9) and Te (2.1) are close to that of H (2.1). Of these elements, boron stands out as by far the lightest and therefore most interesting element with regard to applications in the field of hydrogen storage.[1] That group 13 element compounds are in principle interesting in this context has been shown by our group with a very simple example, namely the diatomic Ga_2 (Ga being the heavier "sister" of B). The Ga_2 dimer, which can be stabilized with the help of the matrix isolation technique, readily takes up dihydrogen to form a cyclic $Ga(\mu\text{-}H)_2Ga$ molecule [see Equation (1)].[2] The reaction barrier, estimated on the basis of the IR spectra recorded in experiments with mixtures of H_2 and D_2, amounts to ca. 40 $kJ\,mol^{-1}$, a value which is in good agreement with the results of quantum chemical calculations.[3]



(1)

These experiments therefore demonstrated that low reaction barriers are indeed possible. However, Ga_2 is not stable under normal conditions and therefore not directly relevant for application purposes. It would also be more interesting to find B compounds, which are lighter than their Ga counterparts. Therefore we searched for suitable dinuclear B compounds in low oxidation states in which the two B atoms can establish a direct B–B bond. In general, this can be achieved by bridging the two B atoms with one or more suitable ligands. If the two bridging ligands coordinate, the general reaction sequence (2) describes the possible uptake or release of H_2 for these molecular compounds (E being preferably B).



(2)

In the hpp ligand, which is obtained after H abstraction from hppH (1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine), we have now found a first example of a ligand where this concept might work. This ligand has been used extensively to bring together two transition-metal atoms in dinuclear compounds and engage them in direct and sometimes multiple metal–metal bonding. Examples of this in-

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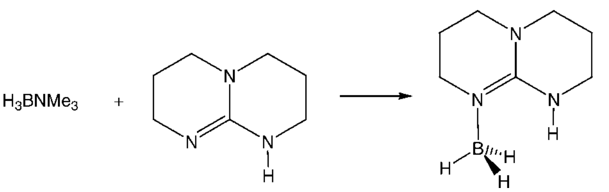
clude the complexes $Nb_2(hpp)_4$[4] and $M_2(hpp)_4Cl_2$ (where, for example, M = Ru,[5] W, Os and Pt[6]). Reaction sequence (2) then describes the conversion of a mononuclear E^{III} compound into a dinuclear E^{III} compound, which then eliminates dihydrogen to form a dinuclear E^{II} and finally a dinuclear E^{I} compound, the latter two featuring direct E–E bonding. It has also been shown recently that activation of hydrogen by subvalent compounds featuring direct E–E bonds is possible for the dinuclear compound Ar′GeGeAr′ [Ar′ = C_6H_3-2,6(C_6H_3-2,6-*i*Pr_2)$_2$], which can add one, two or three equivalents of H_2 to give first Ar′(H)GeGe(H)Ar′, then Ar′H_2GeGeH_2Ar′ and finally Ar′GeH_3.[7] It should also be noted that catalytic H_2 elimination from amine–borane adducts such as H_3BNMe_2H has been extensively studied recently.[8]

Results and Discussion

First we prepared the monomeric compound $H_3B{\cdot}hppH$ [see Equation (3)]. It is the first example of a structurally characterized 1:1 adduct of hppH to a group 13 element hydride, and it can be used as a precursor to the desired dinuclear hydrides. $H_3B{\cdot}hppH$ was synthesized by heating a solution containing equimolar quantities of $H_3B{\cdot}NMe_3$ and hppH for a period of 18 h at 60 °C. The analogous reaction between $H_3Ga{\cdot}NMe_3$ and hppH resulted in the direct formation of the dinuclear compound $[H_2Ga(hpp)]_2$,[9] even at 0 °C, and it proved impossible to isolate this adduct. In the crystal structure of $H_3B{\cdot}hppH$ illustrated in Figure 1[10] are featured two intramolecular as well as two intermolecular H···H contacts that are established between positively and negatively polarized H atoms.



(3)

These contacts are important, since they lower the barrier for H_2 elimination (vide infra). The intramolecular H···H contacts between two of the H atoms attached to the B atom and the H atom attached to the N atom of the same molecule are 223 and 224 pm (217 and 218 pm when normalized E–H distances are used[11]), respectively, and the corresponding intermolecular contacts measure 228 and 236 pm (220 and 228 pm). The B–N bond length is 157.5 pm. This value is shorter than the B–N bonds of borane–amine adducts. To name two recently reported examples, the B–N bond distances in the BH_3 adducts of $PhCH_2N(CH_3)_2$[12] and $HC(CH_2CH_2)_3N$[13] have been determined to be 162.0(2) and 160.8(5) pm, respectively. The distance is also shorter than that reported for imine adducts such as the *N*-benzyl (Bn) imine adduct $Ph_2C{=}N(Bn){\cdot}B(C_6F_5)_3$ featuring a B–N bond length of 164.2(8) pm.[14] The B–H bond lengths measure 110(2) (no H···H contacts), 112(1) and 112(2) pm, and the N–H bond is 89(2) pm long. Calculations were carried out to determine whether the inter- or intramolecular H···H contacts are responsible for the conformation of the BH_3 group. Calculations for an isolated molecule returned a conformation very close to that observed, and thus the intramolecular H···H contacts determine the geometry. This is also in line with the smaller observed values for the intramolecular H···H distances. In Figure 2 the relative energy is plotted as a function of the dihedral angle between the C–N–B and the N–B–H planes as calculated by using MP2/SVP.[15] It can be seen that the barrier for rotation around the B–N axis is no more than 4.5 kJ mol^{-1}.

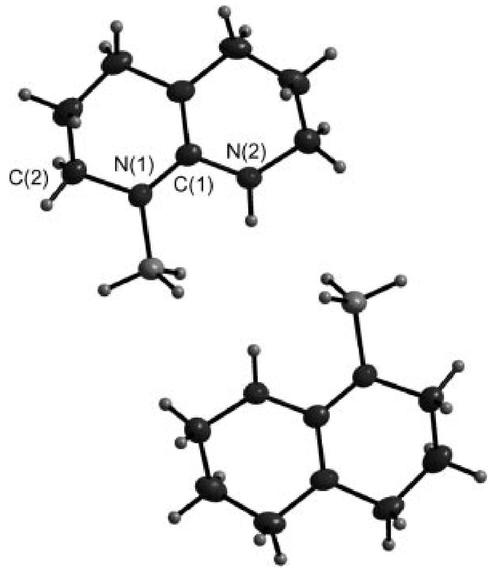


Figure 1. Molecular structure of $H_3B{\cdot}hppH$ in the crystalline phase showing the arrangement of two symmetrically equivalent molecules. The thermal ellipsoids are drawn at the 50 % probability level. Selected bond parameters (distances in pm, bond angles in degrees): B–H 110(2), 112(1), 112(2); B–N(1) 157.5(2); N(2)/N(1)–C(1) 134.8(2)/132.1(2); N(2)–H 89(2); B–N(1)–C(1) 122.3(1); B–N(1)–C(2) 117.8(1); N(1)–C(1)–N(2) 118.0(1).

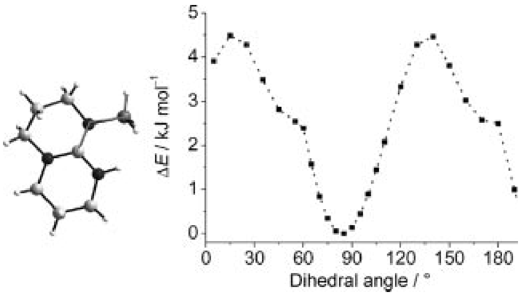


Figure 2. Relative energy as a function of the dihedral angle C–N–B–H as calculated with MP2/SVP.

Hydrogen is eliminated if a solution of the precursor $H_3B{\cdot}hppH$ is heated in toluene to 110 °C for 20 h. Interestingly, we did not obtain $[H_2B(hpp)]_2$ as the product of this reaction, as in the reaction of the corresponding Ga homologue,[9] but rather $[HB(hpp)]_2$ was produced directly [see

Equation (4)]. The barrier for H_2 elimination from $[H_2B(hpp)]_2$ is so small that this process occurs at temperatures below 110 °C. $[HB(hpp)]_2$ is the product of a redox reaction and features two B atoms in the formal oxidation state +2. In the case of $[H_2Ga(hpp)]_2$, we observed H_2 elimination even at 25 °C, and all signs indicated that $[HGa(hpp)]_2$ was the product.[9] However, we have so far been unable to structurally characterize this species. In the case of the boron compound, we have obtained good-quality crystals from toluene solutions, and Figure 3 illustrates the crystal structure derived from our X-ray diffraction data.[10] $[HB(hpp)]_2$ features a B–B single bond measuring 177.2(3) pm and a *cis*-bent arrangement of the H–B–B–H fragment [with B–H distances of 115(3) and 106(4) pm]. The value of the B–B bond length is in a range typical for B–B single bonds. For example, gas-phase electron diffraction measurements of $B_2(NMe_2)_4$ and $B_2(OMe)_4$ indicated B–B bond lengths of 176.2(1.1) and 172.0(6) pm.[16] The four B–N bond lengths are almost equal: 158.2(3), 156.3(3), 157.2(3) and 157.1(3) pm. The two five-membered BBNCN rings are almost planar, and the dihedral angle between them is 67.80(8)°. The IR spectrum contains absorptions in a region typical for terminal B–H stretches (2398–2230 cm^{-1}).

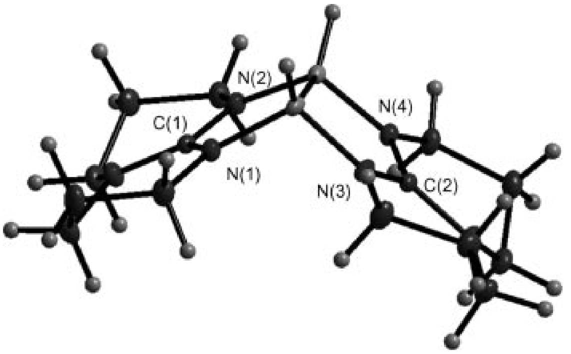
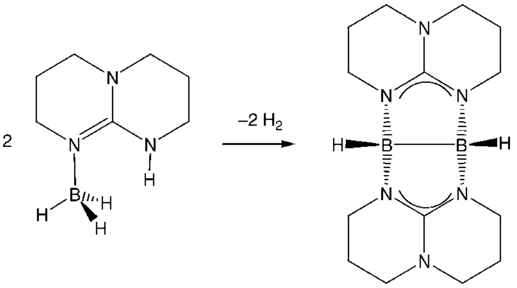
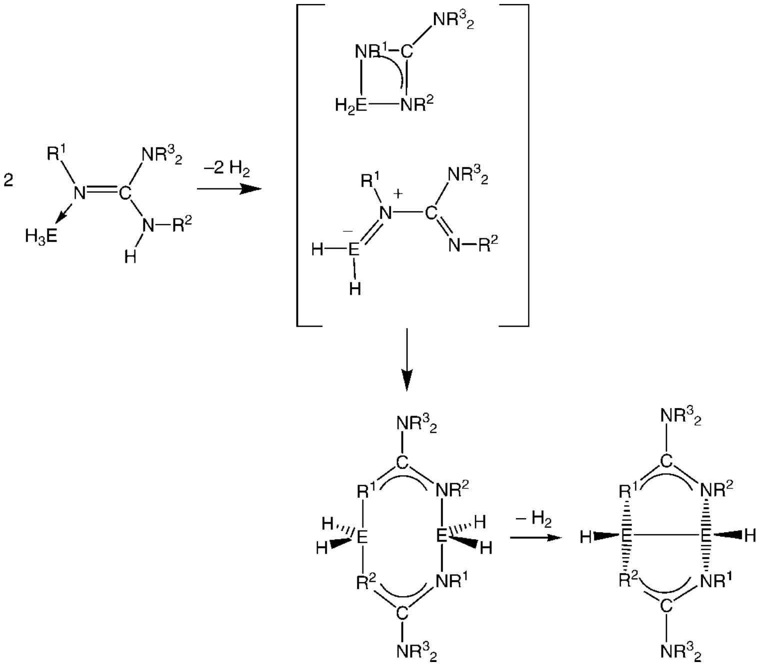


Figure 3. Molecular structure of $[HB(hpp)]_2$ in the crystalline phase. The thermal ellipsoids are drawn at the 50% probability level. Selected bond parameters (distances in pm, bond angles in degrees): B–H 115(3), 106(4); B–B 177.2(3); B–N 157.1(2), 157.2(3), 156.3(3), 158.2(3); N(1)/N(2)–C(1) 133.1(2), 134.3(2); N(3)/N(4)–C(2) 133.8(2), 133.4(2); N(1)–C(1)–N(2) 115.6(2); N(3)–C(2)–N(4) 115.3(2); N(1)/N(2)–B–N(3)/N(4) 111.0(2), 110.8(2).



(4)

The reaction pathway proposed on the basis of quantum chemical calculations leading from $H_3B{\cdot}hppH$ to $[HB(hpp)]_2$ is illustrated in reaction sequence (5) (generalized to guanidine derivatives). Intramolecular H_2 elimination from $H_3B{\cdot}hppH$ is facilitated by intramolecular H···H contacts and leads to a diene-type intermediate. The reaction energy and the standard Gibbs free energy for this first step are +74 (+46 with zero-point vibrational energy corrections) and +17 kJ mol^{-1}, respectively.[14] This diene-type intermediate is in equilibrium with a four-membered ring structure



(5)

in which the guanidinate ligand adopts a chelating binding mode. The standard Gibbs free energy change between the diene and the four-membered ring is calculated to be no more than 3 kJ mol^{-1} (in favour of the four-membered ring). The diene subsequently undergoes a [4+4] cycloaddition to give $[H_2B(hpp)]_2$. This second step is associated with an energy change of –109 (–118 including zero-point vibrational energy corrections) kJ mol^{-1} and a standard Gibbs free energy change of –87 kJ mol^{-1}. Finally, and most importantly, the reaction energy and standard Gibbs free energy for the formation of $[HB(hpp)]_2$ by H_2 elimination from $[H_2B(hpp)]_2$ come out to be +32 (+1 including zero-point vibrational energy corrections) and –30 kJ mol^{-1}, respectively. Solvation effects for this particular reaction were estimated by using the COSMO method[17] with $\varepsilon_r = 2.38$ for toluene. As expected, the effects are very small (ΔE decreases to +30 kJ mol^{-1}, and ΔG^0 increases slightly to –27 kJ mol^{-1}). Figure 4 shows ΔG for the decomposition reaction of $[H_2B(hpp)]_2$ to give $[HB(hpp)]_2$ and H_2 as a function of temperature at a pressure of 1 bar. Experiments will be undertaken to analyze whether the H_2 elimination can be accomplished reversibly. We are also extending our work to related compounds featuring two B atoms connected by one or two bridging guanidinate or amidinate ligands.

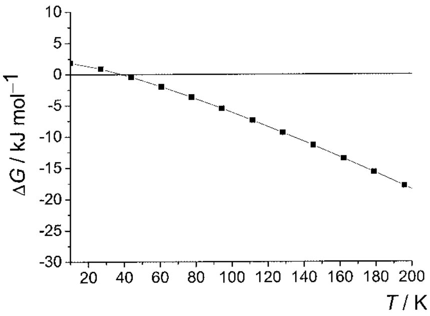


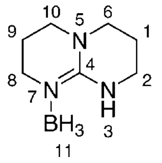
Figure 4. ΔG for the reaction $[H_2B(hpp)]_2 \rightarrow [HB(hpp)]_2 + H_2$ as a function of temperature at a constant pressure of 1 bar.

Conclusion

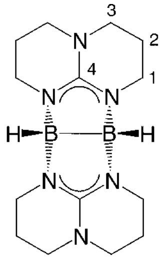
The base exchange reaction between $H_3B{\cdot}NMe_3$ and the guanidine derivative hppH affords the new borane adduct $H_3B{\cdot}hppH$. Intramolecular BH···HN contacts are established therein, facilitating H_2 elimination, which was observed around 110 °C. Dimerization and repeated H_2 elimination leads directly to the new diborane (4) derivative $[HB(hpp)]_2$. X-ray diffraction measurements reveal the presence of a trigonal prismatic central B_2N_4 unit in this hydride. Quantum chemical calculations were carried out to analyse the reaction pathway. These calculations suggest the formation of a diene-type intermediate upon intramolecular H_2 elimination followed by cycloaddition and elimination of a second H_2 molecule to give the observed product. Future experiments concentrate on the synthesis of other derivatives of this class of compounds, which might also be interesting for H_2 activation, and on the synthesis of the intermediate $[HB(hpp)]_2$ by catalytic dehydrocoupling reactions.

Experimental Section

All reactions were carried out under a dry argon atmosphere by using standard Schlenk techniques. All solvents were dried by using standard methods followed by distillation. $H_3B{\cdot}NMe_3$ and hppH were purchased from Aldrich and used as received.



$H_3B{\cdot}hppH$: A solution of $H_3B{\cdot}NMe_3$ (0.524 g, 7.18 mmol) in toluene (20 mL) was added to a solution of hppH (1.00 g, 7.18 mmol) in toluene (20 mL) by syringe, and the reaction mixture was stirred for 18 h at 60 °C. The colourless solution was concentrated, and *n*-pentane (ca. 10 mL) was added to obtain a white precipitate in 70% yield (0.70 g, 5.03 mmol). Crystals suitable for X-ray diffraction were grown from a hexane/toluene (2:1) mixture at –20 °C. $C_7H_{16}BN_3$ (153.03): calcd. C 54.94, H 10.54, N 27.46; found C 54.36, H 10.38, N 26.91. ^1H NMR (400 MHz, C_6D_6): δ = 6.29 (s, 1 H, NH), 3.34 (t, ^3J = 5.9 Hz, 2 H, 8-H), 2.83 (br. q, ^1J = 93 Hz, 3 H, BH_3), 2.27 (t, ^3J = 5.9 Hz, 2 H, 6-H), 2.13 (t, ^3J = 6.0 Hz, 2 H, 10-H), 2.03 (t, ^3J = 6.0 Hz, 2 H, 2-H), 1.17 (quint, ^3J = 6.0 Hz, 2 H, 9-H), 0.91 (quint, ^3J = 6.0 Hz, 2 H, 1-H) ppm. $^{13}C\{^1H\}$ NMR (100.55 MHz, C_6D_6): δ = 150.69 (C-4), 47.47 (C-8), 47.27 (C-10), 46.82 (C-2), 38.38 (C-6), 21.80 (C-9), 21.57 (C-1) ppm. ^{11}B NMR (128.30 MHz, C_6D_6): δ = –19.15 (q, ^1J = 93 Hz, BH_3) ppm. HRMS (EI+): *m/z* (%) = 152.14 (100.0) $[M - H]^+$, 138.10 (28.2) $[hpp]^+$, 122.09 (5.6) $[M - CH_3NH_2]^+$, 113.00 (5.1) $[M - CH_3NB]^+$, 95.07 (2.8) $[M - C_2H_9NB]^+$. IR (solid CsI): $\tilde{\nu}$ = 3352 (s) (N–H val), 2960 (m) (C–H val), 2872 (m) (C–H val), 2363 (m) (B–H), 2301 (m) (B–H), 2253 (m) (B–H), 1625 (s) (C=N val.), 1570 (s) (N–H def.), 1447 (w) (C–H def.), 1322 (m), 1174 (m) (B–N), 1148 (m) cm^{-1}.



$[HB(hpp)]_2$: A solution of $H_3B{\cdot}NMe_3$ (0.21 g, 2.9 mmol) in toluene (15 mL) was slowly added to a solution of hppH (0.4 g, 2.9 mmol) in toluene (15 mL). The reaction mixture was heated under reflux for 20 h at 110 °C. The solution was concentrated, and colourless crystals of the toluene solvate were obtained from these solutions after storage for several days at –20 °C. ^1H NMR (600 MHz, $[D_8]$toluene): δ = 3.23 (t, ^3J = 5.8 Hz, 2 H, 1-H), 2.57 (t, ^3J = 6.6 Hz, 2 H, 3-H), 1.56 (quint, 2 H, 2-H) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $[D_8]$toluene): δ = 47.96 (C-3), 47.19 (C-1), 24.21 (C-2) ppm. $^{11}B\{^1H\}$ NMR (192.5 MHz, $[D_8]$toluene): δ = –2.39 (BH) ppm. MS (EI+): *m/z* = 299.4 $[C_{14}H_{26}B_2N_6]^+$, 138.2 $[hpp]^+$. IR (solid CsI): $\tilde{\nu}$

= 2964 (m) (C–H), 2852 (m) (C–H), 2398–2230 (m) (B–H), 1565 (s) (C–N), 1321 (m) (B–N) cm^{-1}. It should be noted that the NMR spectra provided evidence for a second species in very small quantities. This might be the isomer of $[HB(hpp)]_2$ featuring hpp ligands which are coordinated to only one B atom. This second species is characterized by the following NMR spectra: ^{1}H NMR (600 MHz, [D$_8$]toluene): δ = 3.48 (m, 1 H, C_AH_2), 3.39 (m, 1 H, C_AH_2), 2.52 (m, 1 H, C_CH_2), 2.42 (m, 1 H, C_CH_2), 1.59 (m, 1 H, C_AH_2), 1.49 (m, 1 H, C_AH_2) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, [D$_8$]toluene): δ = 47.59 (C_C), 45.81 (C_A), 23.37 (C_B) ppm. ^{11}B{^{1}H} NMR (192.5 MHz, [D$_8$]toluene): δ = –1.12 (BH) ppm.

Acknowledgments

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[10] $H_3B\cdot hppH$: $C_7H_{16}BN_3$, M_r = 153.04; 0.30 × 0.30 × 0.20 mm^3, orthorhombic, space group *Pbca*; a = 8.459(2) Å, b = 13.534(3) Å, c = 15.111(3) Å, V = 1730.0(6) Å^3, Z = 8, d_{calc} = 1.175 Mg m^{-3}, Mo-K_α radiation (graphite monochromated, λ = 0.71073 Å), T = 173(2) K, θ range 3.1 to 27.5°. Reflections measured: 3671, independent: 1977, R_{int} = 0.033, empirical absorption correction. Final R indices $[I > 2\sigma(I)]$: R_1 = 0.044, wR_2 = 0.1148, maximum residual electron density 0.16 e Å^{-3}. All non-hydrogen atoms were given anisotropic displacement parameters. The hydrogen atom positions on the N and B atoms were taken from difference Fourier syntheses and refined with individual isotropic displacement parameters. All other hydrogen atoms were input in calculated positions. $[HB(hpp)]_2$: $C_{14}H_{26}B_2N_6\cdot C_7H_8$, M_r = 392.16; 0.30 × 0.15 × 0.15 mm^3, monoclinic, space group *Pn*; a = 8.1843(5) Å, b = 8.3965(6) Å, c = 15.5586(10) Å, β = 100.9340(10)°, V = 1049.77(12) Å^3, Z = 2, d_{calc} = 1.241 Mg m^{-3}, Mo-K_α radiation (graphite monochromated, λ = 0.71073 Å), T = 100(2) K, θ range 2.4 to 32.1°. Reflections measured: 25932, independent: 3513, R_{int} = 0.050, semiempirical absorption correction.[18] Final R indices $[I > 2\sigma(I)]$: R_1 = 0.0457, wR_2 = 0.1161. All non-hydrogen atoms were given anisotropic displacement parameters. All hydrogen atom positions (except those of the methyl group, which was refined as a variable metric rigid group with hydrogen atoms input at calculated positions) were taken from difference Fourier syntheses and refined with individual isotropic displacement parameters. A maximum residual electron density of 0.80 e Å^{-3} was found above the centre of and attributed to the boron–boron bond. Structure solution by using direct methods: SHELXS-97,[19] refinement by full-matrix least-squares on F^2: SHELXL-97.[20] CCDC-642232 ($H_3B\cdot hppH$) and CCDC-642233 {$[HB(hpp)]_2$} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] Corrections which take into account thermal elongations and the effect of high-electron-density gradients generally leading to too short E–H bond lengths in the X-ray structures.

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