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Article

First Dinuclear B(II) Monocations with Bridging Guanidinate Ligands: Synthesis and Properties

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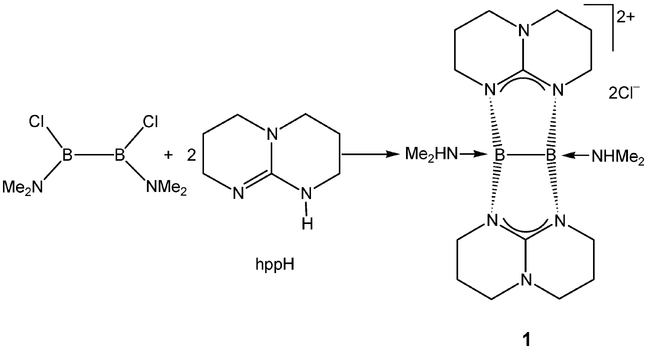
Reaction between the diborane (4) $B_2Cl_2(NMe_2)_2$ and Li(hpp) ($hpp^- = 1,3,4,6,7,8$-hexahydro-2H-pyrimido[1,2-a]-pyrimidinate) leads to $[(Me_2N)B(\mu\text{-hpp})]_2$. This species can be protonated by $HCl \cdot OEt_2$ to give $[(Me_2HN)B(\mu\text{-hpp})]_2Cl_2$featuring two B(II) cations with direct B−B bonding. The unsymmetrical monocation $[(Me_2N)B_2(\mu\text{-hpp})_2(NHMe_2)]^+$ is also obtained. $[(Me_2HN)B(\mu\text{-hpp})]_2Cl_2$ eliminates $NHMe_2$ in a slow reaction leading to $[ClB_2(\mu\text{-hpp})_2(NHMe_2)]Cl$ and ultimately, presumably, to $[ClB(\mu\text{-hpp})]_2$. We report the crystal structures of the two monocations $[ClB_2(\mu\text{-hpp})_2(NHMe_2)]Cl$ and $[(Me_2N)B_2(\mu\text{-hpp})_2(NHMe_2)]Cl$. The experimental results are accompanied by some quantum chemical density-functional theory calculations.

Introduction

Recently we reported, in a preliminary communication, the synthesis of the compound $[(hpp)B(NMe_2H)]_2Cl_2$ (hpp^- = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinate), **1**, which can be prepared by reaction between the diborane(4) derivative $B_2Cl_2(NMe_2)_2$ and the guanidine base hppH (see Scheme 1).[1] Compound **1** is the first example for a new class of dimeric cationic B(II) species. The two B and four N atoms bound directly in **1** adopt a rooftop-like structure. We postulated that the reaction proceeds in two steps via the bisamide intermediate $[(\mu\text{-hpp})BNMe_2]_2$, **2a**, which reacts with the additionally formed HCl to give **1**. Diborane **1** crystallizes from a CH_2Cl_2/hexane mixture as a CH_2Cl_2 solvate (see Table 1 for selected bond parameters). A thermogravimetric analysis showed that the two dimethylamine ligands in **1** can be removed at temperatures below 200 °C.[1] The relative weakness of the $B-NMe_2H$ bonds makes these dicationic compounds interesting for catalytic applications.

In this article we now report the first synthesis and characterization of two new related monocationic compounds, namely, $[(Me_2N)B_2(\mu\text{-hpp})_2(NHMe_2)]Cl$ and $[ClB_2(\mu\text{-hpp})_2(NHMe_2)]Cl$. ESI^+ spectra indicate that $[ClB_2(\mu\text{-hpp})_2(NHMe_2)]Cl$ dimerizes to give tetranuclear boron complexes. Furthermore, new experiments reported herein are fully consistent with the previously proposed pathway leading to **1**.

Scheme 1



Experimental Section

All reactions were performed under a dry argon atmosphere using the standard Schlenk technique. All solvents were dried using standard methods and then distilled. $B_2Cl_2(NMe_2)_2$ was prepared according to literature procedure.[2] $B_2(NMe_2)_4$ and hppH (98%) were purchased from Boron Molecular Pty Ltd. and Aldrich, respectively, and used as delivered. NMR spectra were measured with a Bruker Avance II 400 spectrometer. Deprotonation of hppH was accomplished using ^{n}BuLi to form the corresponding hpp^- guanidinate anion. A solution of hppH (1.86 g, 13.4 mmol) in 20 mL of toluene

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10.1021/ic8000812 CCC: $40.75

Table 1. Selected Bond Distances (in pm) and Angles (in degrees) As Measured for **1**, **2b**, **3**, and **4**[a]

	1	**2b**	**3**	**4**
B1−B2	174.6(2)	177.2(3)	175.3(4)	170.6(7)
B1−N1	155.2(4)	1.571(2)	156.2(4)	155.5(6)
B2−N2	154.3(4)	1.582(3)	153.9(4)	155.0(6)
B1−N4	155.1(4)	1.572(3)	156.3(4)	152.9(6)
B2−N5	153.9(4)	1.563(3)	154.8(4)	153.0(5)
N1−C1	134.5(4)	1.342(2)	133.7(4)	135.2(5)
N2−C1	134.9(4)	1.331(2)	134.4(4)	133.6(5)
C1−N3	133.8(4)	1.365(2)	134.1(4)	135.6(5)
N4−C8	134.4(4)	1.338(2)	132.8(4)	135.2(5)
N5−C8	133.9(4)	1.334(2)	134.5(4)	134.7(5)
C8−N6	134.5(4)	1.358(2)	134.6(4)	133.9(5)
B1−N7	160.1(4)		153.7(4)	
B1−Cl				192.2(5)
B2−N8	160.6(4)		160.3(4)	
B2−N7				161.0(6)
N−H	100.08/89.1		0.92(4)	0.936(19)
N•••Cl	308.3/311.1		313.1	311.2
H•••Cl	209.4/224.5		225.7	218.3
N1−B1−N4	111.8(2)	111.04(15)	110.7(2)	114.1(4)
N2−B2−N5	112.2(2)	110.75(15)	113.2(2)	114.5(3)
N1−C1−N2	115.0(2)	115.55(16)	114.8(3)	115.8(4)
N4−C8−N5	115.2(2)	115.34(16)	115.6(2)	115.4(3)
N7−B1−B2	130.7(2)		134.5(3)	
Cl1−B1−B2				125.1(3)
N8−B2−B1	130.1(2)		125.7(2)	
N7−B2−B1				122.7(4)
B1−H1		1.15(3)		
B1−H2		1.772(3)		

[a] Please note that the atom numbering for **2b** differs from that in ref 13 to make it similar to that of the other compounds.

was cooled to 0 °C and 1 equiv. of ^{n}BuLi (1.6 M solution in hexane) added. The solution was allowed to warm to room temperature and stirred for 1 h. $B_2Cl_2(NMe_2)_2$ (1.21 g, 6.7 mmol) was slowly added to a stirred solution of Li(hpp) (13.4 mmol) in 20 mL of toluene. The reaction mixture was stirred for 3 h at room temperature, during which time formation of a white precipitate was observed. The LiCl was removed by filtration, and the filtrate was evaporated to afford crude **2a**.

NMR Spectra: 1. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.90$ (septet, H8, *2H*, ^{3}J(H8−H15) = 5.5), 3.67 (dt, H2a, *4H*, ^{2}J(H2a−H2b) = 12.8 Hz, ^{3}J(H2a−H3) = 5.0 Hz), 3.30 (dt, H2b, *4H*, ^{2}J(H2b−H2a) = 12.8 Hz, ^{3}J(H2b−H3) = 6.3 Hz), 3.19 (dt, H4a, 4*H*, ^{2}J(H4a−H4b) = 11.9 Hz, ^{3}J(H4a−H3) = 5.0 Hz), 3.12 (dt, H4b, 4*H*, ^{2}J(H4b−H4a) = 11.9 Hz, ^{3}J(H4b−H3) = 6.5 Hz) 2.42 (d, H-15, *12H*, ^{3}J(H15−H8) = 5.5 Hz), 1.89 (q, H3, *8H*, ^{3}J(H3−H) = 5.0 Hz, ^{3}J(H3−H) = 6.5 Hz). ^{13}C-{^{1}H} NMR (100.56 MHz, CD_2Cl_2): $\delta = 158.36$ (C-1), 47.79 (C-4), 40.39 (C-2), 39.86 (C-15), 22.18 (C-3). ^{11}B {^{1}H} NMR (128.3 MHz, CD_2Cl_2): $\delta =$ 1.43. **2a**: The ^{1}H NMR spectra showed, as expected, no signal due to an NH proton, the typical signals expected for the hpp^{-} ligands, and the signals of the two NMe_2 groups. However, the ^{11}B NMR spectra showed two signals at 2.25 and 0.17 ppm. Of these, the signal at 0.17 ppm most likely belongs to another B containing species (which, however, does not contain hpp). Tentative ^{1}H NMR of **2a**: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 3.46$ (m, H2, *8H*), 3.14 (m, H4, *8H*), 2.30 (s, H15, *12H*), 1.86 (m, H3, *8H*). ^{13}C-{^{1}H} NMR (100.56 MHz, CD_2Cl_2): $\delta = 48.07$ (C-4), 40.64 (C-15), 39.89 (C-2), 22.69 (C-3). ^{11}B{^{1}H} NMR (128.3 MHz, CD_2Cl_2): $\delta = 2.25$ and $\delta = 0.17$. **4**: ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 8.72$ (m, H8, 1H), 3.76 (dt, H2a, 2H, ^{2}J(H2a−H2b) = 12.9 Hz, ^{3}J(H2a−H3) = 4.7 Hz), 3.43 (m, H7a, 2H), 3.16 (H2b, H4, H5, H7b, 12 H), 2.43 (d, H15, 6H, ^{3}J(H15−H7) = 5.4 Hz), 1.89 ppm (m, H3, H6, 8H). ^{13}C NMR (100.56 MHz, CD_2Cl_2): $\delta = 157.57$ (C1), 47.71 (C4), 47.62 (C5), 40.75 (C2), 39.41 (C7), 37.99 (C15), 22.53 (C3), 22.23 ppm (C6). ^{11}B NMR (128.3 MHz, CD_2Cl_2): $\delta = 3.11$ (B1), 1.07 ppm (B2).

X-ray Crystallographic Studies. Crystals of **3** and **4** were grown from CH_2Cl_2/hexane solutions. Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a glass capillary. Measurements were made on a Nonius-Kappa CCD diffractometer with a low-temperature unit using graphite-monochromated Mo Kα radiation. The temperature was set to 200 K. The data collected were processed using the standard Nonius software.[3] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[4,5] Graphical handling of the structural data during solution and refinement was performed with XPMA.[6] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations.

Crystallographic data (excluding structure factors) for structures **3** and **4** reported in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-674639 and CCDC-674640. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk]. Summary of the crystallographic data: **3**·CH_2Cl_2: $C_{16}H_{39}B_2Cl_3N_8$, $M_W = 507.55$; temperature, 200 K; wavelength, 0.71073 Å; triclinic, $P\bar{1}$, $a = 985.9(2)$ pm, $b = 1031.3(2)$ pm, $c = 1488.3(3)$ pm, $\alpha = 74.73(3)°$, $\beta = 83.50(3)°$, $\gamma = 62.60(3)°$, $V = 1296.0(5) \times 10^6$ pm^3, $Z = 2$, $\rho_{calc} = 1.301$ Mg m^{-3}, $F_{000} = 540$; crystal size, 0.50 × 0.50 × 0.40 mm; θ range for data collection, $2.29° \leq \theta \leq 27.58°$; reflexions measured, 48680; unique reflections, 5767; $R_{int} = 0.0341$; observed reflections ($I > 2\sigma(I)$), 3957; refinement method, full-matrix least-squares on F; parameters refined, 332; goodness of fit, 1.036; R_1, 0.0635; $wR = 0.1626$; min./max. residual electron density, –0.784/0.70 × 10^{-6} e pm^3. **4**·1.2 CH_2Cl_2: $C_{16}H_{31}B_2Cl_{12}N_7$·1.2 CH_2Cl_2, $M_W = 257.95$; temperature, 200 K; wavelength, 0.71073 Å; monoclinic, P2(1)/c, $a = 1057.9(2)$ pm, $b = 2951.7(6)$ pm, $c = 1660.2(3)$ pm, $\beta = 96.73(3)°$, $V = 5148.4(18) \times 10^6$ pm^3, $Z = 16$, $\rho_{calc} = 1.331$ Mg m^{-3}, $F_{000} = 2163$; crystal size, 0.80 × 0.80 × 0.60 mm; θ range for data collection, $1.38° \leq \theta \leq 27.52°$; reflexions measured, 22676; unique reflections, 11789; $R_{int} = 0.0666$; observed reflections ($I > 2\sigma(I)$), 6591; refinement method, full-matrix least-squares on F; parameters refined, 580; goodness of fit, 1.031; R_1, 0.0753; w$R = 0.2065$; min/max. residual electron density, –0.539/1.082 × 10^{-6} e pm^3.

Results and Discussion

Figure 1 displays the structure of **1** as determined by X-ray diffraction and also a representative ^{1}H NMR spectrum of **1**.[1] **2a**, the proposed intermediate in the synthesis of **1**, can be synthesized by reaction between $B_2Cl_2(NMe_2)_2$ and

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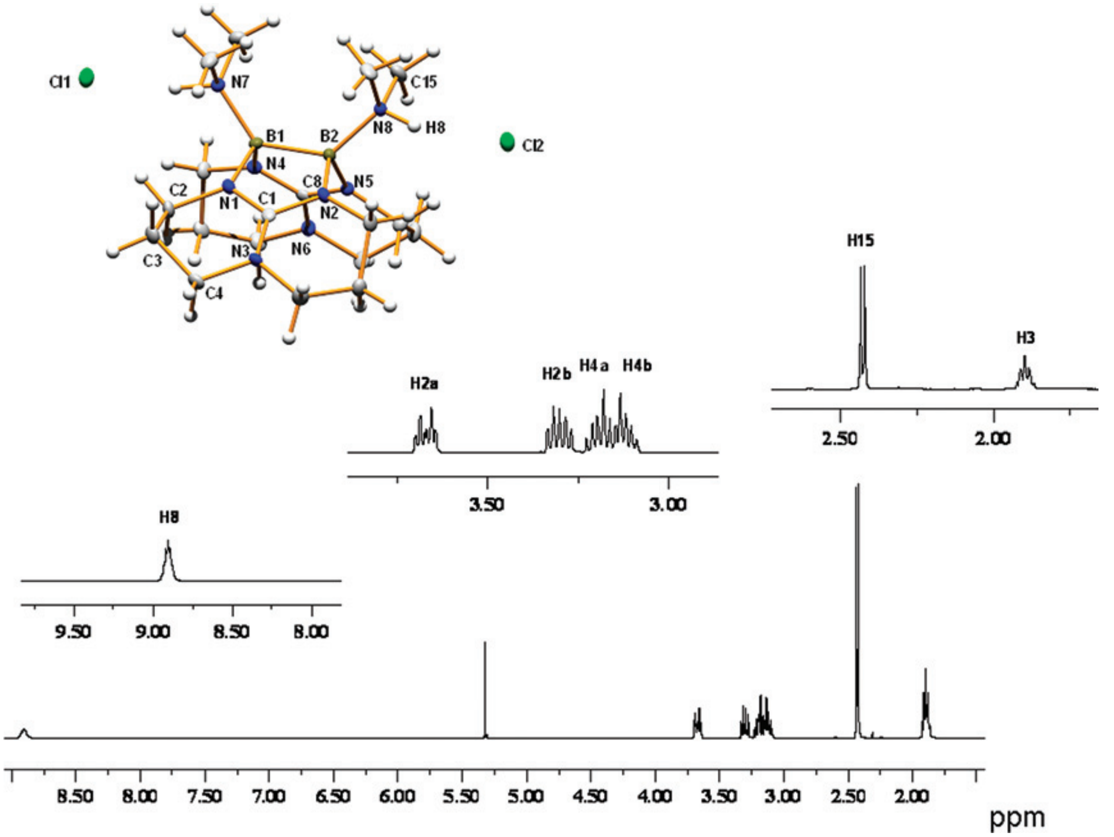
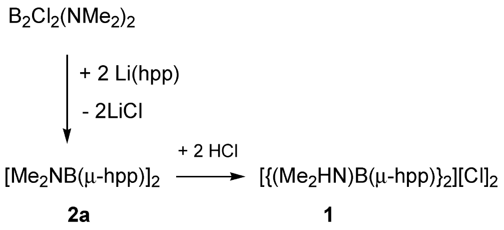


Figure 1. Crystal structure from X-ray diffraction (ellipsoids are drawn at the 50% probability level) and NMR spectra (chemical shifts in ppm) obtained for **1**.

Scheme 2



Li(hpp) (see Scheme 2). This species turned out to be extremely reactive, and we were unfortunately not able to characterize it adequately. Quantum chemical density-functional theory (DFT) calculations were performed with TURBOMOLE,[7] and the resulting minimum structure is depicted in Figure 2. The BP86 functional[8] as well as the B3LYP hybrid functional[9] were applied. For all atoms the def2-TZVPP basis set was chosen.[10] The calculated structure (see Table 2 for selected bond parameters and the Supporting Information for coordinates and vibrational properties) resembles that of the previously characterized $[HB(\mu\text{-hpp})]_2$, **2b**.[11] Similar to the structure of **1**, the characteristic feature is a slightly distorted trigonal prismatic central B_2N_4 unit. The B−B bonds in **2b** (177.2(3) pm) and **1** (174.6(2) pm) are in the typical region for B−B single bonds, so that **2a** should also exhibit such a bond, in agreement with the results of the calculations suggesting a B−B bond distance of 179.7 pm. Addition of $HCl\cdot Et_2O$ to **2a** gives **1** in a clean reaction (as followed by NMR spectroscopy), showing that the experimental data are consistent with the proposed pathway.

Although we were not able to get crystals of **2a**, we managed to isolate a small amount of an intermediate of its reaction with HCl, namely $[Me_2NB(\mu\text{-hpp})_2B(NMe_2H)]^+Cl^-$, **3**. A few crystals of $\mathbf{3}\cdot CH_2Cl_2$ were grown from CH_2Cl_2/hexane. The structure as determined by X-ray diffraction is shown in Figure 3. The B−B bond distance in **3** was determined to be 175.3(4) pm and is thus slightly larger than that in **1**, where 174.6(2) pm were measured.[1] As anticipated, the $B-NMe_2$ distance [153.7(4) pm] is significantly shorter than the $B-NMe_2H$ distance [160.3(4) pm]. For comparison, in **1** the $B-NMe_2H$ distances amount to 160.1(4) and 160.6(4) pm. Like **2a**, **3** is a reactive species, and we were not able to separate it from compound **1**. Because the NMR spectra of these compounds are similar, an ambiguous NMR spectroscopic characterization turned out to be impossible because of lack of enough pure samples.

1 undergoes a slow decomposition reaction when kept for several weeks in a CH_2Cl_2/hexane solution in which one or

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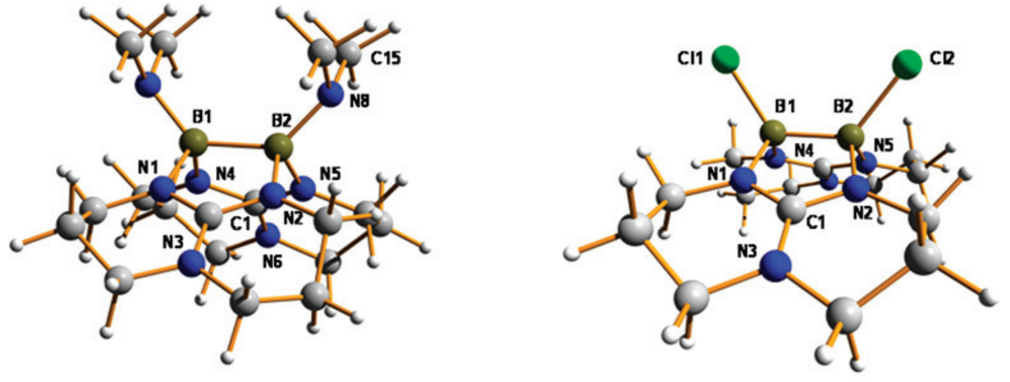


2a **5**

Figure 2. Illustration of the structures from quantum chemical calculations of **2a** and **5**.

Table 2. Selected Bond Distances (in pm) and Angles (in degrees) As Calculated for **2a** and **5**

	2a	5
B1−B2	179.7	173.1
B1−N1	159.2	156.2
B2−N2	159.6	156.2
B1−N4	159.6	156.4
B2−N5	159.2	156.0
N1−C1	134.3	134.7
N2−C1	134.3	134.8
C1−N3	137.2	136.9
N4−C8	134.3	134.9
N5−C8	134.3	134.7
C8−N6	137.2	136.5
B1−N7	153.4	
B1−Cl1		189.6
B2−N8	153.4	
B2−Cl2		189.8
N1−B1−N4	108.9	113.8
N2−B2−N5	108.9	114.0
N1−C1−N2	116.2	115.8
N4−C8−N5	116.2	115.8
N7−B1−B2	132.2	
Cl1−B1−B2		124.9
N8−B2−B1	132.2	
Cl2−B2−B1		124.9

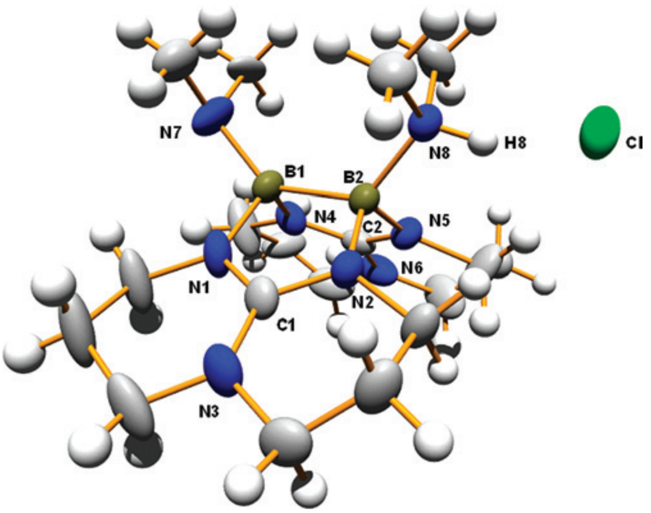
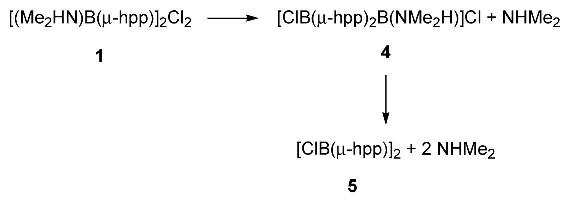


Figure 3. Crystal structure from X-ray diffraction for **3**. Ellipsoids are drawn at the 50% probability level.

Scheme 3



even both $NHMe_2$ groups are eliminated leading to the species $[ClB(\mu\text{-hpp})_2B(NMe_2H)]^+Cl^-$, **4**, and ultimatively presumably $[(\mu\text{-hpp})BCl]_2$, **5** (see Scheme 3). Compound **4** was obtained in larger amounts and can also clearly be characterized by NMR spectra recorded for solutions of the crystalline material. The observed loss of $NHMe_2$ is in full agreement to the thermogravimetric and quantum chemical studies[1] which already indicated a relatively weak B−$NHMe_2$ bonding. Colorless crystals of **4** suitable for X-ray analysis were obtained from the CH_2Cl_2/hexane solutions. Figure 4 illustrates the structure of **4** as determined by X-ray diffraction. Table 1 compares selected bond distances and angles with those obtained for related compounds. With 170.6(7) pm, the B−B bond is significantly shorter than in **1** or **2b**. The B−Cl distance measures 192.2(5) pm and is thus relatively long. For comparison, in $[BCl(NMe_3)]_2$[12] B−Cl bond distances of 186 and 189 pm have been measured. These values are much larger than those adopted in three-coordinated diborane species (e.g., 181.9(4) pm in $[BCl(NH\textit{i}Pr_2)]_2$[13] and 177.0(5)/177.4(4) pm in $[BCl(Mes)]_2$ (Mes = mesityl)).[14] The B←$NHMe_2$ donor bond is again more than 5 pm larger than the B−N bonds to the hpp^- ligands. ESI^+ spectra (see Supporting Information) indicate that **4** dimerizes to give $[B_4Cl_4(hpp)_4(NMe_2H)_2]$ or a salt $[B_4Cl_3(hpp)_4(NMe_2H)_2]Cl$. Thus, in addition to the signals due to M^+ and $[M - NMe_2H]^+$ at $m/z = 378$ and 333, a large signal appeared in the spectrum of **4** at about $m/z = 792$ which can be assigned on the basis of the mass and the isotopic pattern to the $[B_4Cl_3(hpp)_4(NMe_2H)_2]^+$ cation. Unfortunately we were so far unable to isolate and crystallize this interesting tetramer. Of course, it is in principle also possible that the cation is formed in the gas-phase. However, signals from **1**

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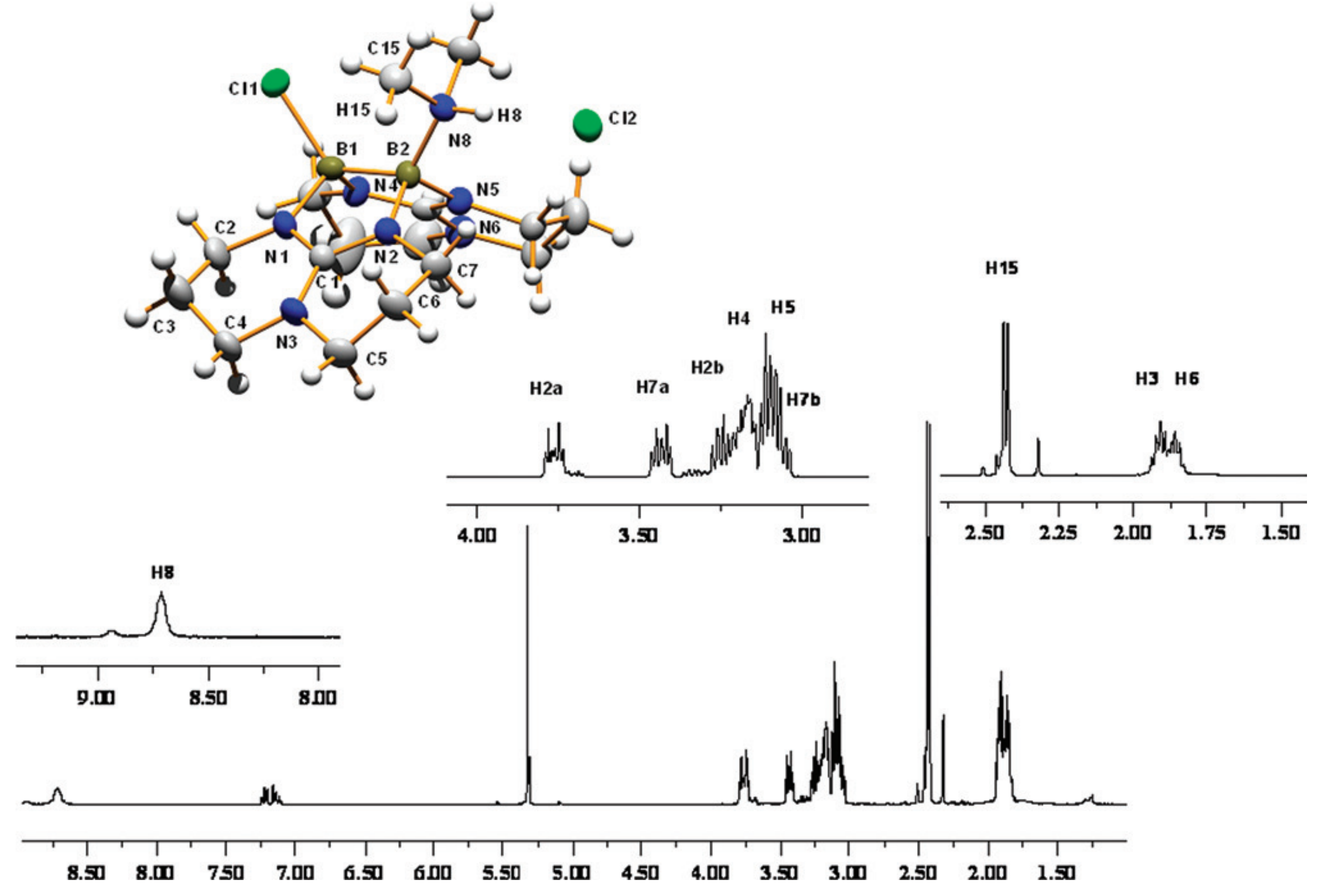

Figure 4. Crystal structure from X-ray diffraction (ellipsoids are drawn at the 50% probability level) and NMR spectra (chemical shifts in ppm) obtained for **4**.

are absent in the ESI spectra; therefore, a gas-phase process is not very likely. The elusive structure of **5** was calculated using the same method and basis set as for **2a**, and selected bond distances and angles are included in Table 2.

Conclusions

In summary, this article presents the structures of the first B(II) monocations $[(Me_2N)B_2(\mu\text{-hpp})_2(NHMe_2)]Cl$, **3**, and $[ClB_2(\mu\text{-hpp})_2(NHMe_2)]Cl$, **4**, and sheds some light on their reactivity. With 170.6(7) pm, the B−B bond in **4** is the shortest of the compounds for which XRD data are available (**1**, **2b**, **3**, and **5**), in line with the electronegativity of the Cl ligand, and with 177.2(3) pm, the B−B bond in the neutral compound **2b** is the longest. The B−B bond distance of **1** (174.6(2) pm) and **3** (175.3(4) pm) are in between. Current work in our group is directed into the analysis of their reactivity with special emphasis on possible applications in the area of homogeneous catalysis.

Acknowledgment. The authors thank the *Deutsche Forschungsgemeinschaft* and the *Fond der Chemischen Industrie* for their continuous financial support.

Supporting Information Available: Crystallographic data of **3** and **4** in CIF format, 2d NMR spectra and ESI spectra for **4**, and calculated coordinates and vibrational properties of **2a** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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