Zinc Halide and Alkylzinc Complexes of a Neutral Doubly Base-Stabilized Diborane(4)

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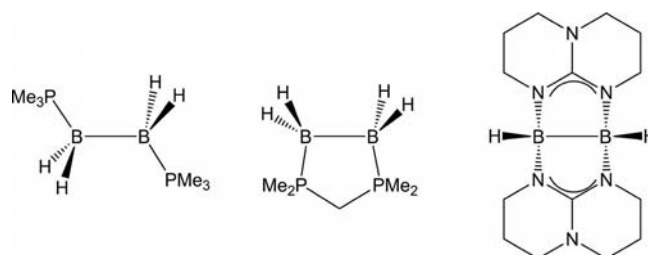The doubly base-stabilized diborane(4) [HB(μ-hpp)]$_2$ (hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinate) was used as a ligand in the first authenticated example of a dialkylzinc complex and the second example of a zinc halide complex featuring a neutral boron hydride as ligand. The three complexes [ZnCl$_2${HB(μ-hpp)}$_2$] (**2**), [ZnBr$_2${HB(μ-hpp)}$_2$] (**3**),

and [ZnMe$_2${HB(μ-hpp)}$_2$] (**4**) were fully characterized. The bonding properties were analysed in detail. This analysis indicated a complex bonding situation involving not only the two hydrogen atoms, but also the two boron atoms of the [HB(μ-hpp)]$_2$ ligand.

Introduction

Anionic boron hydrides have been shown to exhibit a rich coordination chemistry. Nevertheless, examples of structurally characterized alkylzinc complexes featuring anionic boron hydride ligands and B–H–Zn bridges are restricted to a few compounds, which include MeZnBH$_4$[1] and [(MeZn)$_2$B$_3$H$_7$]$_2$.[2] Up to date, no alkylzinc compound of a neutral boron hydride is known. In the light of the great synthetic potential of alkylzinc compounds and boron hydrides, such compounds are of considerable interest. The neutral boron hydride bis(trimethylphosphanyl)diborane(4), B$_2$H$_4$(PMe$_3$)$_2$, and the related B$_2$H$_4$(PMe$_2$CH$_2$PMe$_2$) (see Scheme 1) have been shown to be versatile ligands, which are generally bonded through two of the hydrido substituents to the metal center. Examples of structurally characterized complexes of this kind include [ZnCl$_2$-{B$_2$H$_4$(PMe$_3$)$_2$}] (**1**),[3] [Cu{B$_2$H$_4$(PMe$_3$)$_2$}]I,[4] [M(CO)$_4$-{B$_2$H$_4$(PMe$_3$)$_2$}] (M = Cr, Mo or W),[5,6] and [Cr(CO)$_4$]$_2$-[B$_2$H$_4$(PMe$_2$CH$_2$PMe$_2$)].[7] Unfortunately, the structures of the free ligands B$_2$H$_4$(PMe$_3$)$_2$ and B$_2$H$_4$(PMe$_2$CH$_2$PMe$_2$) are up to date unknown, so that a direct comparison of the structural changes upon coordination is not possible.[8] Additional information on the ligand properties of these diboranes(4) were derived from the IR spectra recorded for carbonyl complexes, such as [M(CO)$_4${B$_2$H$_4$(PMe$_3$)$_2$}] (M = Cr, Mo or W) or the structurally uncharacterized [Ni(CO)$_2$-{B$_2$H$_4$(PMe$_3$)$_2$}].[9] These complexes are generally stable at room temperature, at least in the solid state.[10]
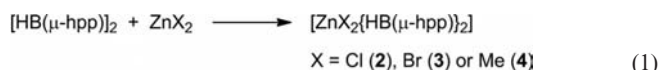

Scheme 1.

Recently, we showed that the doubly base-stabilized diborane(4) [HB(μ-hpp)]$_2$ (see Scheme 1) (hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinate) can easily be prepared by catalytic dehydrogenation of the adduct H$_3$B·hppH,[11–13] and also reported its structural properties. Oxidative insertion reactions into its B–B bond were in the focus of our first reactivity studies. Hence, protonation was shown to lead to the cationic boron hydride and B$_2$H$_5$$^+$ analogue [B$_2$H$_3$(μ-hpp)$_2$]$^+$.[12] Sulfuration with elemental sulfur gives eventually, after passing several coloured (and spectroscopically characterized) intermediate stages, the neutral hydride [HB(μ-hpp)]$_2$(μ-S).[13] Here we now analyse a new aspect of the reactivity of [HB(μ-hpp)]$_2$, namely its use as a ligand. In contrast to B$_2$H$_4$(PMe$_3$)$_2$ and related diborane(4) species, [HB(μ-hpp)]$_2$ exhibits no rotational freedom around the B–B bond, and the B–H groups are already ideally oriented for complex formation.

We report in the following the second example of a zinc halide with a neutral boron hydride as ligand, namely [ZnCl$_2${HB(μ-hpp)}$_2$], as well as the first example of an alkylzinc complex of this kind, namely [ZnMe$_2${HB(μ-hpp)}$_2$] [see Equation (1)]. The structure and bonding in the two complexes will be discussed by taking into account the results of quantum chemical calculations.

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$$[HB(\mu\text{-hpp})]_2 + ZnX_2 \longrightarrow [ZnX_2\{HB(\mu\text{-hpp})\}_2]$$

$$X = Cl \; (\mathbf{2}), \; Br \; (\mathbf{3}) \; \text{or} \; Me \; (\mathbf{4}) \qquad (1)$$

Results and Discussion

Reaction between [HB(μ-hpp)]$_2$, prepared as already reported by catalytic dehydrogenation of the adduct H$_3$B·hppH,[12] and ZnCl$_2$ in dichloromethane/diethyl ether solutions at room temp. yielded the new boron-containing product **2**. The ^{11}B{^{1}H} NMR spectrum of **2** shows a single signal at δ = –8.61 ppm. For comparison, the [HB(μ-hpp)]$_2$ reactant gave rise to an ^{11}B NMR signal at δ = –1.14 ppm. The signal of **2** splits into a doublet if proton coupling is allowed [$^1J(^1H^{11}B)$ = 70 Hz], arguing for the presence of one hydrogen atom bonded directly to the boron atom. The IR spectrum of **2** contains two intense absorptions centered at 2180 and 2152 cm^{-1}, which can be assigned to B–H stretching modes. The position is considerably redshifted in comparison to [HB(μ-hpp)]$_2$ (2272 and 2249 cm^{-1} for the in-phase and out-of-phase combination of the two B–H oscillators, respectively). Crystals of **2**·CH$_2$Cl$_2$ were grown from dichloromethane solution, and the compound was finally identified unambiguously as the complex [ZnCl$_2$-{HB(μ-hpp)}$_2$]. Its molecular structure derived from single-crystal X-ray diffraction data is illustrated in Figure 1. The unit cell contains two slightly different, C_S-symmetric molecules, together with one CH$_2$Cl$_2$ molecule. The Zn and the two Cl atoms as well as the midpoint of the B–B bond lie within the mirror plane. Like in **1**, the ZnH$_2$B$_2$ five-membered ring is almost planar. The Zn–B distance in **2** measures 220.0(2) pm in one and 221.5(2) pm in the other molecule within the unit cell and is thus considerably shorter than in **1**[3] (226.4/227.6 pm). With 183.4(4) and 184.1(4) pm, the B–B bonds in **2** are significantly elongated relative to the free diborane(4) [HB(μ-hpp)]$_2$ [177.2(3) pm].[14] They also are longer than the B–B bond in **1**[3] [181.4(6) pm]. The Cl–Zn–Cl angles of 122.34(3) and 119.08(3)° in **2** compare with 114.7(1)° in **1**.[3] The angle B–Zn–B was measured to be 49.25(10)°/49.13(10)°.

In a similar way the corresponding Br compound [ZnBr$_2${HB(μ-hpp)}$_2$] (**3**) was prepared from [HB(μ-hpp)]$_2$ and ZnBr$_2$. Crystals were again grown from dichloromethane. The molecular structure of **3** is illustrated in Figure 2. The unit cell features again two slightly different molecules, together with two molecules of CH$_2$Cl$_2$. Some structural and spectroscopic data accumulated for the two complexes are compiled in Table 1. According to this comparison, the bonding properties appear to be similar.

The differences in the structural properties of the ligand [HB(μ-hpp)]$_2$ before and after coordination argue for a strong metal–ligand interaction. The measured structural and spectroscopic parameters also indicate that the bonding to ZnCl$_2$ is much stronger for [HB(μ-hpp)]$_2$ than for B$_2$H$_4$(PMe$_3$)$_2$. Motivated by these results, we tested coordination of [HB(μ-hpp)]$_2$ to the much weaker Lewis acid ZnMe$_2$. Surprisingly, complex formation was observed simply after stirring of a mixture of [HB(μ-hpp)]$_2$ and ZnMe$_2$
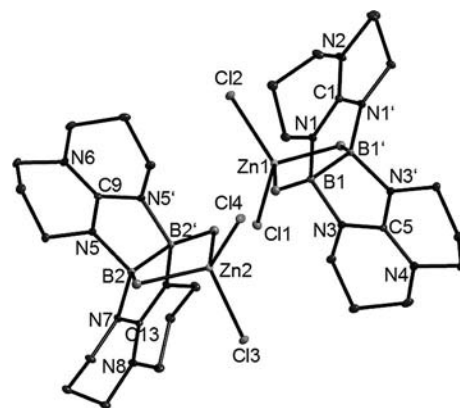

Figure 1. Molecular structure of **2**. Vibrational ellipsoids drawn at the 50% probability level. The hydrogen atoms of the two hpp groups are omitted. Selected structural parameters (bond lengths in pm, bond angles in °): Zn1–B1 220.0(2), Zn2–B2 221.5(2), Zn1–Cl1 221.82(8), Zn1–Cl2 222.85(8), Zn2–Cl3 222.13(8), Zn2–Cl4 219.01(8), B1–B1′ 183.4(4), B2–B2′ 184.1(4), B1–N1 152.7(3), B1–N3 153.6(2), B2–N5 153.5(2), B2–N7 152.6(2), N1–C1 135.1(2), N2–C1 134.0(3), N3–C5 134.36(19), N4–C5 134.5(3), N5–C9 134.9(2), N6–C9 133.7(3), N7–C13 134.1(2), N8–C13 134.7(3); Cl1–Zn1–Cl2 122.34(3), Cl3–Zn2–Cl4 119.08(3), N1–C1–N1′ 114.4(2), N3–C5–N3′ 114.5(2), N5–C9–N5′ 114.1(2), N7–C13–N7′ 114.9(2), N1–B1–N3 117.14(16), N5–B2–N7 115.90(15), B1–Zn1–B1′ 49.25(10), B2–Zn2–B2′ 49.13(10), B1′–B1–H 125.2(12), B2′–B2–H 135.0(12).
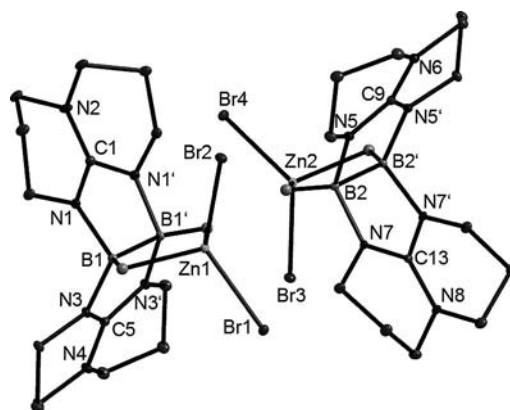

Figure 2. Molecular structure of **3**. Vibrational ellipsoids drawn at the 50% probability level. The hydrogen atoms of the two hpp groups are omitted. Selected structural parameters (bond lengths in pm, bond angles in °): Zn1–B1 2.212(3), Zn2–B2 2.204(3), Zn1–Br1 2.3454(7), Zn1–Br2 2.3655(7), Zn2–Br3 2.3568(7), Zn2–Br4 2.3235(8), B1–B1′ 1.832(6), B2–B2′ 1.851(6), B1–N1 1.523(4), B1–N3 1.531(4), B2–N5 1.538(4), B2–N7 1.530(4), N1–C1 1.352(3), N2–C1 1.331(6), N3–C5 1.342(3), N4–C5 1.353(5), N5–C9 1.344(3), N6–C9 1.354(6), N7–C13 1.348(3), N8–C13 1.342(5); Br1–Zn1–Br2 122.56(3), Br3–Zn2–Br4 119.02(2), N1–C1–N1′ 113.9(4), N3–C5–N3′ 114.9(3), N5–C9–N5′ 114.6(4), N7–C13–N7′ 114.4(3), N1–B1–N3 118.2(3), N5–B2–N7 115.8(2), B1–Zn1–B1′ 48.94(15), B2–Zn2–B2′ 49.67(15), B1′–B1–H 131(2), B2′–B2–H 126(2).

in toluene at room temperature, and crystals were grown directly from the reaction mixture at a temperature of 3 °C. Figure 3 shows the structure of this complex {[ZnMe$_2${HB(μ-hpp)}$_2$] (**4**)}, which represents the first authenticated dialkylzinc complex to a neutral boron hydride.

Table 1. Comparison between some salient exp. parameters for $[ZnX_2\{HB(\mu\text{-hpp})\}_2]$ (X = Cl, Br or CH_3) (bond lengths in pm, bond angles in °, frequencies in cm^{-1}, chemical shifts in ppm).

	X = Cl (**2**)	X = Br (**3**)	X = CH₃ (**4**)	$[HB(\mu\text{-hpp})]_2$
d(B–B)	183.4(4)/184.1(4)	183.2(6)/185.1(6)	180.5(4)	177.2(3)
d(B–Zn)	220.0(2)/221.5(2)	221.2(3)/220.4(3)	247.4(3)/246.0(3)	–
$\angle$(B–Zn–B)	49.25(10)/49.13(10)	48.94(15)/49.67(15)	42.91(9)	–
$\angle$(X–Zn–X)	122.34(3)/119.08(3)	122.56(3)/119.02(2)	138.65(11)	–
ν(B–H)	2180/2152	2175	2219	2272/2249
δ(^{11}B)	–8.61	–7.93	–1.75	–1.14

Selected structural parameters along with spectroscopic information for **4** are compiled together with those obtained for **2** and **3** in Table 1. As expected, the data clearly point to a much weaker coordinative link in **4**. The position of the ^{11}B NMR signal increases in the order **2** (δ = –8.61 ppm) < **3** (δ = –7.93 ppm) << **4** (δ = –1.75 ppm) < $[HB(\mu\text{-hpp})]_2$ (δ = –1.14 ppm). With 2219 cm^{-1}, the wavenumber measured for the B–H stretching mode is much higher in **4** than in **2** (2180/2152 cm^{-1}) or **3** (2175 cm^{-1}), being closer to that of the free ligand $[HB(\mu\text{-hpp})]_2$ (2272/2249 cm^{-1}). The B–B bond length shrinks in the order **2** [183.4(4)/184.1(4) pm] ≥ **3** [183.2(6)/185.1(6) pm] > **4** [180.5(4) pm] > $[HB(\mu\text{-hpp})]_2$ [177.2(3) pm]. The distance B–Zn of 247.4(3)/246.0(3) pm in **4** is by more than 25 pm longer than those in **2** or **3** [220.0(2)/221.5(2) and 221.2(3)/220.4(3) pm, respectively]. Finally, the N–B–N angle [111.87(19)/112.66(19)°] in **4** is much closer to that of the free ligand $[HB(\mu\text{-hpp})]_2$ [111.0(2)/110.8(2)°] than in the complexes **2** [117.14(16)/115.90(15)°] and **3** [118.2(3)/115.8(2)°].
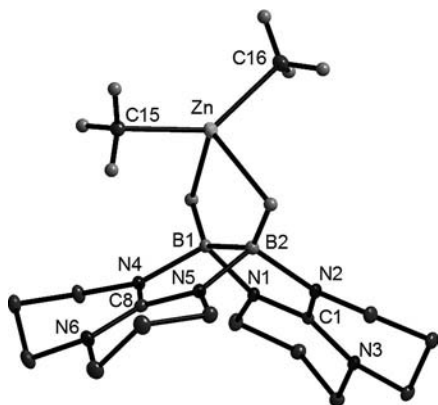

Figure 3. Molecular structure of **4**. Vibrational ellipsoids drawn at the 50% probability level. The hydrogen atoms of the two hpp groups are omitted. Selected structural parameters (bond lengths in pm, bond angles in °): Zn–B1 247.4(3), Zn–B2 246.0(3), Zn–C15 200.7(2), Zn–C16 199.6(3), B1–B2 180.5(4), B1–N1 155.7(3), B1–N4 154.6(3), B2–N2 155.7(3), B2–N5 155.5(3), N1–C1 133.8(3), N2–C1 133.8(3), N3–C1 135.6(3), N4–C8 134.0(3), N5–C8 134.2(3), N6–C8 135.3(3); C15–Zn–C16 138.65(11), N1–C1–N2 115.1(2), N4–C8–N5 115.3(2), N1–B1–N4 111.87(19), N2–B2–N5 112.66(19), B1–Zn–B2 42.91(9), B1–B2–H 131.8(16), B2–B1–H 129.2(16).

The differences in bonding between the dialkylzinc complex **4** and the two zinc halide complexes **2** and **3** can be rationalized by the differences in the Lewis acidity of the metal center. Nevertheless, a closer inspection of the bonding properties is worthwhile. The metal–diborane(4) bond-

ing could in principal be composed of two different contributions, as sketched in Scheme 2. In the first contribution (see Scheme 2a), which is expected to dominate, the diborane(4) acts as a chelating ligand, with the negatively polarized hydrogen atoms bonded to the metal center. In this way, the bonding in the previously studied complexes of $B_2H_4(PMe_3)_2$ and $B_2H_4(PMe_2CH_2PMe_2)$ was explained. In the second contribution (which is expected to be less important), the B–B bond coordinates to the metal atom (see Scheme 2b). From the experimental parameters (see Table 1) it is clear that this second contribution is more relevant for **2** or **3** than for **4**. Hence, the significant increase of the B–B bond length in the course of complexation with $ZnCl_2$ leading to **2** [from 177.2(3) pm before to 183.4(4)/184.1(4) pm after complexation] is indeed in line with this second contribution. Furthermore, the B–Zn distances in **2** and **3** are relatively short (ca. 221 pm). They are indeed significantly shorter than e.g. the 229 pm measured in the complex $[Zn(\eta^2\text{-}BH_4)Cl(tmen)]$ (**5**) (tmen = tetramethylethylenediamine, see Scheme 3), with the boron atoms in the oxidation state +III and no sign of direct B–Zn bonding,[15] but still longer than the 208.8(3)/208.7(3) pm adopted in complex **6** (see Scheme 3, Dip = 2,6-diisopropylphenyl) with the boron atoms in the formal oxidation state +I and two B–Zn bonds.[16]
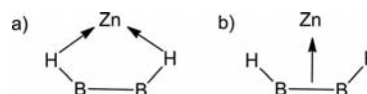
Scheme 2.
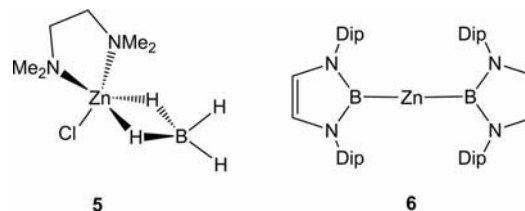
Scheme 3.

It appeared to be not possible to answer the question regarding the nature of the coordinative link in the complexes purely on the basis of the experimental results. Additional information was therefore acquired from an analysis of the topology of the electron density distribution from quantum chemical calculations. The bonding in B_2H_6 was recently analysed on the basis of the experimentally derived electron-density distribution,[17] and quantum chemical cal-

Table 2. Comparison between selected exp. and calcd. parameters for **2** (bond lengths in pm, bond angles in °, frequencies in cm^{-1}).

	Exp.	RI-MP2/def2-TZVPP	B3LYP/def2-TZVP[a]	BP/def2-TZVP	B3LYP/6-311++G(d,p)
d(B–B)	183.4(4)/184.1(4)	181.63	180.85	181.90	181.10
d(B–Zn)	220.0(2)/221.5(2)	223.95	233.83	229.49	230.67
d(Zn–Cl)	221.82(8)/222.85(8)	219.23	221.92	221.17	222.55
∠(B–B–H)	125.2(12)/135.0(12)	129.1	129.1	129.3	129.0
∠(Cl–Zn–Cl)	122.34(3)/119.08(3)	139.4	133.3	132.8	133.0
ν(B–H)	2180/2152	not calcd.	not calcd.	2240 /2229	2292 /2280

[a] = Hydrogen atoms boded to boron atoms were calculated by using B3LYP/def2-TZVPP.

culations based on functional/basis set combination B3LYP/6-311++G(d,p) were shown to reproduce the electron-density distribution in B$_2$H$_6$ satisfactorily.[12] Therefore, it appeared reasonable to employ this combination also for the calculations on **2** and **4**. In Table 2, some structural parameters for **2** as derived experimentally are compiled together with the calculated ones. It can be seen that the B–Zn distances are heavily overestimated with B3LYP/6-311++G(d,p). The additionally quoted parameters derived from an RI-MP2 calculation show a much better agreement. Complex **4** was also calculated with B3LYP/6-311++G(d,p), and a comparison of some parameters is given in the Supporting Information. With 265.64 pm, the calculations again overestimate the B–Zn distance [experimentally derived values of 247.4(3)/246.0(3) pm]. The calculated topologies of the electron-density distribution for **2** and **4** are illustrated in Figure 4, which in addition shows the positions of the bond (3,–1) and ring (3,+1) critical points (highlighted by triangles and crosses, respectively, in Figure 4). As expected, three critical points are located along the B–B and the two B–H bonds. In the case of **2** only one other critical point was detected, which is located in the center of the B–Zn–B triangle. Critical points along the lines connecting the Zn atom with the two H atoms are missing. This finding is consistent with a complex binding situation involving all five atoms (the Zn atoms, the two H and the two B atoms). A slightly different bonding situation is present in **4**. Hence, two additional bond critical points were found between H and Zn together with two ring critical points. Although the difference in electron density is

very small, the results of the calculations are consistent with the presence of a significant Zn–B$_2$ bonding contribution, which is stronger in **2** than in **4**.

Conclusions

The doubly base-stabilized diborane(4) [HB(μ-hpp)]$_2$ was used in this work as a ligand in the first authenticated example of a dialkylzinc complex and the second example of a zinc halide complex featuring a neutral boron hydride as ligand. The three complexes [ZnCl$_2${HB(μ-hpp)}$_2$] (**2**), [ZnBr$_2${HB(μ-hpp)}$_2$] (**3**), and [ZnMe$_2${HB(μ-hpp)}$_2$] (**4**) were fully characterized. The bonding properties were analysed in detail. This analysis indicated a complex bonding mode involving not only the two hydrogen atoms, but also the two boron atoms of the [HB(μ-hpp)]$_2$ ligand. In ongoing work we are currently extending our research to other transition metals, especially those relevant for catalytic hydrogenation of [HB(μ-hpp)]$_2$.

Experimental Section

General: The reactions were carried out under argon by using standard Schlenk techniques. All solvents were rigorously dried by applying standard procedures prior to their use. The synthesis of [HB(μ-hpp)]$_2$ was accomplished as reported previously.[12] ZnCl$_2$ and ZnBr$_2$ were obtained from Acros and Aldrich, respectively, and stored in a glove box (MBraun LABmaster dp, MB-20-G) under argon.

2: A solution of dry ZnCl$_2$ (68 mg, 0.50 mmol) in diethyl ether (10 mL) was added to a solution of [HB(μ-hpp)]$_2$ (150 mg, 0.50 mmol) in dichloromethane (10 mL). After stirring at room temp. for 17 h, the solvent was removed, and the colourless residue was recrystallized from dichloromethane solutions to give colourless crystals in 24% yield (52 mg, 0.12 mmol). C$_{14}$H$_{26}$B$_2$Cl$_2$N$_6$Zn·CH$_2$Cl$_2$ (518.06): calcd. C 34.56, H 5.41, N 16.12; found C 34.97, H 5.42, N 16.38. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ = 3.31 [t, ^3J(H,H) = 5.8 Hz, 8 H, NCH$_2$], 3.20–3.09 (m, 8 H, NCH$_2$), 1.98–1.85 (m, 8 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$): δ = 157.0 (2 C, C), 46.4 (4 C, NCH$_2$), 44.7 (4 C, NCH$_2$), 21.8 (4 C, CH$_2$) ppm. ^{11}B NMR (128 MHz, CD$_2$Cl$_2$): δ = –8.61 [d, ^1J(H,B) = 70 Hz, 2 B, BH] ppm. IR (KBr): ṽ = 3038 (w) (C–H val.), 2960 (s) (C–H val.), 2935 (s) (C–H val.), 2858 (s) (C–H val.), 2760 (w) (C–H val.), 2180 (m) (B–H val.), 2152 (m) (B–H val.), 2118 (w), 2088 (w), 2047 (s), 1607 (s) (C=N val.), 1517 (s) (C=N val.), 1477 (m), 1460 (m), 1441 (m), 1400 (m), 1370 (m), 1350 (w), 1318 (s), 1278 (s), 1226 (s), 1191 (m), 1103 (s), 1063 (s), 1050 (s) cm^{-1}. Crystal data for 2[ZnCl$_2${HB(μ-hpp)}$_2$]·CH$_2$Cl$_2$:
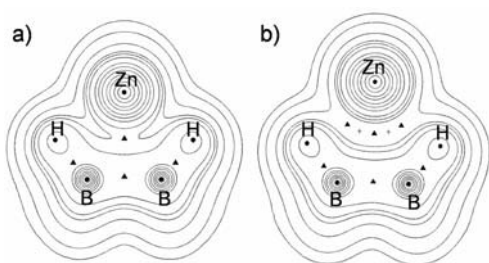

Figure 4. Topology of the electron-density distribution of (a) **2** and (b) **4** in the plane defined by the two B atoms and the Zn atom. Electron density (av., in e Å^{-3}) at the (3,–1) bond critical points (triangles): (a) B–H 0.1567, B–B 0.1315, (B–B)–Zn 0.0538; (b) B–H 0.1593, B–B 0.1454, (B–B)–Zn 0.0268, Zn–H 0.0269 and the (3,+1) ring critical points (crosses): 0.0266. Lines were drawn at electron densities of 0.004, 0.008, 0.02, 0.04, 0.052, 0.08, 0.2, 0.4, 0.8, 2, 4, 8 and 20 e Å^{-3}.

$C_{29}H_{54}B_4Cl_6N_{12}Zn_2$, Mr = 957.56, $0.35 \times 0.30 \times 0.30$ mm, orthorhombic, space group $Pmc2(1)$, a = 12.154(2), b = 10.619(2), c = 17.041(3) Å, V = 2199.4(8) Å^3, Z = 4, $d_{calcd.}$ = 1.446 Mg m^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 2.39–33.17°. Reflections measd. 8185, indep. 8182, R_{int} = 0.0209. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0312, wR_2 = 0.0683.

3: A solution of dry $ZnBr_2$ (113 mg, 0.50 mmol) in diethyl ether (3 mL) was added to a solution of [HB(µ-hpp)]$_2$ (150 mg, 0.50 mmol) in dichloromethane (10 mL). After stirring at room temp. for 17 h, the solvent was removed, and the colourless residue was recrystallized from dichloromethane solutions to give colourless crystals in 53% yield (139 mg, 0.26 mmol). $C_{14}H_{26}B_2Br_2N_6Zn$ (525.24): calcd. C 32.01, H 4.99, N 16.00; found C 32.38 H 5.05, N 15.93. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.31 [t, ^3J(H,H) = 5.8 Hz, 8 H, NCH$_2$], 3.21–3.09 (m, 8 H, NCH$_2$), 2.00–1.84 (m, 8 H, CH$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ = 157.2 (2C, C), 46.4 (4 C, NCH$_2$), 44.8 (4 C, NCH$_2$), 21.8 (4 C, CH$_2$) ppm. ^{11}B NMR (100 MHz, CD_2Cl_2): δ = –7.93 [d, ^1J(B,H) = 72 Hz, 2 B, BH] ppm. IR (KBr): ṽ = 2959 (s) (C–H val.), 2935 (s) (C–H val.), 2858 (s) (C–H val.), 2760 (w) (C–H val.), 2366 (w), 2344 (w), 2175 (m) (B–H val.), 2042 (m), 1598 (s) (C=N val.), 1517 (s) (C=N val.), 1475 (m), 1458 (m), 1440 (m), 1401 (m), 1371 (m), 1317 (s), 1279 (s), 1227 (s), 1187 (m), 1105 (s), 1060 (s) cm^{-1}. Crystal data for [ZnBr$_2${HB(µ-hpp)}$_2$]·CH$_2$Cl$_2$: $C_{15}H_{28}B_2Br_2Cl_2N_6Zn$, Mr = 610.14, $0.44 \times 0.40 \times 0.38$ mm, orthorhombic, space group $Pmc2(1)$, a = 12.243(2), b = 10.849(2), c = 17.113(3) Å, V = 2273.0(8) Å^3, Z = 4, $d_{calcd.}$ = 1.783 Mg m^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 2.22–33.15°. Reflections measd. 8471, indep. 8471, R_{int} = 0.0209. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0348, wR_2 = 0.0829.

4: A 1.2 M solution of Me$_2$Zn in toluene (0.45 mL, 0.55 mmol) was added to a solution of [HB(µ-hpp)]$_2$ (150 mg, 0.50 mmol) in toluene (15 mL). After stirring at room temp. for 17 h, the solution was concentrated and stored at 3 °C to give colourless crystals. They were filtered and dried to give clean product in 57% yield (113 mg, 0.29 mmol). $C_{16}H_{32}B_2N_6Zn$ (394.22): calcd. C 48.95, H 8.16, N 21.25; found C 48.85, H 8.05, N 21.87. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 3.33–3.27 (m, 4 H, NCH$_2$), 3.17–3.11 (m, 4 H, NCH$_2$), 2.36–2.10 (m, 8 H, NCH$_2$), 1.52–1.43 (m, 4 H, CH$_2$), 1.38–1.29 (m, 4 H, CH$_2$), –0.17 (s, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 156.8 (2 C, C), 46.7 (4 C, NCH$_2$), 45.9 (4 C, NCH$_2$), 22.8 (4 C, CH$_2$), –11.8 (2 C, CH$_3$) ppm. ^{11}B NMR (128 MHz, C$_6$D$_6$): δ = –1.75 (br. s, 2 B, BH) ppm. IR (KBr): ṽ = 2957 (s) (C–H val.), 2925 (s) (C–H val.), 2883 (s) (C–H val.), 2850 (s) (C–H val.), 2814 (s) (C–H val.), 2219 (m) (B–H val.), 2047 (w), 1575 (s) (C=N val.), 1474 (m), 1457 (m), 1439 (m), 1398 (m), 1369 (m), 1307 (s), 1274 (s), 1219 (s), 1179 (m), 1134 (w), 1100 (m), 1061 (s) cm^{-1}. Crystal data for [ZnMe$_2${HB(µ-hpp)}$_2$]: $C_{16}H_{32}B_2N_6Zn$, Mr = 395.49, $0.25 \times 0.20 \times 0.20$ mm, monoclinic, space group $P2_1/c$, a = 15.506(3), b = 8.3700(17), c = 14.634(3) Å, β = 90.69(3)°, V = 1899.1(7) Å^3, Z = 4, $d_{calcd.}$ = 1.383 Mg m^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 2.63–28.67°. Reflections measd. 9561, indep. 4878, R_{int} = 0.0207. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0444, wR_2 = 0.1118.

CCDC-814126 (compound **2**), -814125 (compound **3**) and -814124 (compound **4**) 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.

Details of the Quantum Chemical Calculations: See Supporting Information. The AIM 2000[18] guise of program was used to calculate the topology of the electron-density distribution for complexes **2** and **4**.

Supporting Information (see footnote on the first page of this article): ^{1}H, ^{11}B and ^{11}B{^{1}H} NMR spectra of **2**, **3** and **4**; comparison between selected exp. and calcd. parameters for **4**; details of the X-ray crystallographic studies and details of the quantum chemical calculations.

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