

Mono- and diboronates derived from tridentate ONO ligands and arylboronic acids

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Abstract

The syntheses of eight [4.3.0] heterobicyclic boronates containing a N → B coordinative bond are described. The monomeric compounds were prepared by reaction of arylboronic acids with a tridentate ligand having the ONO donor set of atoms. It was shown that substituents at the *para*-position of the B-phenyl moiety transmit electronic effects to the C=N bond which in turn is polarized by formation of the N → B coordination bond. At the same time, related tridentate ligands were also reacted with 1,4-benzenediboronic acid in order to prepare benzene diboron complexes. The structure of this type of compounds was confirmed by X-ray analysis for one of the derivatives.

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Keywords: Tridentate ligands; Boron; Schiff base; Hammett equation; 1,4-benzene diboronic acid

1. Introduction

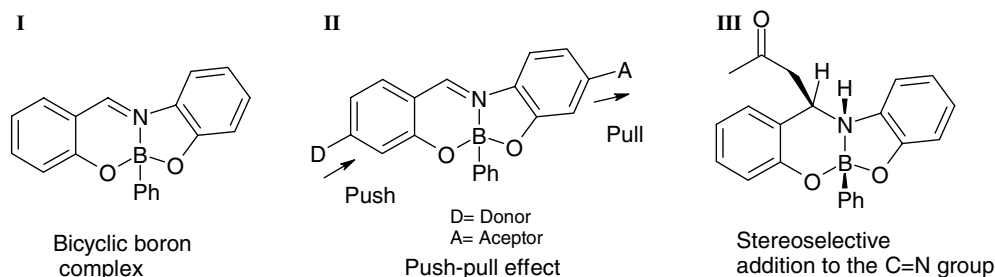
The use of tridentate ligands in coordination chemistry provides a facile means to stabilize transition metals [1] and main group elements [2] taking advantage of the chelate effect. Thus, it has been reported that tridentate ligands having an ONO donor set of atoms react with main group elements to give stable heterocycles [3]. In many cases, the stabilization of the complexes has been increased by the presence of coordinative bonds between the nitrogen atom and the corresponding main group element [2c,4].

In the course of our studies on the reaction of tridentate ONO ligands, we have established the synthesis of several monomeric and dimeric boron complexes [5] and have found that the formation of the different com-

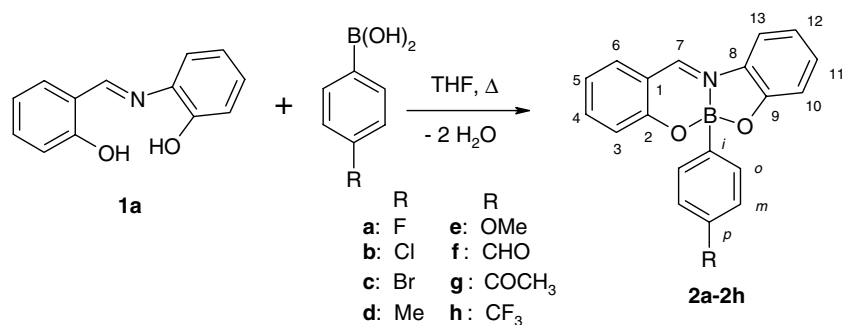
pounds depends on the conformation and structure of the ligand. For example, the reaction of phenylboronic acid with the tridentate ligand derived from salicylaldehyde and 2-aminophenol, leads to a [4.3.0] bicyclic boron compound (Scheme 1, I) [6] which is stabilized by the presence of an intramolecular N → B coordinative bond. The existence of electronic charge transfer complexes (Scheme 1, II) [7], suggests that the electronic delocalization present in the free ligand is retained upon formation of the coordinative bond. Nonetheless, coordination of the nitrogen atom to the boron atom polarizes the C=N double bond, as evidenced by the changes in ¹H NMR chemical shifts of the azomethine group and IR bands [5,6]. This polarization is confirmed also by the facile, stereoselective addition of acetone in these compounds (Scheme 1, III) [8] but not in the free ligand. At present, there is increasing interest in this type of compounds, because some of them are useful in propylene polymerization reactions [9] via the formation of a boron cation.

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Scheme 1. Examples of some monomeric boron compounds. (I) Heterobicycle formed by the presence of an intramolecular N → B coordination bond. (II) Electronic charge transfer boron complex with a push–pull effect. (III) The addition of acetone to compound I is stereoselective.



Scheme 2. Synthesis of the monomeric boron complexes **2a–2h**.

In the present work, several new monomeric boron complexes analogous to **I** that contain different substituents at the *para*-position of the B-aryl moiety (Scheme 2) were synthesized to evaluate the transmission of electronic effects to the C=N bond as a means to control and predict, in the future, the reactivity of the azomethine group. Additionally, the new diboronates described herein allow evaluation of the effect of alternate conjugated systems on the electronic structure of the complex.

2. Results and discussion

2.1. Preparation and characterization of the monomeric boron complexes **2a–2h**

Addition of different arylboronic acids to tridentate ligand **1a** derived from salicylaldehyde and 2-aminophenol [6] containing the ONO donor set of atoms, lead to formation of the monomeric compounds **2a–2h**. As mentioned above, the arylboronic acids selected for this study enclose different substituents at the *para*-position of the phenyl moiety (R = F, Cl, Br, Me, OMe, CHO, COCH₃, and CF₃), in order to evaluate the influence of electronic effects on the C=N bond (Scheme 2). The [4.3.0] heterobicyclic boronates **2a–2h** were obtained in moderate yields and are stable to moisture due to the presence of two B–O covalent bonds and a N → B coordinative bond, in addition to the chelate effect.

The formation of monomeric boron compounds was confirmed by EI-mass spectra. In all eight cases, the molecular ion [M]⁺ was observed and the base peak (*m/z* = 222) corresponds to the loss of the aryl group attached to boron atom [M – Ar]⁺. The C=N stretching band in the IR spectra is found between 1626 and 1634 cm⁻¹, and is shifted to lower wave numbers with respect to the free ligand ($\Delta\nu = 2\text{--}12\text{ cm}^{-1}$) owing to the formation of the N → B coordination bond.

The influence that is generated on the C=N group by the substituents at the *para*-position of the B-aryl moiety, can be analyzed from the NMR data. As a direct consequence of the formation of the N → B bond, the ¹H NMR data shows that the signals corresponding to the azomethine group (H-7), are shifted to lower frequencies in the boron complexes ($\delta = 8.30\text{--}8.42\text{ ppm}$) when compared to the free ligand ($\delta = 8.97\text{ ppm}$). The differences in the shifts can be attributed to the electronic changes induced by the substituents; the signals shifted to lower frequencies ($\delta = 8.30, 8.31\text{ ppm}$) correspond to compounds **2d** and **2e** which contain electron donor groups (Me and MeO), while those at higher frequency ($\delta = 8.41, 8.42\text{ ppm}$) correspond to compounds **2g** and **2h**, which have an electron withdrawing effect due to the presence of the –CF₃ and –COMe groups. Fig. 1 shows that there is a linear correlation between the σ Hammett values [10] and the ¹H NMR chemical shifts (δ), giving evidence of the electronic effect produced by the *para*-substituents in the B-phenyl moiety. Substituent effects are also evident in the B–C_{Ph} bond

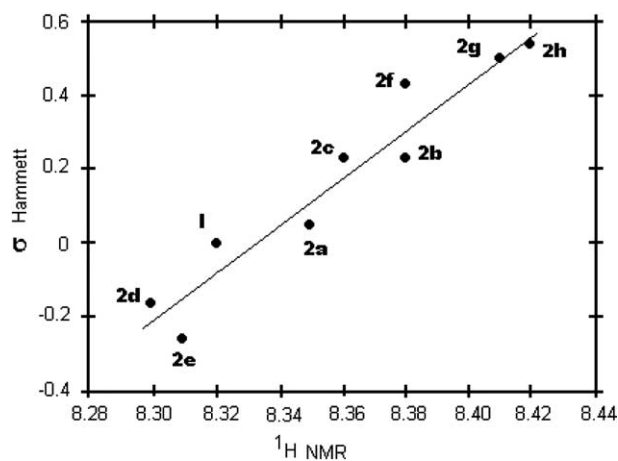


Fig. 1. Correlation between the ^1H NMR chemical shifts (δ) of the imine proton versus the σ Hammett values for the *para*-substituents in the monomeric boron complexes. Equation: σ Hammett = $6.45 \cdot (\delta, ^1\text{H}) - 54.119$, $R = 0.9614$. The chemical shift value for **I** was taken from [6].

lengths, as has been shown for a series of dimeric boron complexes [11].

A similar behavior was observed in the ^{13}C NMR data in relation to the C=N group. In all compounds, the signal corresponding to the C=N group is shifted to lower frequency (ca. $\Delta\delta = 12.0$ ppm) compared to that of the free ligand; particularly complexes containing electron donor groups showed the lowest frequency values. The fact that the boron atoms are in a tetrahedral environment was deduced from the ^{11}B NMR spectra, wherein the chemical shifts were observed in a range of $\delta = 7\text{--}8$ ppm, that is typical for this type of complexes [5].

Crystals of compound **2c** that were suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution of **2c** in CHCl_3 . Crystallographic data and selected geometrical parameters are listed in Tables 1 and 2. The molecular structure is shown in Fig. 2 confirming the formation of a monomeric compound, in which an intramolecular N \rightarrow B coordinative bond forms the [4.3.0] heterobicycle. In the crystal lattice, two enantiomeric molecules of **2c** are located at the same site, as a consequence, the C=N group was disordered in a statistic probability of 50:50, to refine this disorder the PART instruction was used [12]. The N \rightarrow B bond lengths were found to be comparable with that of compound **I**; (1.611(8)/1.625(13) Å for **2c** and 1.613(5) Å for **I**). The two B–O bond distances in compound **2c** are equivalent ($d_{\text{B-O}} = 1.470(6)/1.477(6)$) most probably because of the disorder, since they are an average of those found in compound **I** ($d_{\text{B-O}} = 1.459(5)/1.503(5)$ Å). The most important difference between compounds **2c** and **I** is the C=N bond distance, which is shorter in **I** (1.249(4) Å) than in compound **2c** (1.285(8)/1.285(15) Å). This variation can be attributed to the electronic effect of the bromine atom at the

Table 1
Crystallographic data for **2c** and **3e**

	2c	3e
Empirical formula	$\text{C}_{19}\text{H}_{23}\text{BBrNO}_2$	$\text{C}_{38}\text{H}_{34}\text{B}_2\text{N}_2\text{O}_4 \cdot \text{CHCl}_3$
Formula weight	378.20	723.52
Crystal size (mm^3)	$0.5 \times 0.3 \times 0.3$	$0.48 \times 0.36 \times 0.32$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	5.8960(10)	9.051(2)
<i>b</i> (Å)	17.342(3)	19.368(4)
<i>c</i> (Å)	15.840(3)	11.796(2)
β ($^\circ$)	93.39(3)	99.21(3)
Volume (Å^3)	1616.8(5)	2041.2(7)
<i>Z</i>	4	4
D_{calc} (g/cm^3)	1.553	1.372
Absorption coefficient (mm^{-1})	2.553	0.464
Collected reflections	3189	3792
Independent reflections	2826	3558
Parameters	237	244
Final <i>R</i> indices	$R = 0.0477$	$R = 0.0485$
[$I > 2\sigma(I)$]		
<i>R</i> indices (all data)	$wR = 0.1407$	$wR = 0.1699$
Goodness-of-fit	1.004	1.011

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for **2c** and **3e**

	2c ^a	3e
<i>Bond distances</i> (Å)		
B(1)–N(1)	1.611(8)/1.625(13)	1.616(5)
B(1)–O(1)	1.470(6)	1.467(5)
B(1)–O(2)	1.477(6)	1.449(5)
B(1)–C _{Ph}	1.604(6)	1.620(5)
N(1)–C(7)	1.285(8)/1.285(15)	1.290(4)
N(1)–C(8)	1.412(8)	1.486(5)
<i>Bond angles</i> ($^\circ$)		
O(1)–B(1)–N(1)	114.3(4)/123.0(5)	105.6(2)
O(1)–B(1)–O(2)	111.9(3)	113.5(2)
O(1)–B(1)–C _{Ph}	112.0(4)	113.9(3)
O(2)–B(1)–N(1)	94.4(4)/86.8(5)	98.4(2)
O(2)–B(1)–C _{Ph}	112.5(3)	109.9(2)
N(1)–B(1)–C _{Ph}	110.6(4)/108.0(5)	114.5(3)

^a There are two positions for the C(7) and N(1) atoms because of the presence of two enantiomeric molecules at the same site in the crystal lattice.

para-position of the B-phenyl moiety, giving additional evidence for the polarization change in the C=N group.

2.2. Preparation and characterization of the diboronate complexes **3a–3e**

When the same ligand used for the preparation of monomeric derivatives was allowed to react with 1,4-benzenediboronic acid in a 1:1 ratio, the monochelated complex was not formed but instead the diboronate **3a** was obtained in low yields (ca. 40%). The yield was increased to 89%, when the reaction was carried out in a

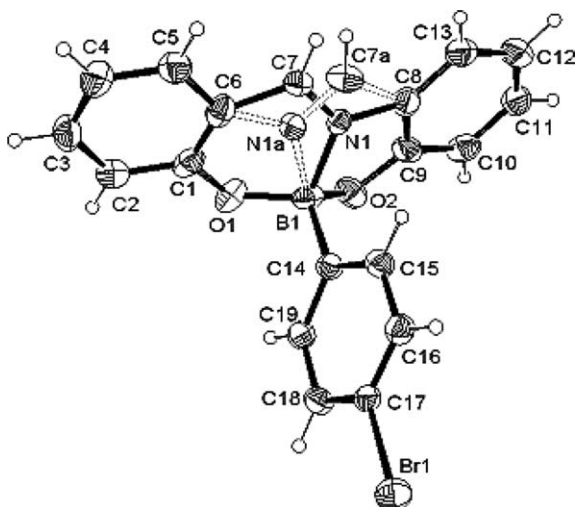


Fig. 2. Molecular structure of compound **2c**.

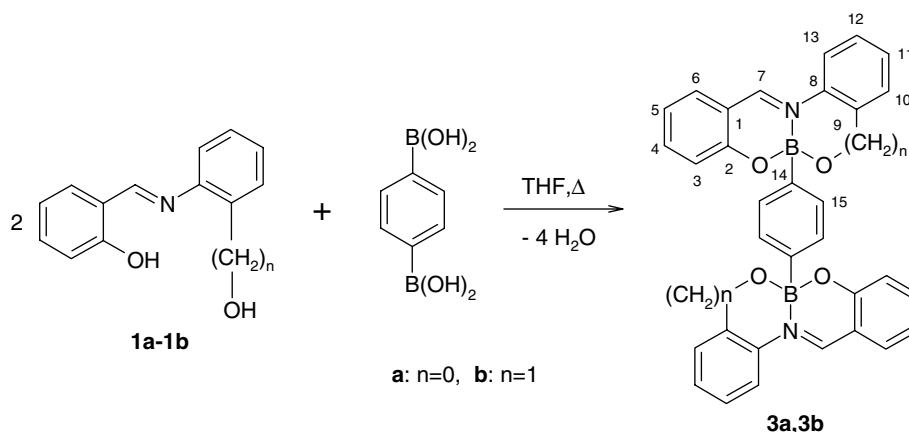
2:1 ratio (Scheme 3). Additionally, ligand **1b** was used for the reaction with diboronic acid to determine if diboronate [4.4.0] heterobicycles are also formed.

The formation of diboronates **3a** and **3b** was established by FAB-mass spectrometry, which permitted to observe peaks for the molecular ions $[M]^+$. The NMR spectra showed only signals for half of the molecule, which indicate the symmetric nature of the complex (at least in solution). The ^1H NMR spectrum of compound **3a** shows that the signal corresponding to the hydrogen atom of the C=N group, is shifted to high frequency ($\Delta\delta = 0.17$ ppm) with respect to the free ligand and also in relation to the monomeric boronates (**2a–2h**). This observation suggests that the boron atom located at the *para*-position creates a deshielding effect on the hydrogen of the imine group. These results are supported by the fact that the signal for the carbon atom (C-7) in the ^{13}C NMR spectrum, is shifted to high frequency ($\delta = 152.4$ ppm) in relation to the chemical shift observed for the analogous carbon atoms in compounds **2a–2h**. Similar results concerning the symmetry and

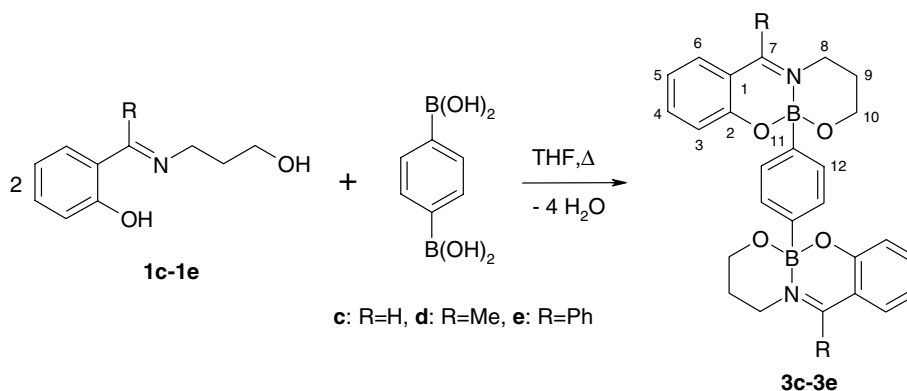
chemical shifts were found for compound **3b**, in this case, the signal for H-7 observed in ^1H NMR was shifted to $\delta = 9.25$ ppm, and for C-7 at $\delta = 158.5$ ppm in ^{13}C NMR. The hydrogen and carbon atoms at position 15 gave signals at $\delta = 6.87/130.2$ and $6.84/130.6$ ppm, for **3a** and **3b**, respectively. The ^{11}B NMR spectra showed signals at $\delta = 7.6$ and 6.7 ppm for **3a** and **3b**, respectively, evidencing the tetrahedral character of the atoms.

For comparison, related compounds were synthesized by reaction of tridentate ligands **1c–1e** with 1,4-benzenediboronic acid. Ligands **1c–1e** have H, Me and Ph groups at the imine position and are derived from propanol amine; this type of ligands favor the formation of complexes with a N \rightarrow B coordinative bond containing two six-membered rings around each boron atom (Scheme 4). The diboronate compounds **3c–3e** were obtained and their structure was confirmed by observation of the corresponding molecular ion $[M]^+$ in the FAB-mass spectra.

The spectroscopic data also established the symmetrical nature of these compounds. The IR spectra of compounds **3c–3e** showed strong bands for the C=N group at 1628, 1618 and 1606 cm^{-1} , respectively. The ^1H NMR spectra showed diastereotopic signals in the range of $\delta = 1.50$ and 4.00 ppm, which correspond to the CH_2 groups. As a consequence of the inductive effect of the organic group (H, Me, and Ph) present at the C=N moiety, the hydrogen atoms of the aromatic bridge (H-12) presented different shifts, $\delta = 7.09$, 7.20 and 7.47 ppm for **3c–3e**, respectively, all of them shifted to higher frequency in relation to **3a** and **3b** whereby the planarity of the ligand produced a shielding effect. In the case of compound **3c**, the signal corresponding to the hydrogen atom of the HC=N fragment was observed at $\delta = 7.09$ ppm. The ^{13}C NMR spectra showed signals at $\delta = 171.9$ and 170.3 ppm for **3d** and **3e**, respectively, corresponding to the azomethine group (C-7); while the signals for C-12 were observed at $\delta = 131.3$ and 131.2 ppm for **3d** and **3e**. The ^{13}C NMR spectrum for **3c** could not



Scheme 3. Synthesis of the diboronate complexes **3a–3b**.



Scheme 4. Synthesis of the diboronate complexes **3c–3e** derived from aliphatic amino alcohols.

be obtained due to poor solubility of the compound. Interestingly, the phenyl group attached to the azomethine moiety in compound **3e** shows two distinct signals for the atoms at the *ortho*- and *meta*-positions in the proton and carbon NMR spectra, probably due to restricted rotation of the aromatic ring.

In addition to the NMR and mass spectrometry analysis, the molecular structure of **3e** was confirmed by X-ray crystallography. The most relevant crystallographic data are summarized in Table 1, selected bond lengths and angles are listed in Table 2. The structure of **3e** contains an inversion center located at the center of the aromatic ring that bridges the two boron chelates and has therefore a C_i punctual group symmetry. The configurations of the boron atoms are *R* and *S*. As can be seen from the molecular structure shown in Fig. 3, compound **3e** contains two fused six-membered rings at each side of the central “ $\text{BC}_6\text{H}_4\text{B}$ ” moiety. Each one of these heterobicycles is formed through a $\text{N} \rightarrow \text{B}$ coordinative, which has a bond length of 1.616(5) Å that is comparable to that of compound **2c**. The six-membered heterocycle containing the $\text{C}=\text{N}$ moiety has an envelop conformation, with the boron atom having the largest deviation from the mean plane ($\Delta = -0.671$ Å). The six-membered heterocycles containing the aliphatic chains have *chair* conformations.

The bond lengths and angles are similar to those of other boronates [5], for instance, the values for the an-

gles around the boron atoms are in the range from 104.2° to 115.1° which is an indication of the distorted tetrahedral geometry of the boron atom. The phenyl group attached to the $\text{C}=\text{N}$ group is oriented nearly perpendicular to the mean plane of the salicylaldehyde, as evidenced by the $\text{C}(12)\text{--C}(11)\text{--C}(7)\text{--C}(1)$ and $\text{C}(12)\text{--C}(11)\text{--C}(7)\text{--N}(1)$ torsion angles which have values of -73.52° and 106.6° , respectively. In a similar way, the $\text{N} \rightarrow \text{B}$ coordination bonds have an eclipsed conformation with respect to the bridging aromatic moiety whereby the torsion angle $\text{C}(19)\text{--C}(17)\text{--B}(1)\text{--N}(1)$ has a value of only 0.80° .

At the supramolecular level the molecules are organized so that two adjacent molecules show interactions involving the aromatic fragments. There is (i) a parallel displacement through $\pi \cdots \pi$ interactions with a distance of 3.71 Å and, (ii) a T-shaped arrangement with an intermolecular $\text{C}\text{--H} \cdots \pi$ distance of 2.87 Å (Fig. 4) [13].

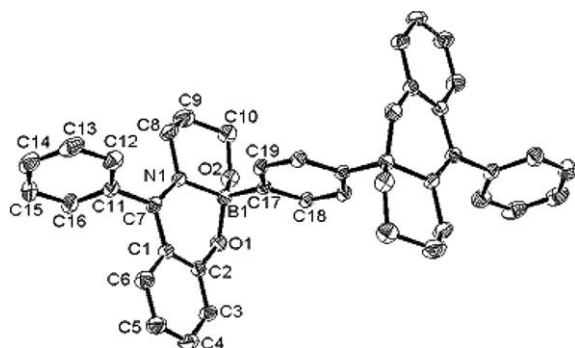


Fig. 3. Molecular structure of compound **3e**.

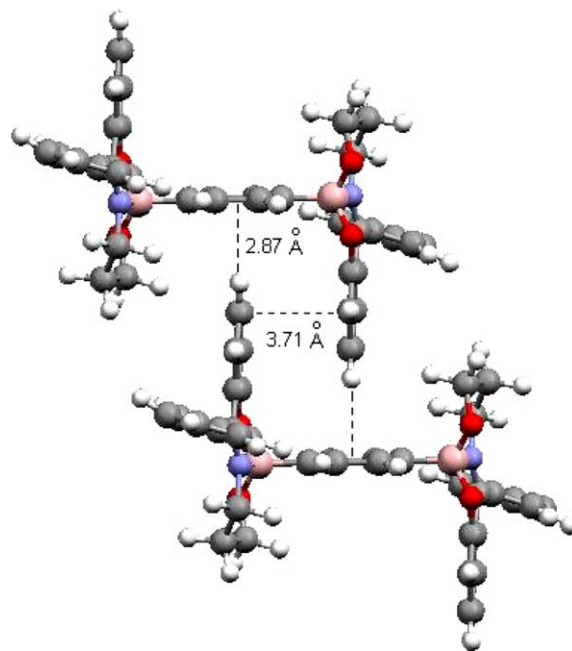


Fig. 4. Schematic representation showing the $\pi \cdots \pi$ and $\text{CH} \cdots \pi$ aromatic interactions presents in **3e**.

2.3. Conclusions

The present study shows that substituents attached to the phenyl moiety of boronates in the *para*-position transmit electronic effects to the C=N bond. Electron withdrawing groups induce a deshielding effect on the azomethine group and electron donating groups cause the opposite effect, as evidenced by the ^1H NMR data. The presence of an additional boronate in the *B*-phenyl moiety (compounds **3a–3e**), enhances the deshielding effect due to increased electronic delocalization between the two chelates present in the diboronates. This possibility to modulate the electrophilicity of the imine bond could allow, in the near future, to control nucleophilic attack on azomethine groups involved in boron complexes. Furthermore, in the case of formation of the diboronate compounds, it was noticed that the presence of aromatic or aliphatic chains in the ligand has no effect on the course of the reaction.

3. Experimental part

3.1. Instrumental

NMR spectra were recorded at room temperature using a Bruker 300 spectrometer. Chemical shifts are given in ppm. Infrared spectra have been recorded on a Perkin–Elmer 16F-PC FT-IR spectrophotometer. Mass spectra were obtained with a HP 5989-A mass spectrometer operating in the electron impact mode. Melting points were determined with a Gallenkamp MFB-595 apparatus.

3.2. X-ray crystallography

Crystal structure determination of 2c and 3e. Crystals suitable for X-ray structure analysis were grown by slow evaporation of concentrated CHCl_3 solutions of the complexes. Intensity data were collected at 293 K with an Enraf-Nonius CAD4 diffractometer, $\text{Mo K}\alpha$ -radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator. Empirical absorption corrections (DIFABS) were applied. The structures were solved by direct methods (SHELXS-86) [14] and refined using SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center as supplementary material Nos. 256294 and 256295 for **2c** and **3e**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

3.3. Preparative part

All reagents were purchased from Aldrich and were used without further purification. All five ligands used (**1a–1e**) [5a,5b,5c,6] as well as 1,4-benzenediboronic acid [15], were synthesized in accordance to reported methods.

3.3.1. General method for the preparation of the monomeric boron complexes **2a–2h**¹

Compounds **2a–2h** were synthesized by reaction of equimolecular quantities of ligand **1a** and the corresponding arylboronic acid. The reaction mixture was dissolved in THF and refluxed. After 1 h under stirring, the water and part of the solvent were removed with a Dean-Stark trap. The solvent was completely removed using a vacuum pump and the product was washed with several portions of hexane.

3.3.1.1. 2-(4-fluorophenyl)-dibenzo-[d,h]-6-aza-1,3-dioxo-2-boracyclonon-6-ene (2a). **2a** was prepared from 0.21 g (1.50 mmol) of **1a** and 0.32 g (1.50 mmol) of 4-fluorophenylboronic acid. A yellow solid was obtained, yield 67% (0.32 g, 1.00 mmol), m.p. = 206–208 °C. IR ν (KBr) 1626 (C=N), 1608, 1550, 1468, 1376, 1174, 952, 824, 742 cm^{-1} . EI-MS m/z (%), 317 (M^+ , 6), 222 ($[\text{M} - \text{C}_6\text{H}_4\text{F}]^+$, 100), 95 (7), 77 (16), 75 (10), 50 (6). ^1H NMR (300 MHz, CDCl_3) δ : 8.35 (1H, s, H-7), 7.57 (1H, ddd, $J = 8.5, 7.2, 1.6$ Hz, H-4), 7.46 (1H, dd, $J = 7.9, 1.3$ Hz, H-10), 7.40 (1H, dd, $J = 7.2, 1.6$ Hz, H-6), 7.37 (1H, td, $J = 7.9, 1.3$ Hz, H-12), 7.33 (2H, dd, $J = 8.9, 2.0$ Hz, H-*o*), 7.21 (1H, d, $J = 8.5$ Hz, H-3), 7.11 (1H, dd, $J = 7.9, 1.3$ Hz, H-13), 6.96 (1H, td, $J = 7.2, 1.6$ Hz, H-5), 6.92 (1H, td, $J = 7.9, 1.3$ Hz, H-11), 6.84, (2H, dd, $J = 8.9, 4.0$ Hz, H-*m*) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ : 158.6 (C-2), 157.4 (C-9), 149.0 (C-7), 138.2 (C-4), 133.0 (C-*o*), 132.6 (C-12, *m*), 131.6 (C-6), 130.5 (C-8), 120.6 (C-5), 120.3 (C-3), 119.2 (C-11, 1), 115.4 (C-13), 115.2 (C-10), 114.2 (C-*p*) ppm. ^{11}B NMR (96 MHz, CDCl_3) δ : 7.7 ($h_{1/2} = 143$ Hz) ppm. Anal. Calc. C, 71.92; H, 4.10; N, 4.42. Found: C, 71.57; H, 4.08; N, 4.36%.

3.3.2. General method for the preparation of diboronate complexes **3a–3e**

Compounds **3a–3e** were synthesized using two equivalents of ligands **1a–1e** and one equivalent of 1,4-benzenediboronic acid. The reaction was refluxed under THF, after 1 h under stirring, the water and part of the solvent was removed with a Dean-Stark trap. The solid was precipitated and filtered; finally the product was washed with several portions of hexane.

¹ Electronic Supplementary Information (ESI) available: experimental and spectroscopic data for complexes **2b–2h** and **3b–3e**.

3.3.2.1. *1,4-Benzene-bis[1-[2-[1-(2-phenolate- κ O)-iminomethyl- κ N]-phenolate- κ O]-boronate (3a)*. **3a** was prepared from 0.50 g (2.34 mmol) of ligand **1a** and 0.19 g (1.17 mmol) of 1,4-benzenediboronic acid. A yellow solid was obtained, yield 89% (0.54 g, 1.04 mmol) slightly soluble in DMSO- d_6 , m.p. = 354–356 °C. IR ν (KBr): 3314, 2942, 1608(C=N), 1572, 1442, 1056, 754, 702 cm^{-1} . FAB-MS m/z : 520. ^1H NMR (300 MHz, DMSO- d_6): 9.14 (1H, s, H-7), 7.74 (1H, d, $J = 7.6$ Hz, H-10), 7.58–7.52 (2H, m, H-12, H-13) 7.30 (1H, t, $J = 7.9$ Hz, H-4), 7.04 (1H, d, $J = 7.6$ Hz, H-6), 6.97 (1H, t, $J = 7.6$ Hz, H-11), 6.94 (1H, d, $J = 7.9$ Hz, H-3), 6.91 (1H, t, $J = 7.9$ Hz, H-5), 6.87 (1H, s, H-15) ppm. ^{13}C NMR (75 MHz, DMSO- d_6) δ : 158.3 (C-2), 157.0 (C-9), 152.4 (C-7), 138.1 (C-4), 132.7 (C-6), 132.3 (C-12), 130.9 (C-8), 130.2 (C-15), 120.7 (C-5), 119.9 (C-1), 119.8 (C-3), 119.7 (C-11), 117.1 (C-13), 114.3 (C-10) ppm. ^{11}B NMR (96 MHz, DMSO- d_6) δ : 7.6 ppm ($h_{1/2} = 960$ Hz). Anal. Calc. C, 73.89; H, 4.26; N, 5.38. Found: C, 73.67; H, 4.08; N, 5.21%.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.01.060](https://doi.org/10.1016/j.jorganchem.2005.01.060).

References

- [1] (a) S. Dutta, A. Chakravorty, *Polyhedron* 13 (1994) 1811; (b) M.J. Clague, N.L. Keder, A. Butler, *Inorg. Chem.* 32 (1993) 5343;
- (c) J.U. Mondal, F.A. Schultz, T.D. Brennan, W.R. Scheidt, *Inorg. Chem.* 27 (1988) 3950;
- (d) E.Y. Tshuva, M. Versano, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Inorg. Chem. Commun.* 2 (1999) 371.
- [2] (a) C.Y. Wong, R. McDonald, *Inorg. Chem.* 35 (1996) 325; (b) M. Caligaris, L. Randaccio, in: G. Wilkinson, R.D. Gillard, J. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, 2, Pergamon Press, Elmsford, NY, 1987; (c) D.A. Atwood, M.J. Harvey, *Chem. Rev.* 101 (2001) 37.
- [3] (a) Y. Li, Y. Liu, W. Bu, J. Guo, Y. Wang, *Chem. Commun.* (2000) 1551; (b) N. Yalçın, A. Kenar, C. Arici, O. Atakol, M. Tastekin, *Main Group Met. Chem.* 24 (2001) 247; (c) H.I. Beltrán, L.S. Zamudio-Rivera, T. Mancilla, R. Santillan, N. Farfán, *Chem. Eur. J.* 9 (2003) 2291; (d) M. Sánchez, O. Sánchez, H. Höpfl, M.E. Ochoa, D. Castillo, N. Farfán, S. Rojas-Lima, *J. Organomet. Chem.* 689 (2004) 811; (e) N. Farfán, H. Höpfl, V. Barba, M.E. Ochoa, R. Santillan, E. Gómez, A. Gutiérrez, *J. Organomet. Chem.* 581 (1999) 70.
- [4] H. Höpfl, *J. Organomet. Chem.* 581 (1999) 129.
- [5] (a) H. Höpfl, M. Sánchez, V. Barba, N. Farfán, S. Rojas, R. Santillan, *Inorg. Chem.* 37 (1998) 1679; (b) V. Barba, D. Cuahutle, M.E. Ochoa, R. Santillan, N. Farfán, *Inorg. Chim. Acta* 303 (2000) 7; (c) V. Barba, R. Xochipa, R. Santillan, N. Farfán, *Eur. J. Inorg. Chem.* (2004) 118.
- [6] H. Höpfl, M. Sánchez, N. Farfán, V. Barba, *Can. J. Chem.* 76 (1998) 1352.
- [7] H. Reyes, B.M. Muñoz, N. Farfán, R. Santillan, S. Rojas-Lima, P.G. Lacroix, K. Nakani, *J. Mater. Chem.* 12 (2002) 2898.
- [8] V. Barba, D. Cuahutle, R. Santillan, N. Farfán, *Can. J. Chem.* 79 (2001) 1229.
- [9] P. Wei, D. Atwood, *Inorg. Chem.* 37 (1998) 4934.
- [10] C.D. Johnson, *The Hammett Equation*, Cambridge University Press, Cambridge, 1973.
- [11] V. Barba, R. Luna, D. Castillo, R. Santillan, N. Farfán, *J. Organomet. Chem.* 604 (2000) 273.
- [12] L.M. Glówka, D. Martynowski, K. Kozłowska, *J. Mol. Struct.* 474 (1999) 81.
- [13] G.M. Sheldrick, *SHELXS-86*, Program for Crystal Structure Solution, University of Goettingen, Germany, 1986.
- [14] G.M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Goettingen, Germany, 1997.
- [15] I.G.C. Coutts, H.R. Goldschmid, C. Musgrave, *J. Chem. Soc. C* (1970) 488.