

# Boron di- and tri-cations†

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Previous work on boron di- and tri-cations is reviewed. The structural chemistry of representative examples of these classes of compound has been probed by determination of the single-crystal X-ray structures of [(4-Mepy)<sub>4</sub>B]Br<sub>3</sub> and [py<sub>3</sub>BH]Br<sub>2</sub>. The electronic structures of the polycations [(py)<sub>3</sub>BH]<sup>2+</sup>, [(py)<sub>3</sub>BBr]<sup>2+</sup>, [(4-Mepy)<sub>3</sub>BH]<sup>2+</sup>, [(4-Mepy)<sub>4</sub>B]<sup>3+</sup>, [(Me<sub>3</sub>P)<sub>3</sub>BH]<sup>2+</sup> and [(Me<sub>3</sub>P)<sub>4</sub>B]<sup>3+</sup> have been examined by DFT methods. The atomic charges on these cations were evaluated by Mulliken, natural population analysis (NPA), Hirschfeld and Voronoi deformation density (VDD) methods.

## Introduction

The first claims to mononuclear boron di- and tri-cations appeared in a patent that was issued over fifty years ago.<sup>1</sup> However, this patent featured little or no characterization data. An interest in this subject resurfaced in the mid-1960's starting with the work of Prasad and Singh,<sup>2</sup> who described species consistent with the formulation [L<sub>3</sub>BCl]Cl<sub>2</sub> (L = amine) but lacking definitive characterization. Two publications appeared in 1967 in which mononuclear boron di-cations were claimed. Thus, Lappert and Srivastara<sup>3</sup> investigated the reactions of various amido-substituted boron dichlorides with pyridine and found that treatment of Et<sub>2</sub>NBCl<sub>2</sub> with three equivalents of pyridine afforded a product of composition [Et<sub>2</sub>NBpy<sub>3</sub>]Cl<sub>2</sub> (**1**), which was characterized by elemental analysis, IR spectroscopy and conductivity measurements. However, compound **1** showed little conductivity in nitrobenzene solution. Ryschkewitsch *et al.*<sup>4</sup> studied the reactions of the Lewis acid–base complex Me<sub>3</sub>NBBr<sub>3</sub> (**2**) with pyridine and substituted pyridines and found that boron di-cation salts of the type [L<sub>3</sub>BBr]Br<sub>2</sub> (**3**, **4**) can be isolated (L = pyridine (**3**), 3,5-dimethylpyridine (**4**)). Using a similar approach, it was also possible to produce the boron tri-cation salts, [L<sub>4</sub>B]Br<sub>3</sub> (**5**) by using the stronger base 4-methylpyridine. Salts **3–5** are water soluble and conductance measurements were consistent with the proposed formulae. Moreover, it was possible to effect anion exchange with KPF<sub>6</sub> or KAsF<sub>6</sub> to afford the corresponding [PF<sub>6</sub>]<sup>−</sup> and [AsF<sub>6</sub>]<sup>−</sup> salts in essentially quantitative yields. Compounds **3** and **4** were also characterized by elemental analysis, IR and UV spectroscopy. Subsequent work revealed that the analogous nucleophilic displacement of two bromide anions from the Lewis acid–base complex R<sub>3</sub>NBBr<sub>2</sub> (R = Me (**6**), Et) afforded high yields of the hydrido-substituted boron di-cations [L<sub>3</sub>BH]X<sub>2</sub> (L = pyridine (**7**) or substituted pyridine; X = Br (**7**), I).<sup>5</sup> As in the

case of the halo-substituted di-cations, the two bromide anions could be substituted by [PF<sub>6</sub>]<sup>−</sup> anions. The foregoing hydridoboron di-cation salts were also characterized by elemental analysis, IR spectroscopy and <sup>1</sup>H and <sup>11</sup>B NMR. In the case of the [py<sub>3</sub>BH]<sup>2+</sup> di-cation, ν<sub>BH</sub> = 2540 cm<sup>−1</sup> and δ<sub>B</sub> = 13.3 ppm with a <sup>1</sup>J<sub>BH</sub> coupling of 115 ± 10 Hz. These hydridoboron di-cations are remarkably inert, being unaffected by cold 0.2 M NaOD in D<sub>2</sub>O, chlorine or refluxing bromine.

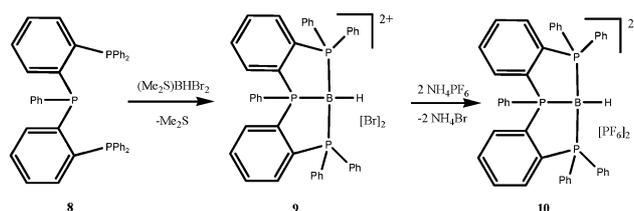
Boron di-cation salts with mixed amine donors have also been isolated starting from Me<sub>3</sub>NBBr<sub>2</sub>.<sup>6</sup> The syntheses of these boron di-cation salts involves three nucleophilic displacements. The use of different amines indicates that there is an initial slow substitution of Me<sub>3</sub>N from Me<sub>3</sub>NBBr<sub>2</sub> by R-py to form (R-py)BHBr<sub>2</sub> and that this step is followed by two rapid sequential bromide eliminations to form [(R-py)<sub>3</sub>BH]Br<sub>2</sub>.

Phosphine donors can also be employed for the support of boron di-cations. Thus, as shown in Scheme 1, the triphosphine **8** reacts readily with Me<sub>2</sub>S·BHBr<sub>2</sub> to displace the Me<sub>2</sub>S and two bromide anions forming the boron di-cation salt **9**.<sup>7</sup> In turn, **9** will undergo facile anion exchange with NH<sub>4</sub>PF<sub>6</sub> to form the corresponding hexafluorophosphate salt **10**. Although crystals of **9** and **10** proved to be unsuitable for X-ray diffraction studies, their identities were established on the basis of mass spectrometric and NMR data. Compound **9** exhibited a broad <sup>11</sup>B NMR resonance at δ −32.3 ppm. Single-crystal X-ray diffraction studies were, however, possible on the acyclic boron di-cation **11** and the bicyclic analogue **12**, which were prepared by treatment of Me<sub>2</sub>S·BHBr<sub>2</sub> with Me<sub>3</sub>P and the tripodal phosphine MeC(CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>, respectively.<sup>8</sup> It was not possible to prepare the Et<sub>3</sub>P analogue of **11** by the same method, presumably because of the increased steric bulk of this phosphine compared with that of Me<sub>3</sub>P. Compound **11** crystallizes as a monohydrate. There are no direct interactions between the cations and either the bromide

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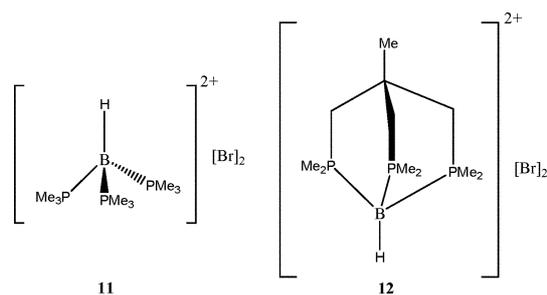
† Electronic supplementary information (ESI) available: Cartesian coordinates of all optimized structures and calculated atomic charges. CCDC reference numbers 692492–692495. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b810575h



Scheme 1

anions or the water molecule. The three crystallographically independent cations possess  $C_3$  symmetry and differ only with respect to conformation. As expected on the basis of steric repulsion, the P–B–P bond angles ( $113.8(2)^\circ$ ) exceed the ideal tetrahedral angle. The P–B distances fall in the expected range for P→B donor–acceptor bonds. The  $^{11}\text{B}$  chemical shift for **11** occurs at  $\delta -47.1$  and the signal comprises a quartet with  $^1J_{\text{BP}} = 95$  Hz. Akin to the amine donor stabilized di-cations  $[\text{L}_3\text{BH}]^{2+}$ , strong bases such as LiH, *n*-BuLi,  $\text{KN}(\text{SiMe}_3)_2$  *etc.* fail to react with **9** or **10**. However, the treatment of **9** or **10** with  $\text{LiNMe}_2$  or NaOMe results in liberation of the phosphines. In the case of the pyridine reaction, the isolated product was a  $[(\text{py})_3\text{BH}]^{2+}$  salt. Clearly, the “umpolung” effect on the hydrogen atoms is incomplete since **9** and **10** are water stable and do not exhibit protic activity. Interestingly, however, the bicyclic di-cation **12** undergoes hydrogen–deuterium exchange in alkaline  $\text{D}_2\text{O}$ , thus implying some protic character on the part of the B–H hydrogen.

There is considerable diversity in the naming of boron di- and tri-cations. Thus, Ryschkeiwitsch *et al.* refer to these species as “divalent and trivalent boron cations”,<sup>4a</sup> “triply charged boron cations”,<sup>4b</sup> “tris(pyridine)hydroboron(III) cation salts”,<sup>5b</sup> and “tris(amine) cations of boron”,<sup>5c</sup> while Schmidbauer *et al.* refer to the phosphine-stabilized derivatives as “dications based on a hydrido(phosphonio)borate skeleton”<sup>7</sup> and “poly(phosphane)borane cations”.<sup>8</sup> In turn, these nomenclature issues beg the question of the charge distributions in boron di- and tri-cations, a theme that will be addressed in the following section. Due to the increasing interest in main group polycations, it might be appropriate to establish a more general and systematic nomenclature for such species. As noted above, some confusion has arisen in the past on this issue. In the context of boron chemistry, a possible solution might be to extend the nomenclature suggested originally by Kölle and Nöth<sup>9</sup> by referring to all coordinatively saturated  $[\text{BL}_4]^{z+}$  species as boronium cations and specifying the overall charge when it differs from +1. Such an approach seems reasonable in view of the extensive delocalization of charge throughout these covalently bonded systems (*vide infra*).



## Results and discussion

### Solid-state structures

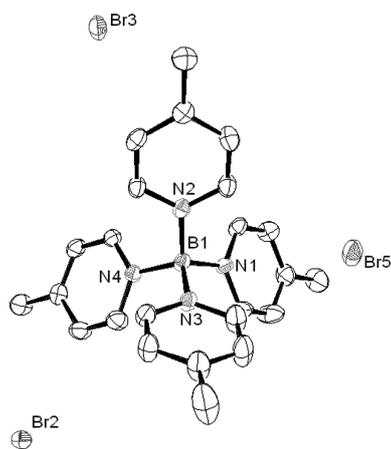
Since neither pyridine nor substituted pyridine-supported boron cations of the types discussed above had been structurally authenticated, we were prompted to repeat the syntheses of representative examples of these boron di- and tri-cation salts with a view to carrying out single-crystal X-ray diffraction studies. The salts  $[(4\text{-Mepy})_4\text{B}]\text{Br}_3$  (**5**) and  $[\text{py}_3\text{BH}]\text{Br}_2$  (**7**) proved to be suitable for such studies. In the interest of completeness we also performed structural assays of the neutral precursors  $\text{Me}_3\text{NBBR}_3$  (**2**) and  $\text{Me}_3\text{NBHBr}_2$  (**6**). Compounds **2**, **5**, **6** and **7** were prepared *via* literature methods.<sup>4–6</sup> Pertinent details of the data collection appear in Table 1 and a selection of metrical parameters is presented in Table 2. The two precursor molecules, **2** and **6**, adopt the classical staggered geometry for Lewis acid–base complexes of this type and the N→B donor bond distances are consistent with those found in the CCDC. Figures of the structures of **2** and **6** are available as ESI.† The tri-cation salt  $[(4\text{-Mepy})_4\text{B}]\text{Br}_3$  (**5**) features two independent ion pairs in the asymmetric unit. However, the metrical parameters for these two ion pairs are very similar, hence only one of these is illustrated in Fig. 1 and complete data are available as ESI.† Individual tri-cations possess approximate  $S_4$  symmetry and the closest B–Br distance, which is 4.395 Å, exceeds the sum of van der Waals radii (3.52 Å).<sup>10</sup> The solid-state structure of **7** consists of an array of  $[\text{py}_3\text{BH}]^{2+}$  cations

**Table 1** Selected crystal data, data collection and refinement parameters for  $(\text{Me}_3)_3\text{N}-\text{BBR}_3$  (**2**),  $[(4\text{-Mepy})_4\text{B}]\text{Br}_3$  (**5**),  $(\text{Me}_3)_3\text{N}-\text{BHBr}_2$  (**6**) and  $[\text{py}_3\text{BH}]\text{Br}_2$  (**7**)

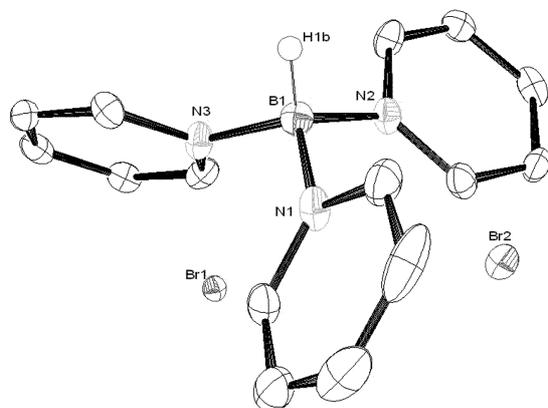
	<b>2</b>	<b>5</b>	<b>6</b>	<b>7</b>
Formula	$\text{C}_3\text{H}_9\text{BBR}_3\text{N}$	$\text{C}_{24}\text{H}_{28}\text{BBR}_3\text{N}_4$	$\text{C}_3\text{H}_{10}\text{BBR}_2\text{N}$	$\text{C}_{15}\text{H}_{20}\text{BBR}_2\text{N}_3\text{O}_2$
Formula weight	309.65	623.04	230.75	444.97
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/m$	$P2_1/c$	$Pnma$	$P\bar{1}$
<i>a</i> /Å	6.626(5)	17.704(4)	11.627(5)	9.3043(4)
<i>b</i> /Å	10.493(5)	17.664(4)	10.811(5)	10.0118(4)
<i>c</i> /Å	6.810(5)	18.891(4)	6.171(5)	12.0149(8)
$\alpha/^\circ$	90.000(5)	90.0	90.00	93.085(3)
$\beta/^\circ$	115.211(5)	99.60(3)	90.00	112.533(3)
$\gamma/^\circ$	90.000(5)	90.0	90.00	117.583(2)
<i>Z</i>	2	8	4	2
<i>D<sub>c</sub></i> /g cm <sup>−3</sup>	2.401	1.421	1.976	1.681
<i>F</i> (000)	288	2480	440	444
Crystal size/nm	0.11 × 0.10 × 0.05	0.40 × 0.25 × 0.20	0.20 × 0.15 × 0.12	0.44 × 0.26 × 0.21
$\theta$ range/ $^\circ$	3.31–27.38	1.86–27.50	3.50–27.44	2.39–27.49
Collected reflections	1631	23 787	2753	19 540
Independent reflections	1023	13 255	918	4019
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0364	0.0608	0.0390	0.0273
<i>wR</i> <sub>2</sub> (all data)	0.0925	0.1690	0.1085	0.0603

**Table 2** Selected bond distances (Å) and angles (°) for Me<sub>3</sub>N–BBr<sub>3</sub> (2), [(4-Mepy)<sub>4</sub>B]Br<sub>3</sub> (5), Me<sub>3</sub>N–BHBr<sub>2</sub> (6) and [py<sub>3</sub>BH]Br<sub>2</sub> (7)

2		5		6		7	
Distances/Å							
B(1)–N(1)	1.594(8)	B(1)–N(1)	1.564(6)	B(1)–N(1)	1.599(10)	B(1)–N(1)	1.583(5)
B(1)–Br(1)	2.002(7)	B(1)–N(2)	1.567(7)	B(1)–Br(1)	2.034(5)	B(1)–N(2)	1.565(4)
B(1)–Br(2)	2.021(4)	B(1)–N(3)	1.562(6)	B(1)–H(1)	0.9794	B(1)–N(3)	1.577(5)
N(1)–C(1)	1.509(5)	B(1)–N(4)	1.564(6)	C(1)–N(1)	1.490(7)	B(1)–H(1b)	1.10(4)
N(1)–C(2)	1.498(7)			C(2)–N1)	1.513(6)		
Bond angles/°							
Br(1)–B(1)–Br(2)	109.2(2)	N(1)–B(1)–N(2)	111.1(4)	Br(1)–B(1)–H(1)	110.3	N(1)–B(1)–N(2)	110.0(3)
N(1)–B(1)–Br(1)	110.4(4)	N(1)–B(1)–N(3)	113.6(4)	N(1)–B(1)–Br(1)	109.0(3)	N(1)–B(1)–N(3)	109.9(3)
N(1)–B(1)–Br(2)	110.3(2)	N(1)–B(1)–N(4)	104.3(4)	N(1)–B(1)–H(1)	110.3	N(2)–B(1)–N(3)	109.1(3)
C(1)–N(1)–B(1)	110.9(3)	N(2)–B(1)–N(3)	105.1(4)	C(1)–N(1)–B(1)	116.4(6)	N(1)–B(1)–H(1b)	109.1(19)
C(2)–N(1)–B(1)	112.3(5)	N(2)–B(1)–N(6)	113.2(4)	C(1)–N(1)–C(2)	107.6(3)	N(2)–B(1)–H(1b)	108.(2)
C(1)–N(1)–C(2)	107.5(3)	N(2)–B(1)–N(4)	109.8(4)			N(3)–B(1)–H(1b)	110.(2)

**Fig. 1** ORTEP diagram of 5 with 40% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

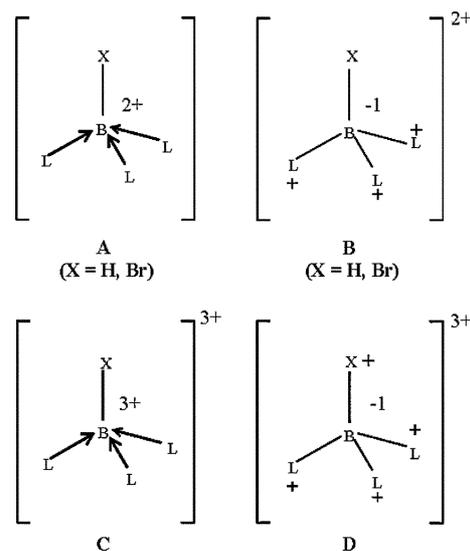
and Br<sup>−</sup> anions. As noted by Ryschkewitch *et al.*,<sup>4b</sup> 7 incorporates two water molecules of crystallization. The closest non-bonded distance is 5.235 Å between B and Br(2). The skeletal geometry of the di-cation is tetrahedral (Fig. 2) and the average N–B–N bond angle [109.7(3)°] is identical to that of the tri-cation [(4-Mepy)<sub>4</sub>B]Br<sub>3</sub> [109.5(4)°]. The py rings of the [py<sub>3</sub>BH]<sup>2+</sup> cation are

**Fig. 2** ORTEP diagram of 7 with 40% probability thermal ellipsoids. Two water molecules and hydrogen atoms are omitted for clarity.

arranged in a propeller fashion, such that the overall symmetry is approximately C<sub>3</sub>. The average B–N bond distances for [(4-Mepy)<sub>4</sub>B]<sup>3+</sup> (1.566(7) Å) and [py<sub>3</sub>BH]<sup>2+</sup> (1.575(5) Å) are identical within experimental error.

### Electronic structures

At the simplest level, the discussion of the electronic structures of boron di- and tri-cations can be couched in terms of a variety of canonical forms, some of which are shown below.



The ligands (L) function as  $\sigma$  donors in A and C, while in B and D they adopt the  $\sigma$ -bonded “onio” form. Other canonical forms can, of course, be drawn for A and B in which the B–X moiety is polarized B <sup>$\delta+$</sup> –X <sup>$\delta-$</sup> . Obviously, the observed structures are expected to lie between the extremes A and B and C and D. In order to gain additional insight into the electronic structures, the atomic charges in the polycations [(py)<sub>3</sub>BH]<sup>2+</sup>, [(py)<sub>3</sub>BBr]<sup>2+</sup>, [(4-Mepy)<sub>3</sub>BH]<sup>2+</sup>, [(4-Mepy)<sub>4</sub>B]<sup>3+</sup>, [(Me<sub>3</sub>P)<sub>3</sub>BH]<sup>2+</sup>, and [(Me<sub>3</sub>P)<sub>4</sub>B]<sup>3+</sup> were examined with DFT methods.<sup>11</sup> The molecular geometries were fully optimized within the generalized gradient approximation using the PW91<sup>12</sup> exchange and correlation functionals and all-electron triple- $\zeta$  basis sets of uncontracted Slater-type orbitals (STOs), augmented with

two auxiliary basis sets of STOs for polarization (TZ2P). The atomic charges were evaluated under the Mulliken,<sup>13–16</sup> natural population analysis (NPA)<sup>17,18</sup> and Hirschfeld<sup>18</sup> schemes as well as the Voronoi deformation density (VDD)<sup>19</sup> method for both the PW91 and the hybrid B3LYP<sup>20</sup> functionals using the TZ2P basis sets. The resulting average values per element are provided in Table 3 (the methyl group of the 4-Mepy ligand is treated as a pseudo atom). Because population-based charges (Mulliken and NPA) are known to be dependent on the basis set and functional, additional atomic charge calculations were performed with the smaller DZP and DZ basis sets and B3LYP; the complete set of results is provided as ESI.† In the present case, the Mulliken charges varied widely and unsystematically, thus precluding a meaningful interpretation. The NPA charges, which are based

on explicitly orthogonalized atomic orbitals, displayed greater consistency between functionals but still showed an important basis set dependency. The methods, based on quantification of the electron density in the immediate surroundings of each atom, are usually consistent and are regarded as more realistic;<sup>19</sup> indeed the values we obtained with the Hirschfeld and VDD schemes were comparable across DFT functionals and basis sets, and were similar in magnitude to each other. These calculations indicate that in each polycation the charge is delocalized throughout the entire molecule. There are, however, some important differences between the pyridine and phosphine derivatives. In the pyridine substituted cations, the boron atom has positive charges of modest magnitude (0.1–0.2 a.u.), which are comparable to the charges on the hydrogen atoms of the organic ligands. The methyl group of

**Table 3** Calculated<sup>a</sup> average charges (in a.u.) of atoms or methyl groups in boron polycations

	Mulliken		NPA		Hirschfeld		Voronoi DD	
<b>[(py)<sub>3</sub>BH]<sup>2+</sup></b>								
B	0.32	(0.88)	0.52	(0.57)	0.13	(0.10)	0.09	(0.07)
N	-0.22	(-0.42)	-0.45	(-0.47)	-0.03	(-0.01)	-0.05	(-0.03)
C	0.19	(0.33)	-0.08	(-0.07)	0.04	(0.04)	0.01	(0.02)
H <sub>C</sub>	-0.02	(-0.15)	0.27	(0.26)	0.09	(0.09)	0.13	(0.12)
H <sub>B</sub>	-0.11	(-0.24)	0.01	(0.00)	-0.05	(-0.05)	-0.07	(-0.07)
<b>[(py)<sub>3</sub>BBr]<sup>2+</sup></b>								
B	0.42	(0.88)	0.71	(0.67)	0.18	(0.16)	0.12	(0.10)
N	-0.23	(-0.44)	-0.51	(-0.48)	-0.04	(-0.02)	-0.05	(-0.03)
C	0.19	(0.33)	-0.07	(-0.08)	0.04	(0.04)	0.01	(0.02)
H <sub>C</sub>	-0.02	(-0.15)	0.26	(0.27)	0.09	(0.08)	0.13	(0.12)
Br	-0.27	(-0.28)	-0.08	(-0.06)	0.03	(0.03)	-0.07	(-0.06)
<b>[(4-Mepy)<sub>3</sub>BH]<sup>2+</sup></b>								
B	0.32	(0.89)	0.57	(0.52)	0.12	(0.10)	0.09	(0.06)
N	-0.23	(-0.43)	-0.48	(-0.46)	-0.04	(-0.02)	-0.06	(-0.04)
C(py)	0.17	(0.29)	-0.03	(-0.04)	0.04	(0.04)	0.01	(0.02)
H <sub>C</sub>	-0.04	(-0.17)	0.25	(0.26)	0.08	(0.08)	0.12	(0.12)
Me	0.16	(0.09)	0.11	(0.12)	0.14	(0.15)	0.17	(0.17)
H <sub>B</sub>	-0.12	(-0.25)	-0.01	(0.01)	-0.05	(-0.05)	-0.08	(-0.07)
<b>[(4-Mepy)<sub>3</sub>B]<sup>3+</sup></b>								
B	0.37	(1.15)	1.02	(0.98)	0.21	(0.19)	0.15	(0.13)
N	-0.27	(-0.50)	-0.54	(-0.51)	-0.05	(-0.03)	-0.09	(-0.07)
C(py)	0.16	(0.29)	-0.03	(-0.04)	0.05	(0.04)	0.01	(0.02)
H <sub>C</sub>	0.23	(0.13)	0.14	(0.15)	0.18	(0.18)	0.21	(0.21)
Me	-0.03	(-0.16)	0.26	(0.27)	0.08	(0.08)	0.13	(0.12)
<b>[(Me<sub>3</sub>P)<sub>3</sub>BH]<sup>2+</sup></b>								
B	-0.10	(-0.31)	-0.80	(-0.78)	-0.08	(-0.09)	-0.16	(-0.16)
P	0.44	(0.82)	1.26	(1.28)	0.40	(0.37)	0.29	(0.28)
C	0.47	(0.49)	-0.96	(-0.94)	-0.12	(-0.11)	-0.14	(-0.13)
H <sub>C</sub>	-0.12	(-0.16)	0.28	(0.27)	0.08	(0.07)	0.10	(0.09)
H <sub>B</sub>	-0.12	(-0.14)	0.11	(0.09)	-0.04	(-0.03)	-0.02	(-0.02)
<b>[(Me<sub>3</sub>P)<sub>3</sub>B]<sup>3+</sup></b>								
B	-0.22	(-0.74)	-0.69	(-0.69)	-0.06	(-0.05)	-0.16	(-0.15)
P	0.39	(0.90)	1.23	(1.24)	0.38	(0.37)	0.29	(0.28)
C	0.47	(0.48)	-0.96	(-0.93)	-0.12	(-0.11)	-0.14	(-0.13)
H <sub>C</sub>	-0.11	(-0.16)	0.28	(0.28)	0.08	(0.08)	0.10	(0.10)

<sup>a</sup> Using B3LYP and PW91 with the TZ2P basis set.

4-Mepy does not appear to influence the charge on boron. In the cases of  $[(\text{Me}_3\text{P})_3\text{BH}]^{2+}$  and  $[(\text{Me}_3\text{P})_4\text{B}]^{3+}$  the positive charge is particularly apparent on the phosphorus atoms (0.3–0.4) and boron acquires a negative charge (*ca.* –0.1). In the two groups of cations, the increase of total charge has only a small effect on boron. Note that in both  $[(\text{py})_3\text{BH}]^{2+}$  and  $[(\text{Me}_3\text{P})_3\text{BH}]^{2+}$ , the hydrogen atom attached to boron ( $\text{H}_\text{B}$ ) possesses a negative charge, which suggests a hydridic character. Experimentally, the tridentate phosphine-stabilized boron di-cation **12** undergoes hydrogen–deuterium exchange in basic solution;<sup>8</sup> our charge analysis suggests that this would be facilitated by the anionic character of boron rather than by the charge of the hydrogen atom itself. It is also interesting to note that the halogen atom of  $[(\text{py})_3\text{BBr}]^{2+}$  constitutes the only case in which the Hirschfeld and VDD methods disagree on the sign of the charge. However, because their magnitudes are close to zero, this mismatch can be attributed to the different approaches used to define atomic volume in these schemes.

The first  $\beta$ -diketiminato-supported boron di-cation,  $[\{\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{B}(\text{bipy})]^{2+}$  (**13**) was isolated recently as its bis(triflate) salt by treatment of  $[\{\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{B}(\text{OTf})_2]$  (**14**) with 2,2'-bipyridine.<sup>21</sup> The  $\text{BN}_2\text{C}_3$  ring of **13** is planar within experimental error and the dihedral angle between this plane and the bipy ligand plane is approximately  $90^\circ$ . The average distance for the B–N(bipy) bonds is 1.591(10) Å, while that for the B–N(diketiminato) bonds is 1.514(9) Å and the closest boron–triflate oxygen distance (3.772 Å) exceeds the sum of van der Waals radii (3.07 Å).<sup>10</sup> Interestingly, **14**, the bis(triflate) precursor to **13**, has one boron–oxygen distance (1.496(5) Å) that is somewhat shorter than the other (1.562(7) Å) and therefore suggestive of incipient ionization toward the mono-cation  $[\{\text{HC}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{B}(\text{OTf})][\text{OTf}]$ .

Some useful insights about the electronic structure of the di-cation **13** were provided by DFT calculations. The experimental geometry was fully optimized as described above. The agreement between the experimental and the calculated structures was satisfactory, the main differences were, as expected, in the C–H distances and the orientations of the methyl groups. Atomic charges were also calculated as before but, because TZ2P is too large, NPA could only be performed with a TZP basis set. Table 4 compiles the average charges obtained with the latter basis set, which were almost identical to the TZ2P values in all the available schemes. The charge on the boron atom is positive and comparable in magnitude to that in  $[(4\text{-Mepy})_4\text{B}]^{3+}$ . This could

be due to the electron-withdrawing effect of the perfluorophenyl groups.

Finally, we note that several interesting boron di- and tri-cations have been investigated computationally by Rasul and Olah using *ab initio* methods.<sup>22</sup> The hydridoboron di-cations  $[\text{BH}_n]^{2+}$  ( $n = 3–8$ ) have reasonably high kinetic barriers for deprotonation. For example, the di-cation  $\text{BH}_7^{2+}$  is a propeller-shaped species of  $C_{3v}$  symmetry that can be regarded as a complex between  $\text{BH}^{2+}$  and three dihydrogen molecules. A structure of lower symmetry ( $C_{2v}$ ) lies only 4.7 kcal mol<sup>–1</sup> higher in energy than the  $C_{3v}$  structure, hence intramolecular hydrogen scrambling is predicted to be facile. The tri-cation  $\text{BH}_8^{3+}$  can be thought of as a complex of four dihydrogen molecules with a  $\text{B}^{3+}$  cation. The minimum energy geometry is one in which the four dihydrogen molecules are oriented in a tetrahedral fashion with respect to the boron center.

## Conclusions

The single-crystal X-ray structures of  $[(4\text{-Mepy})_4\text{B}]\text{Br}_3$  and  $[\text{py}_3\text{BH}]\text{Br}_2$  have been determined and confirm the structures proposed earlier for these compounds by Ryschkewitsch *et al.*<sup>4</sup> on the basis of elemental analyses, conductance measurements, IR and UV spectroscopic assays. Apart from the structures of these and related boron di- and tri-cations, considerable interest is associated with the charge distributions in such species. To address this issue, the atomic charges in the polycations  $[\text{py}_3\text{BH}]^{2+}$ ,  $[\text{py}_3\text{BBr}]^{2+}$ ,  $[(4\text{-Mepy})_3\text{BH}]^{2+}$ ,  $[(4\text{-Mepy})_4\text{B}]^{3+}$ ,  $[(\text{Me}_3\text{P})_4\text{B}]^{3+}$ , and  $[(\text{Me}_3\text{P})_3\text{BH}]^{2+}$  were probed by DFT methods. The charges were evaluated using Mulliken, natural population analysis, Hirschfeld, and Voronoi deformation density (VDD) methods. The Mulliken charges varied widely and had unrealistic values. The most consistent results were obtained with the Hirschfeld and VDD schemes. These calculations indicate that in all cases, the charges are delocalized throughout the polycation structures. In the cases of the pyridine- and 4-methylpyridine-stabilized polycations, the boron atom acquires a small positive charge in the range 0.1–0.2. Interestingly, however, in the phosphine-stabilized polycations  $[(\text{Me}_3\text{P})_4\text{B}]^{3+}$  and  $[(\text{Me}_3\text{P})_3\text{BH}]^{2+}$ , the boron centers acquire small negative charges of the order of –0.1. The foregoing charge distributions are consistent with NMR chemical shift data in the sense that the <sup>11</sup>B chemical shift for  $[\text{py}_3\text{BH}]^{2+}$  is +13.3 ppm, while those for the tris(phosphine)-substituted boron di-cations **9** and **10** appear at –32.3 and –47.1 ppm, respectively (*vide supra*).

**Table 4** Calculated<sup>a</sup> average charges (in a.u.) of atoms or methyl groups in the boron di-cation **13**

	Mulliken		NPA		Hirschfeld		Voronoi DD	
B	0.46	(0.97)	0.91	(0.87)	0.19	(0.16)	0.14	(0.11)
N <sub>diketiminato</sub>	–0.33	(–0.49)	–0.55	(–0.52)	–0.10	(–0.08)	–0.12	(–0.10)
N <sub>bipy</sub>	–0.24	(–0.43)	–0.41	(–0.39)	–0.04	(–0.02)	–0.03	(–0.01)
C <sub>diketiminato</sub>	0.15	(0.21)	0.13	(0.11)	0.06	(0.05)	0.04	(0.03)
Me	0.19	(0.14)	0.11	(0.11)	0.13	(0.14)	0.20	(0.19)
C <sub>Ph</sub>	0.35	(0.34)	0.26	(0.24)	0.07	(0.07)	0.04	(0.04)
C <sub>bipy</sub>	0.19	(0.28)	–0.03	(–0.04)	0.04	(0.04)	0.01	(0.02)
H <sub>diketiminato</sub>	–0.05	(–0.14)	0.26	(0.26)	0.07	(0.08)	0.10	(0.10)
H <sub>bipy</sub>	–0.03	(–0.12)	0.21	(0.21)	0.07	(0.07)	0.10	(0.10)
F <sub>Ph</sub>	–0.38	(–0.37)	–0.27	(–0.25)	–0.05	(–0.04)	–0.02	(–0.01)

<sup>a</sup> Using B3LYP and PW91 with the TZP basis set.

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