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## Boron complexes of redox-active diimine ligandt

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Boron complexes (dpp-bian)BCl<sub>2</sub> (1) and (dpp-bian)BX (X = Cl, 2; Br, 3) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) have been prepared by reacting mixtures dpp-bian–BX<sub>3</sub> (1 : 1) with one (1) and two (2 and 3) equivalents of sodium correspondingly in toluene. Complexes 2 and 3 reveal a moderate stability against ambient oxygen and moisture. The reaction of complex 2 with PhC==CLi gave compound (dpp-bian)B–C==CPh (4). Treatment of 2 with potassium hydroxide afforded complexes (dppbian)B–OH (5) and (dpp-bian)B–OK (6). Boron amide (dpp-bian)B–NH<sub>2</sub> (7) has been isolated from the reaction of compound 1 with sodium in liquid ammonia. Borane (dpp-bian)B–H (8) can be prepared by the reactions of complexes 2 and 3 with LiAlH<sub>4</sub>. Diamagnetic compounds 2–8 have been characterized by IR, <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy; paramagnetic complex 1 has been studied by the ESR method. Molecular structures of 2, 5, 7 and 8 have been determined by X-ray crystallography.

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## Introduction

Nitrogen-based o-donor ligands have provided progress in many fields of modern coordination chemistry. Among most fundamental results obtained are (i) isolation of stable compounds of low-valent main group elements, e.g. N-heterocyclic carbenes (NHC)<sup>1*a,b*</sup> plus their Si,<sup>1*c,d*</sup> Ge,<sup>1*c,e*</sup> Sn,<sup>1*c,e*</sup> P,<sup>1*f-i*</sup> and As<sup>1*f*</sup> analogues; (ii) synthesis of complexes featuring direct metalmetal bonds.<sup>2,3</sup> We have contributed to these fields by synthesizing  $\operatorname{Ge}(\pi)^{4a,b}$  species as well as compounds comprising of M-M bonds (Zn-Zn,<sup>4c</sup> Ga-Ga,<sup>4d</sup> Zn-Ga,<sup>4d</sup> Al-Al,<sup>4e</sup> Ga-Li<sup>4f</sup> and Ga-La<sup>4g</sup>), whose remarkable stability is granted by redox-active N-ligand, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian). One of the most important features of the dppbian is variability of its coordinating facilities in the metal complexes: usually, the dpp-bian serves as neutral,  $5^{5a}$  radicalanionic<sup>5b-d</sup> or dianionic<sup>5b</sup> chelating ligand, although the formation of the tri-anion and tetra-anion of dpp-bian have also been documented.<sup>5b</sup> Further, metal complexes of the dpp-bian reveal an amazing reactivity. For instance, complexes (dppbian)M–M(dpp-bian) (M = Al, $^{4f}$  Ga<sup>6</sup>) are able to bind different alkynes. In the case of gallium this process is reversible. It allows hydroamination (hydroarylation) of alkynes using

<sup>b</sup>Department of Chemistry, N. I. Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Avenue, Nizhny Novgorod, 603950, Russian Federation (dpp-bian)Ga–Ga(dpp-bian) as catalyst.<sup>6b</sup> Looking for new examples of an unusual chemical bonding and reactivity we started synthesis and investigation of the dpp-bian derivatives of boron as the smallest ion in the group 13 metals.

The first 1,3,2-diazaborolines were prepared almost 40 years ago by Niedenzu and Merriam<sup>7a,b</sup> and later by Weber and Schmid.<sup>7c</sup> Synthesis of boron analogues of NHCs have been first attempted at the start of the 21st century,<sup>7d</sup> just immediately after the pioneering work of Schmidbaur and co-workers<sup>8a</sup> on the preparation of potassium salts of the 1,3,2diazagalol [{(tBuNCH)<sub>2</sub>}Ga{K(tmeda)}]<sub>2</sub> including solvent separated gallen-anion [{(tBuNCH)<sub>2</sub>}Ga]<sup>-.8b</sup> However, the first efforts to prepare metal boranides failed due to side reactions. Difficulties have already arisen at the stage of synthesis of diboranes. Thus, reduction of boron precursor {(tBuNCH)<sub>2</sub>}-B-Br with K/Na alloy in DME, TMEDA or toluene resulted 1,3,2-diazaboroles with substituents at the boron atom that were abstracted from the respective reaction media.<sup>7d</sup> First metal boranide, boryllithium  $[{(ArNCH)_2}B-Li(\mu-DME)]_2$  (Ar = 2,6-diisopropylphenyl), has been reported by Segawa, Mashita and Nozaki in 2006.<sup>9a</sup> It has been prepared by the reduction of N,N'-bis(2,6-diisopropylphenyl)-2-bromo-2,3dihydro-1*H*-1,3,2-diazaborole with  $Li[C_{10}H_8]$ . This compound has already found an application as a nucleophile in organic synthesis<sup>9b</sup> as well as in the syntheses of compounds with direct metal-boron bonds.<sup>10</sup> Among the amazing achievements in the field of boron chemistry in the last decade is preparation of mono- and dianionic diboranes with one- and two-electron B–B  $\pi$  bonds accessed by the groups of Berndt and Power through the population of the empty  $\pi$ -bonding orbital between the boron atoms in  $R_2B-BR_2$  (R = alkyl, aryl,

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<sup>+</sup>CCDC 916524 (2), 916525 (5), 916526 (7) and 916527 (8). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33055a

amino, alkoxy).<sup>11</sup> To stabilize a double boron-boron bond in illusive diborene HB=BH, Robinson and co-workers used NHC donor.<sup>12</sup> The most recent landmark in the chemistry of boron is the preparation of diboryne,  $\{(ArNCH)_2\}B=B-\{(ArNCH)_2\}$  (Ar = 2,6-diisopropylphenyl) reported by Braunschweig and co-workers.<sup>13</sup> This ambient temperature stable compound has been synthesized by the reduction of a bis(NHC)-stabilized tetrabromodiborane with four equivalents of sodium naphthalenide.

A sole crystallographically characterized dpp-bian derivative of boron reported so far is the ionic complex  $[(dpp-bian)BCl_2]$ - $[BCl_4]$  formed in the reaction of dpp-bian with  $BCl_3$ .<sup>5*a*</sup> The dpp-bian in this complex acts as neutral chelating ligand. Attempts to reduce  $[(dpp-bian)BCl_2][BCl_4]$  with alkali metals in THF were made, but no pure compounds could be isolated.<sup>5*a*</sup> Here we report on the syntheses and characterisation of a series of boron derivatives of anionic dpp-bian ligands.

#### **Results and discussions**

#### Synthesis and properties of compounds 1-8

Reduction of the dpp-bian with sodium metal in the presence of boron halides allows preparation of acenaphthene-1,2diimine derivatives of boron. The reaction of equimolar amounts of the dpp-bian, Na and  $BCl_3$  in toluene at 80 °C at stirring within 24 h afforded air- and moisture sensitive compound (dpp-bian) $BCl_2$  (1) in good yield (Scheme 1).

Compound **1** is paramagnetic due to the presence of the radical-anion of the dpp-bian. In solution complex **1** exhibits an ESR signal (Fig. 1), whose hyper-fine structure is caused by



**Scheme 1** Synthesis of compound **1**.



**Fig. 1** ESR signal of complex **1** (toluene, 293 K): (a) experimental spectrum; (b) spectrum simulated using WinEPR Simfonia (g = 2.00243;  $A(^{14}N) = 0.40$  (2 N),  $A(^{11}B) = 0.50$  (1 B),  $A(^{10}B) = 0.167$  (1 B),  $A(^{35}CI) = 0.45$  (2 Cl),  $A(^{37}CI) = 0.375$ (2 Cl),  $A(^{1}H) = 0.108$  (4 H) mT).



Scheme 2 Synthesis of compounds 2 and 3.

the coupling of unpaired electron with <sup>14</sup>N, <sup>10</sup>B, <sup>11</sup>B, <sup>35</sup>Cl, <sup>37</sup>Cl and <sup>1</sup>H nuclei. Also the absorption in the range 1500–1600 cm<sup>-1</sup> in the IR spectrum is indicative for the sesquialteral C…N bonds of the dpp-bian radical-anion.<sup>5b-d</sup>

The reactions of the dpp-bian–BX<sub>3</sub> mixtures (1:1) (X = Cl, Br) with two equivalents of sodium in toluene (80 °C, 24 h, stirring) afford new boron complexes of the dianionic dppbian ligand (dpp-bian)B–Cl (2) and (dpp-bian)B–Br (3) (Scheme 2). Although the syntheses of complexes 2 and 3 can be carried out in other solvents (Et<sub>2</sub>O or 1,2-dimethoxyethane) the preferable reaction media is toluene since the products 2 and 3 can be easily crystallised from this solvent after filtration from sodium chloride. When the reactions between dpp-bian, BX<sub>3</sub> and sodium have been tried in THF the formation of a gel has been observed, probably, due to the polymerisation of THF. Note that pure 2 and 3 do not react with THF and can be re-crystallised from this solvent.

In contrast to all the metal complexes of the dpp-bian dianion compounds 2 and 3 are rather stable towards moisture and oxygen: in the crystalline state no decomposition in air could be observed over seven days. For comparison, aluminium and gallium complexes with dpp-bian dianion react immediately even with traces of the oxygen and water.<sup>5d</sup> Noticeable oxidation of 2 with oxygen occurred only in solution: in air in toluene compound 2 (1.3 mmol L<sup>-1</sup>) oxidized completely within 24 hours while stirring at ambient temperature to give free dpp-bian.

Being impressed by reactivity of (dpp-bian)Ga–Ga(dpp-bian) towards alkynes we treated complex 2 with phenylacetylene. Unfortunately these substances do not interact. On the other hand compound 2 readily reacts with Li–C $\equiv$ CPh in THF resulting in compound (dpp-bian)B–C $\equiv$ CPh (4) (Scheme 3). In contrast to 2 and 3 compound 4 reacts with water affording the boronic acid derivative (dpp-bian)B–OH (5). Compound 5 can be also obtained by reacting compound 2 with potassium hydroxide. However, this reaction requires prolonged heating of the reaction mixture accompanied by ultra-sonication treatment (Scheme 3). In its turn compound 5 reacts with an excess of potassium hydroxide yielding (dpp-bian)BOK (6) (Scheme 3).

Due to the lack of suitable single crystals the molecular structures of compounds 4 and 6 could not be determined by X-ray crystallography. However both complexes have been satisfactory characterized by spectroscopic methods and elemental analysis. The IR spectrum of compound 4 reveals absorption at 2182 cm<sup>-1</sup>, which corresponds to the stretching vibrations



Scheme 3 Synthesis of compounds 4, 5 and 6.



Fig. 2 The  $^{1}$ H NMR spectra of 5 (top) and 6 (bottom) (400 MHz, C<sub>6</sub>D<sub>6</sub>, 293 K).

of the C–C triple bond of the phenylethynyl ligand. The <sup>1</sup>H NMR spectrum of 4 also reveals the expected signal set for the organic fragments. The <sup>1</sup>H NMR spectra of 5 and 6 are depicted in Fig. 2. In both spectra the methyl groups of the isopropyl substituents give rise to two doublets (each 12 H). In the spectrum of compound 6 these signals are overlapped with signals of the diethyl ether. The four methine protons of the dpp-bian ligand in 5 and 6 appear in each case as septets at  $\delta$  3.50 and 3.68 ppm, respectively. The singlet signal at  $\delta$  2.77 ppm in the <sup>1</sup>H NMR spectrum of 5 confirms the presence of the OH group in the compound.

Reduction of compounds 2 and 3 with alkali metals in hexane, toluene and THF aimed at the preparation of compounds with boron-boron and alkali metal-boron bonds has been attempted. However, the syntheses of the desired compounds were failed. The use of  $\text{Li}[C_{10}H_8]$  as reducing agent<sup>9a</sup> in THF also resulted in no isolable products. One can suggest



that intermediate boron species formed under reduction with alkali metals react further with reaction media affording an intractable mixture of products. Therefore, reduction of compounds 2 and 3 with sodium dissolved in liquid ammonia at -45 °C has been attempted. According to the literature data at that temperature the formation of NaNH<sub>2</sub> does not happen.<sup>14</sup> Addition of 2 or 3 into a solution of sodium in liquid NH<sub>3</sub> was accompanied by a color change from red to green-brown within a few minutes. Evaporation of ammonia resulted in a yellow-brown powder, which being dissolved in toluene gave a violet solution. Crystallisation from toluene afforded amide (dpp-bian)B–NH<sub>2</sub> (7) as violet needle-like crystals (Scheme 4).

Compounds 2 and 3 react with  $LiAlH_4$  in THF to give boron hydride (dpp-bian)B–H (8) (Scheme 5). In contrast to reported syntheses of boron hydrides using  $LiAlH_4$ ,<sup>15</sup> these reactions proceed only at high temperatures in the presence of an excess of  $LiAlH_4$ .

Compound 8 is quite stable towards oxygen. Also, it is unreactive towards compounds with multiple C-C and C-O, *e.g.* phenylacetylene or benzylideneacetone. The presence of the B-H is confirmed by absorption at 2311 cm<sup>-1</sup> in the IR spectrum.

# Molecular structures and DFT calculations of compounds 2, 5, 7, and 8

Molecular structures of compounds 2, 5, 7, and 8 have been determined by X-ray crystallography and are depicted in Fig. 3–6, respectively. Crystal data and structure refinement details are collected in Table 1. The selected bond lengths determined by single crystal X-ray diffraction together with corresponding distances calculated by DFT B3LYP/6-31G(d) are given in Table 2. All four compounds represent monomeric three-coordinate boron species. The sums of the boron bond angles (360°) in each compound indicate sp<sup>2</sup>-hybridization of the boron atoms. It provides delocalisation of p-electrons over five atoms in the boron cycles. Probably due to this

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Fig. 3 Molecular structure of compound  ${\bf 2}$  at 30% probability level. Hydrogen atoms are omitted.



Fig. 4 Molecular structure of compound 5 at 30% probability level. Hydrogen atoms except atom H(1) are omitted.



Fig. 5 Molecular structure of compound 7 at 30% probability level.

delocalisation compounds 2, 5, 7, and 8 reveal remarkable stability against oxygen and moisture. The aromatic character of 1,3,2-diazaboroles is further evident from their ability to



Fig. 6 Molecular structure of complex 8 at 30% probability level. Hydrogen atoms except atom H(1) are omitted.

form  $\pi$ -complexes, for example ( $\eta^5$ -diazaborolidine)Cr(CO)<sub>3</sub>.<sup>16</sup> In contrast, compounds 2 and 3 do not react with  $Cr(CO)_6$ , probably due to the presence of bulky isopropyl groups in close proximity to the 1,3,2-diazaborole moiety. According to X-ray diffraction analyses of 2, 5, 7 and 8, the five-membered boron cycles N(1)N(2)C(1)C(2)B are planar. Mean deviations of the atoms B, N(1), N(2), C(1) and C(2) from the plane are in the range of 0.001-0.006 Å. The Cl atom in 2 is disposed virtually in the plane of the boron cycle: the displacement from the plane is 0.077 Å. A similar situation is observed for O(1), N(3)and H(1) atoms in 5, 7 and 8: deviations of the atoms O(1), N(3) and H(1) from the boron cycle are 0.033, 0.011 and 0.091 Å, respectively. The B-N bond lengths in compounds 2, 5, 7, and 8 fall into the narrow range 1.429(3)-1.450(2) Å (av. 1.436 Å). They are remarkably shorter than Al-N and Ga-N bonds in other group 13 metal complexes of dpp-bian dianion, e.g. (dpp-bian)AlI(Et<sub>2</sub>O) (av. Al-N 1.836 Å)<sup>17a</sup> and (dpp-bian)-Ga–Ga(dpp-bian) (av. Ga–N 1.860 Å)<sup>4d</sup> (Table 2). The observed differences are in good agreement with the difference in covalent radii of trivalent B, Al and Ga (0.85, 1.26 and 1.24 Å, respectively).<sup>17b</sup> The geometries of N,B-heterocycles in 2, 5, 7, and 8 can be compared with that of acenaphthene-1,2-diimine derived carbene, (dpp-bian)C<sup>1b</sup> (Table 2). As expected the N–C(carbene) bonds in (dpp-bian)C (av. 1.378 Å)<sup>1b</sup> are shorter than B-N bonds in 2, 5, 7, and 8 (av. 1.436 Å). Since in compound 5 the hydroxyl group is connected to the aromatic cycle this compound can be considered as "heterocyclic phenol". Deprotonation of compound 5 with KOH to "phenolate" 6 supports this conclusion. The B-Cl, B-OH, B-NH<sub>2</sub>, and B-H bond lengths in compounds 2, 5, 7, and 8 match well to those distances in related boron compounds.18

Electronic structures of the free dpp-bian<sup>2–</sup> dianion and compounds 2, 5, 7, 8, A, C, D were studied by DFT at the B3LYP/6-31G(d) level of theory. The DFT calculations for complex **B** have been performed earlier.<sup>4d</sup> The optimized bond lengths agree well with the X-ray data (Table 2). The calculated C–C distance in the diimine fragment of the dpp-bian ligand in the complexes studied (1.374–1.393 Å, Table 2) is shorter

	2	5	7	8
Formula	C <sub>36</sub> H <sub>40</sub> BClN <sub>2</sub>	C <sub>36</sub> H <sub>41</sub> BN <sub>2</sub> O	$C_{36}H_{42}BN_3$	$C_{36}H_{41}BN_2$
$M_{ m r}$	546.96	528.52	527.54	512.52
T/K	100(2)	100(2)	100(2)	100(2)
Crystal size/mm <sup>3</sup>	$0.72 \times 0.39 \times 0.07$	$0.58 \times 0.07 \times 0.05$	$0.48 \times 0.19 \times 0.07$	$0.28 \times 0.14 \times 0.10$
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	$P\bar{1}$	P2(1)/n
a/Å	12.9857(16)	12.8866(12)	10.9275(7)	12.8332(13)
b/Å	19.268(2)	18.7947(17)	12.8248(9)	18.739(2)
c/Å	13.4096(17)	13.3897(12)	13.0157(9)	13.4197(14)
$\alpha/^{\circ}$	90	90	94.550(2)	90
β/°	110.856(2)	110.201(2)	113.4610(10)	109.425(3)
$\gamma/^{\circ}$	90	90	108.675(2)	90
$V/Å^3$	3135.3(7)	3043.5(5)	1539.63(18)	3043.6(5)
Z	4	4	2	4
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.159	1.153	1.138	1.119
$\mu/\mathrm{mm}^{-1}$	0.148	0.068	0.066	0.064
F(000)/e	1168	1136	568	1104
<i>hkl</i> range	$-15 \le h \le 15$	$-15 \le h \le 15$	$-13 \le h \le 13$	$-15 \le h \le 15$
	$-22 \le k \le 22$	$-23 \le k \le 23$	$-15 \le k \le 15$	$-23 \le k \le 23$
	$-15 \le l \le 15$	$-16 \le l \le 16$	$-16 \le l \le 16$	$-16 \le l \le 16$
$\theta$ range for data collection/°	1.98 to 25.00	2.17 to 26.00	2.11 to 26.00	1.90 to 26.00
Completeness to $\theta = 25.00^{\circ}$ (%)	99.6	_	—	
Completeness to $\theta = 26.00^{\circ}$ (%)	—	99.2	99.2	99.8
Max. and min. transmission	0.9897 and 0.9007	0.9966 and 0.9616	0.9954 and 0.9692	0.9936 and 0.9824
Refl. measured	23 998	25 678	13 225	25 945
Refl. unique	5491	5936	6010	5975
R <sub>int.</sub>	0.0779	0.0950	0.0332	0.0965
Param. refined	327	383	398	398
$R(F^2)/wR(F^2) \left[I > 2\sigma(I)\right]$	0.1287/0.3196	0.0852/0.1954	0.0591/0.1384	0.0807/0.1914
$R(F^2)/wR(F^2)$ [all data]	0.1548/0.3389	0.1645/0.2267	0.1023/0.1536	0.1685/0.2279
GoF $(F^2)$	1.246	1.008	1.016	0.934
$\Delta  ho_{ m fin}$ (max/min)/e Å <sup>-3</sup>	1.669/-0.583	0.418/-0.306	0.249 / -0.194	0.363/-0.255

Table 1Crystal structure data for 2, 5, 7 and 8

**Table 2** Selected bond lengths (Å) for **2**, **5**, **7**, **8**, (dpp-bian)All(Et<sub>2</sub>O)<sup>17a</sup> (**A**), (dpp-bian)Ga–Ga(dpp-bian)<sup>4d</sup> (**B**), (dpp-bian)C<sup>1b</sup> (**C**) and (dpp-bian)<sup>2–</sup> (**D**) according to single-crystal X-ray diffraction and DFT calculation<sup>b</sup> (*italic*)

Compound	2	5	7	8	Α	В	С	D
N-C	1.385(3)	1.395(3)	1.395(2)	1.398(2)	1.394(8)	1.370(3)	1.387(5)	
	1.395(3)	1.408(3)	1.403(2)	1.391(2)	1.418(9)	1.371(3)	1.389(5)	1.368
	1.400	1.400	1.400	1.394	1.413	1.380	1.388	1.364
	1.397	1.400	1.400	1.394	1.416	1.380	1.388	
C(1)-C(2)	1.362(4)	1.348(3)	1.357(2)	1.357(3)	1.39(1)	1.383(3)	1.373(5)	1.421
	1.374	1.374	1.374	1.376	1.393	1.390	1.372	
N-E <sup>a</sup>	1.433(4)	1.429(3)	1.443(2)	1.435(3)	1.833(6)	1.918(1)	1.379(5)	_
	1.429(4)	1.437(3)	1.450(2)	1.436(3)	1.839(5)	1.924(1)	1.377(6)	
	1.440	1.453	1.458	1.445	1.847	1.894	1.386	
	1.440	1.449	1.458	1.445	1.850	1.894	1.386	
N…N	2.313	2.313	2.317	2.302	2.718	2.678	2.157	3.020
	2.331	2.336	2.337	2.318	2.759	2.645	2.164	

<sup>*a*</sup> E = B for 2, 5, 7, 8; E = Al for A; E = Ga for B; E = C for B. <sup>*b*</sup> DFT results for all complexes except compound  $B^{3e}$  were obtained in this work.

than that in the free dpp-bian<sup>2–</sup> dianion (1.421 Å). The NBO approach describes this C–C bond as a double bond. The corresponding ellipticity parameter (0.380) found from the AIM analysis<sup>19</sup> appears to be very close to that for the C=C bond in ethylene (0.375). On the other hand, the calculated C–N distances increases on going from the dianion to the complexes. These changes are caused by the formation of the coordinative bond (dpp-bian)–E (E = B, C, Al, Ga). A higher electronegativity

of the boron atom as compared to aluminium and gallium results in a more covalent character of the N–B bond. Indeed, the AIM analysis shows that on going from (dpp-bian)-AlCl to 2 the electron density in the (3, -1) critical point of the N–E bond (E = Al, B) increases from 0.090 to 0.195 a.u. Accordingly, the local orbital locator<sup>20</sup> (LOL) profile demonstrates an increase in the LOL value and a substantial shift of the LOL maximum corresponding to the N–E bond towards

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Fig. 7 The LOL contour map (the 0.55–0.70 a.u. range, step 0.05 a.u.) in the plane orthogonal to the metallacycle for the N–Al bond in (dpp-bian)AlCl (right) and the N–B bond in 2 (left).



 
 Table 3
 The frontier orbital energies and HOMO–LUMO energy gaps (eV) in the dpp-bian complexes of boron, aluminium and gallium

Complex	HOMO	LUMO	$\Delta E_{\text{LUMO-HOMO}}$
(dipp-bian)B–Cl (2)	-4.88	-1.75	3.13
(dipp-bian)B-OH (5)	-4.50	-1.56	2.94
$(dipp-bian)B-NH_2(7)$	-4.25	-1.47	2.78
(dipp-bian)B-H (8)	-4.78	-1.64	3.14
(dipp-bian)Al-Cl	-4.43	-1.59	2.84
$(dipp-bian)_2Ga_2$ ( <b>B</b> )	-4.13	-1.58	2.55

the boron atom when one goes from (dpp-bian)AICI to complex 2 (Fig. 7). The LOL increase implies a reduction in the quantum kinetic energy density of electrons caused by the covalent bonding.<sup>21</sup>

The HOMO and LUMO shapes for the boron compounds investigated are very similar. Those of **2** are depicted in Fig. 8. The HOMO is N–B bonding but B–Y (Y = Cl, OH, NH<sub>2</sub>) antibonding. The LUMO is localized mainly on the dpp-bian ligand. Similar MO isosurfaces were found for the dpp-bian gallium complexes.<sup>4d</sup> The frontier orbital energies are given in Table 3. The HOMO energies of the boron complexes decrease in the order 7 > 5 > 8 > 2. They are lower than that of digallane **B**.<sup>4d</sup> It provides a higher stability of the boron derivatives against oxygen. The HOMO–LUMO energy gap increases on going from compound **B** to the boron dpp-bian complexes (Table 3). For example, the  $\Delta E_{LUMO-HOMO}$  value for the 2 molecule is 0.58 eV higher than that for compound **B**. It correlates well with a 0.38 eV blue shift of the lowest absorption band in



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the UV-Vis spectra on going from compound **B** to compound **2** (Fig. 9).

### Conclusions

In conclusion, we have prepared a series of 1,3,2-diazaboroles derived from acenaphthene-1,2-diimine - compounds 2-8. Due to the delocalisation of the p-electrons over the five-membered heterocycles and shielding of boron atom with isopropyl groups the title compounds reveal good stability against oxygen and moisture. In contrast, (dpp-bian)BCl<sub>2</sub>, which contains dpp-bian radical-anion, is air- and moisture sensitive. Attempted syntheses of diboranes starting from chlorine and bromine boron precursors 2 and 3 failed, probably due to the instability of the B-B bonds arising from the sterical hindrances caused by bulky dppbian ligands. In contrast to our expectation compound 2 is not able to add phenylacetylene across B-N-C section in the fivemembered cycle in the way observed in Ga and Al complexes of the dpp-bian dianion. We believe the energy of the HOMO in compound 2 (-4.87 V) is too low to interact effectively with the LUMO of the alkyne to furnish the formation of the cycloadduct.

### Experimental

#### General procedures

All manipulations were carried out using Schlenk techniques. Diimine dpp-bian<sup>22</sup> has been prepared according to literature procedure. Melting points were measured in sealed capillaries and are uncorrected. The solvents were distilled from sodium-benzophenone prior to use. The <sup>1</sup>H NMR spectra were recorded on Bruker DPX-200 NMR and Bruker Advance III 400 spectrometers; IR spectra – on a FSM-1201 spectrometer; ESR spectra – on a Bruker EMX instrument. The yields of the products calculated on the amount of the dpp-bian used in the syntheses.

#### 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneborondichloride (dpp-bian)BCl<sub>2</sub> (1)

To a solution of 0.5 g of dpp-bian (1.0 mmol) in toluene (40 mL) 0.023 g (1.0 mmol) of sodium metal and 0.12 g

(1.0 mmol) of BCl<sub>3</sub> were added. The mixture was stirred at 80 °C till the sodium dissolved completely. The precipitated sodium chloride was filtered off. From the concentrated toluene solution compound (dpp-bian)BCl<sub>2</sub> was isolated as a red microcrystalline powder. Yield 0.38 g (65%). M.p. 290–295 °C. Anal. calcd for C<sub>36</sub>H<sub>40</sub>BCl<sub>2</sub>N<sub>2</sub>: C 74.24, H 6.92, Cl 12.17; found: C 74.28, H 6.95, Cl 12.20. IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 3071m, 3046m, 1938w, 1868w, 1813w, 1680w, 1655w, 1619s, 1596w, 1563s, 1539s, 1501vs, 1452w, 1428w, 1405m, 1370m, 1345s, 1331m, 1314s, 1260m, 1250s, 1227s, 1200s, 1184w, 1115w, 1063m, 1048w, 997m, 967w, 941s, 852s, 828w, 822s, 810vs, 771vs, 758m, 751m, 695m, 656s, 631m. ESR (toluene, 293 K): *g* = 2.00243; *A*(<sup>14</sup>N) = 0.40 (2 N), *A*(<sup>11</sup>B) = 0.50 (1 B), *A*(<sup>10</sup>B) = 0.167 (1 B), *A*(<sup>35</sup>Cl) = 0.45 (2 Cl), *A*(<sup>37</sup>Cl) = 0.375 (2 Cl), *A*(<sup>14</sup>H) = 0.108 (4 H) mT.

#### 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneboronchloride (dpp-bian)BCl (2)

To a solution of 0.5 g of dpp-bian (1.0 mmol) in toluene (40 mL) 0.05 g (2.2 mmol) of sodium metal and 0.12 g (1.0 mmol) of BCl<sub>3</sub> were added. The mixture was stirred at 80 °C till the sodium dissolved completely. The precipitated sodium chloride was filtered off. From toluene compound (dpp-bian)BCl was isolated in the form of red crystals. Yield 0.43 g (79%). M.p. 247-253 °C. Anal. calcd for C<sub>36</sub>H<sub>40</sub>BClN<sub>2</sub>: C 79.05, H 7.37, Cl 6.48; found: C 78.65, H 7.50, Cl 6.40. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , ppm):  $\delta$  7.31 (dd, 2 H<sub>arom</sub>, 6.8 and 8.3 Hz), 7.23 (2 d, 4 H<sub>arom</sub>, 6.8 and 8.3 Hz), 7.19 (d, 2 H<sub>arom</sub>, 8.3 Hz), 6.89 (dd, 2 H<sub>arom</sub>, 6.8 and 8.3 Hz), 6.71 (d, 2 H<sub>arom</sub>, 6.8 Hz), 3.43 (sept, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>, 6.8 Hz), 1.33 (d, 12 H, CH(CH<sub>3</sub>)-(CH<sub>3</sub>), 6.8 Hz), 1.05 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 6.8 Hz). <sup>11</sup>B NMR (128.39 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  24.8 (s, 1 B). IR (Nujol, cm<sup>-1</sup>): *ν* = 3067w, 2725w, 2672w, 1931w, 1860w, 1786w, 1719w, 1613s, 1589m, 1533s, 1399m, 1339m, 1307m, 1244s, 1221s, 1194s, 1177m, 1107w, 1059s, 961w, 936s, 814vs, 804vs, 764vs, 753m, 689m, 675w, 650m, 644m, 613m, 575s.

#### 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneboronbromide (dpp-bian)BBr (3)

To a solution of 0.5 g of dpp-bian (1.0 mmol) in toluene (40 mL) 0.05 g (2.2 mmol) of sodium metal and 0.25 g (1.0 mmol) of BBr<sub>3</sub> were added. The mixture was stirred at 80 °C till the sodium dissolved completely. The precipitated sodium bromide was filtered off. From toluene compound (dpp-bian)BBr was isolated in the form of red crystals. Yield 0.49 g (83%). M. p. 295 °C. Anal. calcd for C<sub>36</sub>H<sub>40</sub>BBrN<sub>2</sub>: C 73.11, H 6.82, Br 13.51; found: C 73.17, H 6.73, Br 13.43. <sup>1</sup>H NMR (200 MHz,  $C_6D_6$ , ppm):  $\delta$  7.45–7.19 (m, 8 H<sub>arom</sub>), 6.99 (dd, 2  $\rm H_{arom},~6.8$  and 8.2 Hz), 6.81 (d, 2  $\rm H_{arom},~6.8$  Hz), 3.52 (sept, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>, 6.8 Hz), 1.45 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 6.8 Hz), 1.19 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 6.8 Hz). IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 3067m, 3049m, 3040m, 2361w, 1958w, 1929m, 1912w, 1861w, 1798w, 1788w, 1720w, 1614s, 1589w, 1531s, 1508w, 1422m, 1399s, 1364s, 1337s, 1300s, 1254s, 1238s, 1220s, 1186s, 1140m, 1108m, 1059s, 1041m, 1032m, 1000w, 960m,

936s, 905w, 893w, 814vs, 803vs, 766vs, 760vs, 755s, 688s, 638s, 613s, 573w, 554s, 540w, 519m, 481m, 463w.

#### 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneboronphenylacetylenide (dpp-bian)BC==CPh (4)

To a solution of 0.55 g (1.0 mmol) of (dpp-bian)BCl in THF (30 mL) 0.25 g (2.5 mmol) of phenylacetylene and 0.014 g (2.0 mmol) of lithium were added. The mixture was stirred at 80 °C till the metal dissolved completely. The precipitated lithium chloride was filtered off. Solvent was removed in vacuum and the residue was dissolved in hexanes. Compound (dpp-bian)BC=CPh was isolated from hexanes as needle like deep red crystals. Yield 0.2 g, (33%). M.p. 270-275 °C. Anal. calcd for C44H45BN2: C 86.26, H 7.40; found C 86.13, H 7.51. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , ppm):  $\delta$  7.31 (dd, 2 H<sub>arom</sub>, 6.8 and 8.3 Hz), 7.23 (2 d, 4 H<sub>arom</sub>, CH 6.8 and 8.3 Hz), 7.19 (d, 2 H<sub>arom</sub>, 8.3 Hz), 6.89 (dd, 2 H<sub>arom</sub>, 6.8 and 8.3 Hz), 6.71 (d, 2 Harom, 6.8 Hz), 3.43 (sept, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>, 6.8 Hz), 1.33 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 6.8 Hz), 1.05 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 6.8 Hz).  $^{11}\text{B}$  NMR (128.39 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  24.8 (s, 1 B). IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 3065m, 3046m, 3020m, 2182m, 1929w, 1862w, 1794w, 1613s, 1596m, 1491w, 1400m, 1350w, 1344m, 1335w, 1277w, 1254m, 1217m, 1187w, 1175m, 1107w, 1068w, 1058m, 1030w, 937m, 916w, 816s, 806m, 768s, 754vs, 690s, 665m, 613m, 579w, 561w, 537m, 494w, 437w.

#### 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneboronhydroxide (dpp-bian)BOH (5)

(a) To a solution of 0.55 g (1.0 mmol) of (dpp-bian)BCl in THF (30 mL) 0.056 g (1.0 mmol) of potassium hydroxide was added. Over the course of stirring at 80 °C for 24 h the reaction mixture turned violet. The precipitate of potassium chloride was filtered off. THF was removed under vacuum and the residue was dissolved in diethyl ether. From the concentrated solution compound (dpp-bian)BOH was isolated as violet prismatic crystals. Yield 0.36 g (68%). (b) To a solution of 0.61 g (1 mmol) of (dpp-bian)BC=CPh in diethyl ether 0.018 g (1 mmol) of distilled water was added by condensation. From the concentrated solution compound (dpp-bian)BOH was isolated as violet prismatic crystals. Yield 0.32 g (61%). M.p. 225-230 °C. Anal. calcd for C<sub>36</sub>H<sub>41</sub>BN<sub>2</sub>O: C 81.81, H 7.82; found: C 81.78, H 7.77. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): δ 7.30 (dd, 2 H<sub>arom</sub>, 6.5 and 8.8 Hz), 7.23 (2d, 4 H<sub>arom</sub>, 6.5 and 8.8 Hz), 7.16 (d, 2  $\rm H_{arom},$  8.3 Hz), 6.89 (dd, 2  $\rm H_{arom},$  7.0 and 8.3 Hz), 6.66 (d, 2 H<sub>arom</sub>, 7.0 Hz), 3.50 (sept, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>, 6.8 and 7.0 Hz), 2.77 (s, 1 H, OH), 1.27 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 6.8 Hz), 1.13 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 7.0 Hz). <sup>11</sup>B NMR (128.39 MHz,  $C_6D_6$ , ppm):  $\delta$  24.0 (s, 1 B). IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 3636m, 3175w, 2724w, 2672w, 1937w, 1910w, 1868w, 1792w, 1717w, 1667w, 1611m, 1587m, 1539s, 1425w, 1397w, 1253m, 1219w, 1208w, 1173m, 1154w, 1102w, 1058m, 1044w, 995m, 969w, 947w, 937w, 925w, 916w, 900w, 835w, 814s, 806s, 766s, 750m, 735s, 723s, 695m, 675w, 660m, 613m.

# Potassium-1,2-bis[(2,6-diisopropylphenyl)imino]acenaph-the neborolate (dpp-bian)BOK (6)

To a solution of 0.55 g (1.0 mmol) of (dpp-bian)BCl in THF (30 mL) 0.2 g (3.6 mmol) of potassium hydroxide was added. Over the course of stirring at 80 °C for 24 h the reaction mixture turned deep blue. The precipitated solid was filtered off. THF was removed under vacuum and the residue was dissolved in diethyl ether. From the concentrated solution compound (dpp-bian)BOK was isolated as deep blue prismatic crystals. Yield 0.36 g (63%). M.p. > 300 °C. Anal. calcd for C<sub>36</sub>H<sub>40</sub>BN<sub>2</sub>OK: C 76.31, H 7.12; Found: C 76.23, H 7.19. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , ppm):  $\delta$  7.14 (m, 8 H<sub>arom</sub>), 6.92 (dd, 2 H<sub>arom</sub>, 6.8 and 8.3 Hz), 6.59 (d, 2 H<sub>arom</sub>, 6.8 Hz), 3.68 (sept, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>, 7.0 Hz), 3.24 (q, 4 H, (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>O, 7.0 Hz), 1.16 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 7.0 Hz), 1.13 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 7.0 Hz), 1.01 (t, 6 H,  $(CH_3CH_2)_2O$ , 7.0 Hz) – <sup>11</sup>B NMR (128.39 MHz,  $C_6D_6$ , ppm):  $\delta$  21.0 (s, 1 B). <sup>13</sup>C NMR (100.62 MHz, ppm): 147.8, 140.69, 133.16, 130.63, 127.14, 126.37, 123.37, 123.08, 116.13, 65.55, 28.31, 23.77, 23.16, 15.21. IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 3032w, 2722w, 1607w, 1555m, 1543w, 1514s, 1497s, 1393m, 1360w, 1342w, 1333w, 1250m, 1213w, 1200m, 1175w, 1163w, 1148m, 1118w, 1075w, 1055m, 974m, 936w, 808vs, 792m, 780w, 760vs, 743m, 722w, 704s, 673s, 614m.

#### 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneboronamide (dpp-bian)BNH<sub>2</sub> (7)

To a solution of 0.023 g (1.0 mmol) of sodium in liquid ammonia (20 mL) at -45 °C 0.55 g (1.0 mmol) of (dpp-bian)-BCl was added. Within several minutes stirring at -45 °C the reaction mixture changed from red to green-brown. Ammonia was evaporated at reduced pressure and the residue was dissolved in toluene (20 mL) resulting in a violet solution. Precipitated sodium chloride was filtered off. From concentrated toluene solution complex (dpp-bian)BNH<sub>2</sub> was isolated as needle like violet crystals. Yield 0.34 g (65%). M.p. 230-233 °C. Anal. calcd for C36H42BN3: C 81.96, H 8.02; found: C 82.08, H 7.94. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , ppm):  $\delta$  7.32 (dd, 2 H<sub>arom</sub>, 6.5 and 8.8 Hz), 7.25 (2d, 4 H<sub>arom</sub>, 6.5 and 8.8 Hz), 7.15 (d, 2 H<sub>arom</sub>, 8.3 Hz), 6.89 (dd, 2 H<sub>arom</sub>, 7.0 and 8.3 Hz), 6.64 (d, 2 H<sub>arom</sub>, 7.0 Hz), 3.56 (sept, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>, 7.0 Hz), 1.37 (s, 2 H, NH2), 1.28 (d, 12 H, CH(CH3)(CH3), 7.0 Hz), 1.14 (d, 12 H, CH (CH<sub>3</sub>)(CH<sub>3</sub>), 7.0 Hz). <sup>11</sup>B NMR (128.39 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  -30.2 (s, 1 B). IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 3507m, 3426m, 3066m, 1933w, 1864w, 1784w, 1611m, 1586vs, 1540s, 1399m, 1364w, 1346w, 1308w, 1253m, 1217w, 1208w, 1177m, 1152w, 1107w, 1059m, 1042w, 978w, 947w, 935m, 895w, 812vs, 806s, 762vs, 710w, 681w, 671w, 654s, 614m, 578w, 561w, 528w.

#### 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphtheneborane (dpp-bian)BH (8)

To a solution of 0.55 g (1.0 mmol) of (dpp-bian)BCl in THF (30 mL) 0.1 g (2.63 mmol) of LiAlH<sub>4</sub> was added. The reaction mixture was stirred at reflux for 60 h. To the solid left after evaporation of THF toluene (25 mL) was added. An excess of

LiAlH<sub>4</sub> was filtered off. From concentrated toluene solution compound (dpp-bian)BH was isolated in the form of needle like prismatic crystals. Yield 0.46 g (90%). M.p. 298 °C. Anal. calcd for C<sub>36</sub>H<sub>41</sub>BN<sub>2</sub>: C 84.36, H 8.06; found: C 84.28, H 8.12. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, ppm):  $\delta$  7.33 (dd, 2 H<sub>arom</sub>, 9.2 and 5.4 Hz), 7.26 (2 d, 4 H<sub>arom</sub>, 9.2 and 5.4 Hz), 7.21 (d, 2 H<sub>arom</sub>, 8.2 Hz), 6.92 (dd, 2 H<sub>arom</sub>, 8.2 and 6.8 Hz), 6.74 (d, 2 H<sub>arom</sub>, 6.8 Hz), 3.47 (sept, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>, 6.8 Hz), 1.28 (d, 12 H, CH(CH<sub>3</sub>)-(CH<sub>3</sub>), 6.8 Hz), 1.14 (d, 12 H, CH(CH<sub>3</sub>)(CH<sub>3</sub>), 6.8 Hz). <sup>11</sup>B NMR (128.39 MHz, ppm):  $\delta$  24.8 (s, 1 B). <sup>13</sup>C NMR (100.62 MHz, C<sub>6</sub>D<sub>6</sub>, ppm): 146, 137, 135, 130, 128, 128, 127, 124, 118, 68, 29, 25, 25, 23. IR (Nujol, cm<sup>-1</sup>):  $\nu$  = 3069m, 3042m, 2724w, 2585s, 2311s, 1920w, 1859w, 1796w, 1613s, 1589m, 1532s, 1422m, 1400s, 1364m, 1335m, 1254s, 1231w, 1219s, 1175s, 1169s, 1140w, 1122w, 1109m 1094m, 1059m, 1044m, 999w, 965w, 937s, 893m, 848m, 814vs, 805vs, 781w, 765vs, 760vs, 670m, 625m, 550w, 499m.

#### DFT calculations

The DFT calculations were carried out with the Gaussian03 program package<sup>23</sup> using the 6-31G(d) basis set<sup>24</sup> and the B3LYP hybrid functional.<sup>25</sup> The molecular geometries were fully optimized and the vibration frequencies were analytically computed. The absence of imaginary frequencies testified for the energy minimum. The NBO<sup>26</sup> and AIM<sup>19</sup> analyses were also performed. For calculation of the AIM charges the AIMALL program<sup>27</sup> was employed. The LOL values were obtained with the Multiwfn multifunctional wavefunction analyzer.<sup>28</sup>

#### Single-crystal X-ray structure determination

The data for 2, 5, 7 and 8 were collected on a Bruker SMART APEX diffractometer, using graphite monochromated MoKa radiation ( $\omega$ -scan technique,  $\lambda = 0.71073$  Å). The structures were solved by direct methods using SHELXS-97<sup>29a</sup> and were refined on F<sup>2</sup> using SHELXL-97.<sup>29b</sup> SADABS<sup>29c</sup> was used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined in the "riding-model" ( $U_{iso}(H) = 1.5U_{eq.}(C)$  in CH<sub>3</sub>-groups and  $U_{iso}(H)$ =  $1.2U_{eq.}(C)$  in other ligands), except for those of OH and NH<sub>2</sub> groups in 5, 7 and H(1) at the boron atom in 8, which were obtained from differential Fourier-synthesis and refined isotropically. In complexes 5, 7 and 8 the i-Pr groups are disordered over two positions. CCDC 916524 (2), 916525 (5), 916526 (7) and 916527 (8) contain the supplementary crystallographic data for this paper.

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