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Bisoxazaborolidines and boron complexes derived from tetradentate ligands: synthesis and spectroscopic studies

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Abstract

A series of tetradentate ligands were synthesized and their reaction with arylboronic acids was studied. Two classes of tetradentate ligands are discussed, which are mainly based on ONNO and ONOO donor sets and involve 2-aminophenol derivatives and Schiff bases. The reaction of phenylboronic acid with tetradentate ligands derived from 2-aminophenol leads to bisoxazaborolidines containing five-membered rings formed by CCNBO atoms, where the boron atoms have a trigonal geometry. In contrast, tetradentate ligands derived from Schiff bases lead to monomeric and dimeric boron complexes, in which the boron atoms have a tetrahedral geometry stabilized by an intramolecular N–B dative bond. The structures of two boron compounds were established by X-ray diffraction analysis.

Keywords: Tetradentate ligand; Aminophenol; Oxazaborolidine; Boron; Schiff base

1. Introduction

Tetradentate ligands of the N_2O_2 type have been extensively studied, including their reaction with main group elements and transition metals [1–6]. The versatility of these ligands permits the isolation with transition metals of both mononuclear and dinuclear complexes. However, for group 13 elements, mainly dinuclear complexes with boron [7–9], aluminum [10] and gallium [10] are known.

Compared to the salen derivatives which are readily available by condensation of primary amines with carbonyl compounds, such as salicylaldehyde and 2-hydroxyphenyl ketones [12,13]; tetradentate ligands derived from aminophenol have been less explored mainly due to the fact that their synthesis requires several steps [13–15]. It has been observed that the reactivity of tetradentate N_2O_2 ligands of the salen type containing sp^2 nitrogen atoms is quite different to that of ligands having sp^3 nitrogen atoms and phenolic oxygens. In recent years, dimetallic boron compounds with salen ligands have been used as Lewis acid activators or as dinuclear catalysts in dealkylation reactions of a wide range of phosphate esters [16,17].

In continuation of our studies on bi- and tridentate ligands with different boron reagents [18–20], we set to investigate the reactivity of tetradentate ligands with arylboronic acids. The boron complexes described herein contain tetradentate ligands with ONNO and ONOO donor moieties. Complexes **2a**–**2g** have boron atoms with trigonal geometry and a C_2 fold axis. The advantages associated with the use of ligands with C_2 symmetry for enantioselective catalysis have been highlighted in the literature [21].

Moreover, compounds having two Lewis acid sites have great potential for application in both catalysis [22] and synthesis [23] and there are a number of biologically important reactions that are mediated by two Lewis

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acidic metals in close proximity [24]. Also, derivatives from tetradentate ligands such as phenols and transition metals are useful model for the simulation of enzymatic systems [25].

2. Experimental

2.1. Materials and instrumentation

All reagents were purchased from Aldrich and used without further purification. NMR spectra were recorded at room temperature using the following spectrometers: Jeol GSX 270, Bruker 300 and Jeol eclipse + 400. 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. Elemental microanalyses were performed by Oneida Research Services (Whitesboro, NY. 13492).

Crystal structure determination: single crystals of **2e** and **5b** suitable for X-ray structure analysis were grown by slow evaporation of a THF solution of the complex. Crystal data and details of the structure determinations are listed in Table 1. Intensity data were collected at 293 K with an Enraf-Nonius CAD4 diffractometer for compound **2e** and a Bruker Smart 6000 diffractometer with a CCD area detector for **5b**, Mo Kα-radiation, $\lambda = 0.71073$ Å, graphite monochromator. Empirical absorption corrections (DIFABS) were applied. The structures were solved by direct methods (SHELXS-86) [26] and refined using SHELXL-97 [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. Crystallographic data for the structures have been deposited at the Cambridge Crystallographic Data Center as supplementary material Nos. 223333 and 223334 for complexes **2e** and **5b**, respectively. Copies of 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.

2.2. Synthesis of the complexes

Ligands **1a**–**1d** were prepared by methods previously described in the literature [13].

2.2.1. General procedure for the preparation of ligands *1e*–*1g*

A mixture of 1,3-dibromopropane and 2 equivalents of *o*-aminophenol was placed into a sealed tube and heated in an oil bath to 120–125 °C. After 14 h of heating, a 10 M NaOH solution was added with stirring. The organic phase was extracted by using several portions of dichloromethane. Finally, the solvent was removed under vacuum and the product washed twice with 10 ml of hexane.

*2.2.1.1. 2, 2′-(1,3-Propanediamine)bisphenol **1e**.* Compound **1e** was prepared from 2.0 g (18.3 mmol) of *o*-aminophenol and 0.93 ml (9.2 mmol) of 1,3-dibromopropane. A white solid was obtained with yield of 32 % (0.76 g, 2.90 mmol). M.p. = 154–156 °C. IR (KBr)ν = 3358, 3318, 3058, 2916, 2848, 1596, 1512,

Table 1
Crystallographic data for **2e** and **5b**

Identification code	**2e**	**5b**
Empirical formula	$C_{27}H_{24}B_2N_2O_2$	$C_{20}H_{22}B_1N_1O_4$
Formula weight	430.10	351.20
Crystal size (mm^3)	$0.51 \times 0.43 \times 0.38$	$0.40 \times 0.30 \times 0.25$
Temperature (K)	273	293
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a (Å)	14.550(3)	8.1627(3)
b (Å)	9.240(2)	15.1214(6)
c (Å)	17.210 (3)	14.5944(5)
β (°)	90.92(3)	105.149(1)
V (Å^3)	2313.4(8)	1738.81(11)
Z	4	4
D_{calc} (g/cm^3)	1.235	1.342
Absorption coefficient (mm^{-1})	0.077	0.386
Collected reflections	4887	11339
Independent reflections	4704	3415
Parameters	299	238
Final R indices [$I > 2$sigma(I)]	$R = 0.0682$	$R = 0.0563$
R indices (all data)	$wR = 0.1827$	$wR = 0.1579$
Goodness-of-fit	1.038	1.053
Largest differential peak and hole (e/Å^3)	0.009/−1.954	0.044/0.001

1490, 1440, 1378, 1276, 1254, 1198, 748 cm^{-1}. MS (EI, 70 eV, DIP) *m/z* (%): 258 [M^+, 63], 149 (40), 132 (35), 120 (100), 109 (42), 77 (35), 53 (18). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.17 (1H, s, NH), 6.65 (1H, d, $J = 7.7$ Hz, H-6), 6.62 (1H, ddd, $J = 7.7$, 6.9, 1.1 Hz, H-4), 6.49 (1H, d, $J = 6.9$ Hz, H-3), 6.40 (1H, td, $J = 7.7$, 1.1 Hz, H-5), 3.35 (1H, s, OH), 3.13 (2H, t, $J = 6.8$ Hz, H-7), 1.84 (2H, qn, $J = 6.8$ Hz, H-8) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 144.6 (C-1), 137.9 (C-2), 120.2 (C-4), 116.1(C-5), 113.9 (C-6), 110.2 (C-3), 40.2 (C-7), 28.9 (C-8) ppm.

*2.2.1.2. 2,2′-(1,3-Propanediamine)-4,4′-dimethylbisphenol (**1f**).* Compound **1f** was prepared from 2.0 g (16.2 mmol) of 2-amino-4-methylphenol and 0.86 ml (8.1 mmol) of 1,3-dibromopropane. A pale pink solid was obtained with yield of 45% (1.04 g, 3.63 mmol). M.p. = 169–170 °C. IR (KBr)ν = 3332, 3118, 2962, 2920, 1522, 1508, 1478, 1438, 1374, 1306, 1278, 1254, 1214, 1124, 808, 770 cm^{-1}. MS (EI, 70 eV, DIP) *m/z* (%): 286 [M^+, 67], 266 (27), 213 (42), 185 (28), 134 (100), 123 (43), 77 (34), 41 (20). ^1H NMR (400 MHz, DMSO-d_6) δ: 8.99 (1H, s, NH), 6.50 (1H, d, $J = 7$ Hz, H-6), 6.29 (1H, s, H-3), 6.17 (1H, d, $J = 7.0$ Hz, H-5), 3.63 (1H, s, OH), 3.10 (2H. t, $J = 8.3$ Hz, H-7), 2.11 (3H, s, CH_3) 1.82 (2H, qn, $J = 8.3$ Hz, H-8) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 142.3 (C-1), 137.7 (C-2), 128.5 (C-4), 116.2 (C-5), 113.7 (C-6), 111.1 (C-3), 40.2 (C-7), 28.9 (C-8), 21.4 (CH_3) ppm.

*2.2.1.3. 2,2′-(1,3-Propanediamine)-5,5′-dimethylbisphenol (**1g**).* About **1g** was prepared from 2.0 g (16.2 mmoles) of 2-amino-5-methylphenol with 0.86 ml (8.1 mmol) of 1,3-dibromopropane. A pale yellow solid was obtained with yield of 24% (0.55 g, 1.92 mmol). M.p. = 166–168 °C. IR (KBr)ν = 3326, 3084, 3032, 2960, 2916, 2802, 1530, 1468, 1420, 1288, 1272, 1248, 1212, 1136, 798, 584 cm^{-1}. MS (EI, 70 eV, DIP) *m/z* (%) 286 [M^+, 87], 266 (1), 242 (2), 164 (2), 136 (69), 134 (100), 91 (25), 77 (26), 28 (7). ^1H NMR (400 MHz, DMSO-d_6) δ: 9.08 (1H, s, NH), 6.48 (1H, s, H-6), 6.43 (1H, d, $J = 7.3$ Hz, H-4), 6.37 (1H, d, $J = 7.3$ Hz, H-3), 4.47 (1H, s, OH), 3.07 (2H, t, $J = 6.2$ Hz, H-7), 2.02 (3H, s, CH_3), 1.80 (2H, qn, $J = 6.2$ Hz, H-8) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ: 144.0 (C-1), 135.5 (C-2), 124.9 (C-5), 120.3 (C-4), 115.0 (C-6), 110.5 (C-3), 41.7 (C-7), 29.0 (C-8), 20.8 (CH_3) ppm.

*2.2.2. General procedure for the preparation of oxazaborolidines **2a**–**2g***

An equivalent of ligands **1a**–**1g** was added to two equivalents of phenylboronic acid in 30 ml of xylene. The solution was refluxed for 6 h using a Dean-Stark trap to remove the water formed during the reaction and part of the solvent. The solution was evaporated to dryness to give compounds **2a**–**2g** as gray solids, which were dissolved in chloroform, precipitated with hexane and washed with a mixture of hexane:chloroform (9:1).

*2.2.2.1. N,N′-[1,2-ethane-bis[2-phenyl-(benzoxazaborolidine)]] (**2a**).* Compound **2a** was prepared from 0.50 g (2.05 mmol) of **1a** and 0.50 g (4.10 mmol) phenylboronic acid. A pale gray solid was obtained with yield of 34% (0.30 g, 0.72 mmol). M.p. = 195–197 °C. IR (KBr)ν = 3264, 3070, 2370, 1604, 1498, 1458, 1364, 1350, 1192, 1090, 1008, 698, 638, 580 cm^{-1}. MS (EI, 15 eV, DIP) *m/z* (%): 416 (M^+, 100), 368 (11), 338 (27), 330 (41), 252 (29), 208 (92), 180 (36), 122 (71). ^1H NMR (270 MHz, $CDCl_3$) δ: 7.77 (2H, dd, $J = 7.7$, 1.5 Hz, H-*o*), 7.49 (1H, dt, $J = 7.7$, 1.5 Hz, H-*p*), 7.42 (2H, dt, $J = 7.7$, 1.5 Hz, H-*m*), 7.19 (1H, dd, $J = 7.0$, 1.3 Hz, H-6), 7.11 (1H, dt, $J = 7.5$, 1.5 Hz, J= H-4), 7.07 (1H, dt, $J = 7.5$, 1.5 Hz, H-5), 7.05 (1H, d, $J = 7.7$, 1.3 Hz, H-3), 4.26 (2H, s, CH_2) ppm. ^{13}C NMR (68 MHz, $CDCl_3$) δ: 149.3 (C-1), 138.0 (C-2), 133.9 (C-*o*), 130.7 (C-*p*), 128.4 (C-*m*), 121.8 (C-4), 120.6 (C-5), 112.6 (C-6) 108.7 (C-3), 42.8 (CH_2) ppm. ^{11}B NMR (86 MHz, $CDCl_3$) δ: 32.5 ppm ($h_{1/2} = 283$ Hz). Elemental *Anal.* Calc.: C, 75.0; H, 5.30; N, 6.70%. Found: C, 74.56; H, 5.54; N, 6.88%.

*2.2.2.2. N,N′-[1,2-ethane-bis[2-phenyl-(8-methylbenzoxazaborolidine)]] (**2b**).* Compound **2b** was prepared from 0.5 g (1.84 mmol) of **1b** and 0.45 g (3.68 mmol) of phenylboronic acid. A pale gray solid was obtained with yield of 48% (0.41 g, 0.92 mmol). M.p. = 200–201 °C. IR (KBr)ν = 3422, 3048, 3018, 2850, 1616, 1494, 1468, 1348, 1324, 1302, 1274, 1232, 1194, 1114, 1064, 1022, 800, 742, 692, 648, cm^{-1}. MS (EI, 15 eV, DIP) *m/z* (%): 444 (100), 366 (11), 352 (45), 280 (39), 222 (95), 91 (51). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.64 (2H, dd, $J = 7.9$, 1.2 Hz, H-*o*), 7.44 (1H, dt, $J = 7.9$, 1.2 Hz, H-*p*), 7.32 (2H, dt, $J = 7.9$, 1.2 Hz, H-*m*), 7.11 (1H, d, $J = 8.0$ Hz, H-6), 6.84 (1H, d, $J = 8.0$ Hz H-5), 6.75 (1H, s, H-3), 4.20 (2H, s, CH_2), 2.39 (3H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.4 (C-1), 138.2 (C-2), 133.7 (C-*o*), 131.6 (C-4), 130.5 (C-*p*), 128.2 (C-*m*), 121.1 (C-5), 112.1 (C-6), 109.7 (C-3), 42.7 (CH_2), 21.8 (CH_3) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 34.4 ppm ($h_{1/2} = 584$ Hz). Elemental *Anal.* Calc.: C, 75.70; H, 5.85; N, 6.31%. Found: C, 75.36; H, 5.94; N, 6.47%.

*2.2.2.3. N,N′-[1,2-ethane-bis[2-phenyl-(7-methylbenzoxazaborolidine)]] (**2c**).* Compound **2c** was prepared from 0.50 g (1.84 mmol) of **1c** and 0.45 g (3.68 mmol) of phenylboronic acid. A white solid was obtained with yield of 65% (0.55 g, 1.23 mmol). M.p. = 195–197 °C. IR (KBr)ν = 3220, 3086, 2920, 2370, 2346, 1654, 1496, 1490, 1458, 1420, 1410, 1340, 1302, 1276, 1170, 1118, 790 cm^{-1}. MS (EI, 15 eV, DIP) *m/z* (%): 444 (72), 368 (13), 306 (26), 264 (6), 223 (18), 222 (100), 171 (37), 130 (41), 78 (19). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.60 (2H,

dd, $J = 7.2$, 1.5 Hz, H-*o*), 7.41 (1H, dt, $J = 7.2$, 1.5 Hz, H-*p*), 7.27 (2H, dt, $J = 7.2$, 1.5 Hz, H-*m*), 7.03 (1H, s, H-6), 6.92 (1H, d, $J = 7.9$, 1.5 Hz, H-4), 6.85 (1H, d, $J = 7.9$, H-3), 4.21 (2H, s, CH_2), 2.43 (3H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.8 (C-1), 136.0 (C-2), 133.8 (C-*o*), 130.7 (C-5), 130.5 (C-*p*), 128.3 (C-*m*), 122.6 (C-4), 113.7 (C-6), 108.6 (C-3), 42.9 (CH_2), 21.7 (CH_3) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 33.7 ppm ($h_{1/2} = 546$ Hz). Elemental *Anal*. Calc.: C, 75.72; H, 5.90; N, 6.31%. Found: C, 75.46; N, 5.94; N, 6.57%.

*2.2.2.4. N,N′-[1,2-ethane-bis[2-phenyl-(8-tertbutylbenzoxazaborolidine)]] (**2d**)*. Compound **2d** was prepared from 0.50 g (1.53 mmol) of **1d** and 0.37 g (1.85 mmol) of phenylboronic acid. A white solid was obtained with yield of 55% (0.46g, 0.87 mmol). M.p. = 138–140 °C. IR (KBr)ν = 3082, 2956, 2904, 2864, 1612, 1600, 1490, 1420, 1406, 1342, 1306, 1290, 1236, 1068, 1054, 1024, 756, 696, 692 cm^{-1}. MS (EI, 15 eV, DIP) m/z (%): 528 (29), 368 (56), 312 (38), 264 (100), 208 (66), 152 (43), 96 (44), 44 (25). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.58 (2H, dd, $J = 7.2$, 1.3 Hz, H-*o*), 7.41 (1H, dt, $J = 7.2$, 1.3 Hz, H-*p*), 7.28 (2H, dt, $J = 7.2$, 1.3 Hz, H-*m*), 7.12 (1H, d, $J = 8.4$ Hz, H-6), 7.07 (1H, dd, $J = 8.4$, 1.3 Hz, H-5), 6.97 (1H, s, H-3), 4.34 (2H, s, CH_2), 2.43 (9H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 147.4(C-1), 145.7 (C-4), 138.0 (C-2), 133.8 (C-*o*), 130.6 (C-*p*), 128.4 (C-*m*), 117.9 (C-5), 112.1 (C-6), 106.1 (C-3), 43.0 (CH_2), 35.1 ($C(CH_3)_3$), 32.3 (CH_3) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 32.0 ppm ($h_{1/2} = 1014$ Hz). Elemental *Anal*. Calc: C, 77.27; H, 7.19; N, 5.30%. Found: C, 77.16; H, 7.22; N, 5.49%.

*2.2.2.5. N,N′-[1,3-propane-bis-[2-phenyl-(benzoxazaborolidine)]] (**2e**)*. Compound **2e** was prepared from 0.50 g (1.94 mmol) of **1e** and 0.47 g (3.86 mmol) of phenylboronic acid. A pale gray solid was obtained with yield of 45% (0.39 g, 0.91 mmol). M.p. = 93–94 °C. IR (KBr)ν = 3390, 2918, 2888, 1480, 1468, 1420, 1404, 1364, 1324, 1292, 1242, 1022, 736, 692 cm^{-1}. MS (EI, 15 eV, DIP) m/z (%): 430 (100), 401 (33), 353 (16), 325 (14), 234 (23), 208 (56), 195 (22), 158 (21), 105 (31). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.82 (2H, dd, $J = 6.8$, 1.3 Hz, H-*o*), 7.48 (1H, dt, $J = 6.8$, 1.3 Hz, H-*p*), 7.41 (2H, dt, $J = 6.8$, 1.3 Hz, H-*m*), 7.36 (1H, dd, $J = 7.4$, 1.3 Hz, H-6), 7.14 (1H, dt, $J = 7.4$, 1.3 Hz, H-4), 7.10 (1H, dt, $J = 7.4$, 1.3 Hz, H-5), 7.02 (1H, dd, $J = 7.4$, 1.3 Hz, H-3), 4.05 (2H, t, $J = 7.4$ Hz, NCH_2), 2.42 (2H, qn, $J = 7.4$, NCH_2CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.7 (C-1), 138.5 (C-2), 134.2 (C-*o*), 130.9 (C-*p*), 128.6 (C-*m*), 122.3 (C-4), 120.8 (C-5), 112.8 (C-6), 109.6 (C-3), 41.0 (NCH_2), 30.8 (NCH_2CH_2) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 34.1 ppm ($h_{1/2} = 248$ Hz). Elemental *Anal*. Calc: C, 75.35; H, 5.58; N, 6.51%. Found: C, 75.05; H, 5.60; N, 6.62%.

*2.2.2.6. N,N′-[1,3-propane-bis[2-phenyl-(8-methylbenzoxazaborolidine)]] (**2f**)*. Compound **2f** was prepared from 0.50 g (1.75 mmol) of **1f** and 0.43 g (3.50 mmol) of phenylboronic acid. A pale gray solid was obtained with yield of 72% (0.60 g, 1.31 mmol). M.p. = 136–137 °C. IR (KBr)ν = 3048, 2918, 1602, 1494, 1476, 1448, 1410, 1380, 1352, 1 1296, 1244, 1192, 1022, 802, 692 cm^{-1}. MS (EI, 15 eV, DIP) m/z (%): 458 (100), 366 (10), 352 (44), 280 (29), 222 (95), 91 (51). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.83 (2H, dd, $J = 7.9$, 1.5 Hz, H-*o*), 7.48 (1H, dt, $J = 7.9$, 1.5 Hz, H-*p*), 7.41 (2H, dt, $J = 7.9$, 1.5 Hz, H-*m*), 7.22 (1H, d, $J = 8.0$ Hz, H-6), 6.87 (1H, dd, $J = 8.0$, 1.2 Hz, H-5), 6.78 (1H, s, H-3), 4.02 (2H, t, $J = 8.0$ Hz, NCH_2), 2.41 (2H, qn, $J = 8.0$ Hz, NCH_2CH_2), 2.38 (3H, s, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 147.8 (C-1), 138.5 (C-2), 134.2 (C-*o*), 131.9 (C-4), 130.9 (C-*p*), 128.7 (C-*m*), 121.2 (C-5), 112.3 (C-6), 110.4 (C-3), 40.9 (NCH_2), 30.5 (NCH_2CH_2), 21.9 (CH_3) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 34.2 ($h_{1/2} = 1031$ Hz) ppm. Elemental *Anal*. Calc.: C, 73.11; H, 6.30; N, 5.88%. Found: C, 73.70; H, 6.15; N, 6.32%.

*2.2.2.7. N,N′-[1,3-propane-bis[2-phenyl-(7-methylbenzoxazaborolidine)]] (**2g**)*. Compound **2g** was prepared from 0.50 g (1.75 mmol) of **1g** and 0.43 g (3.50 mmol) of phenylboronic acid. A white solid was obtained with yield of 72% (0.60 g, 1.31 mmol). M.p. = 134–136 °C. IR (KBr)ν = 3422, 2850, 1654, 1648, 1636, 1540, 1508, 1448, 1400, 1356, 1276, 1256, 1132, 1118, 1092, 936, 792 cm^{-1}. MS (EI, 15 eV, DIP) m/z (%): 458 (100), 381 (63), 368 (73), 294 (26), 248 (11), 222 (93), 185 (11), 129 (25), 73 (16), 60 (12). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.79 (2H, dd, $J = 7.7$, 1.4 Hz, H-*o*), 7.47 (1H, dt, $J = 7.7$, 1.4 Hz, H-*p*), 7.39 (2H, dt, $J = 7.7$, 1.4 Hz, H-*m*), 7.20 (1H, s, H-6), 6.92 (1H, d, $J = 7.2$ Hz, H-4), 6.84 (1H, d, $J = 7.2$ Hz, H-3), 4.00 (2H, t, $J = 7.4$ Hz, NCH_2), 2.43 (3H, s, CH_3), 2.37 (2H, qn, $J = 7.4$ Hz, NCH_2CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.7(C-1), 136.0 (C-2), 134.0 (C-*o*), 130.6 (C-*p*), 130.4(C-5), 128.4 (C-*m*), 122.5 (C-4), 113.4 (C-6), 108.9(C-3), 40.8 (NCH_2), 30.7 (NCH_2CH_2), 21.7 (CH_3) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: 34.11 ppm ($h_{1/2} = 608$ Hz). Elemental *Anal*. Calc.: C, 73.11; H, 6.30; N, 5.88%. Found: C, 73.14; H, 6.10; N, 6.09%.

*2.2.2.8. 2-[(1-((3-(5-Hydroxy)aza)pentyl)imine)ethyl] phenol (**3a**)*. Compound **3a** was prepared from 0.50 g (3.67 mmol) of 2-hydroxyacetophenone and 0.38 g (3.67 mmol) of 2-(2-aminoethyl) aminoethanol in 20 ml of ethanol. After 30 min under reflux, the solvent was removed under high vacuum. A yellow solid was obtained and washed with hexane with yield of 98% (0.80 g, 3.60 mmol). M.p. = 102–104 °C, IR (KBr)ν = 3510 (OH), 3248, 2924, 2860, 1614 (C=N), 1500, 1448, 1058, 772, 742 cm^{-1}. MS (EI, 15 eV, DIP) m/z (%): 222 (M^+, 100), 204 (48), 177 (56), 134 (43), 120 (17), 77 (32). ^{1}H NMR

(400 MHz, $CDCl_3$) δ: 7.49 (1H, dd, $J = 7.5$, 1.0 Hz, H-3), 7.27 (1H, ddd, $J = 8.4$, 7.5, 1.0 Hz, H-5), 6.91 (1H, d, $J = 8.4$ Hz, H-6), 6.74 (1H, td, $J = 7.5$, 1.0 Hz, H-4), 3.65–3.70 (4H, m, H-8, H-11), 3.03 (2H, t, $J = 5.1$ Hz, H-10), 2.84 (2H, t, $J = 5.1$ Hz, H-9), 2.36 (3H, s, H–Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.6 (C-7), 164.7 (C-1), 132.8 (C-5), 128.0 (C-3), 119.2 (C-6), 118.9 (C-2), 116.9 (C-4), 60.9 (C-11), 51.1 (C-9), 49.1 (C-8, C-10), 14.6 (Me) ppm.

*2.2.2.9. 2-[(1-((3-(5-Hydroxy)oxa)pentyl)imine)ethyl] phenol (**3b**).* Compound **3b** was prepared using the procedure described for **3a**, from 0.50 g (3.67 mmol) of 2-hydroxyacetophenone and 0.38 g (3.67 mmol) of 2-(2-aminoethoxy) ethanol. The solution was allowed to stand overnight to give a yellow solid with yield of 93% (0.76 g, 3.40 mmol). M.p. = 45–46 °C. MS (EI, 15 eV, DIP) m/z (%): 223 (M^+, 100), 205 (58), 178 (45), 134 (38), 120 (26), 77 (31). IR (KBr)ν = 3382 (OH), 2870, 1620 (C=N), 1614, 1580, 1454, 1128, 756, 486 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.48 (1H, dd, $J = 8.0$, 1.3 Hz, H-3), 7.27 (1H, ddd, $J = 8.4$, 7.1, 1.3 Hz, H-5), 6.90 (1H, dd, $J = 8.4$, 1.2 Hz, H-6), 6.72 (1H, ddd, $J = 8.0$, 7.1, 1.3 Hz, H-4), 3.81 (2H, t, $J = 4.7$ Hz, H-11), 3.76 (2H, t, $J = 4.7$ Hz, H-10), 3.73 (2H, t, $J = 4.8$ Hz, H-8), 3.64 (2H, t, $J = 4.8$ Hz, H-9), 2.34 (3H, s, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.0 (C-7), 165.9 (C-1), 133.4 (C-5), 128.5 (C-3), 119.9 (C-6), 119.0 (C-2), 116.9 (C-4), 73.2 (C-9), 70.3 (C-11), 62.1 (C-10), 48.7 (C-8), 14.9 (Me) ppm.

*2.2.3. Synthesis of compounds **4a**, **4b**, **5a** and **5b***

Compounds **4a** and **4b** were synthesized from equimolar quantities of **3a** and **3b** with phenylboronic acid in 30 ml of THF. The mixture was refluxed for 30 min, then the water formed during the reaction and part of the solvent were removed using a Dean-Stark trap and, finally the product was dried under high vacuum. Compounds **5a** and **5b** were prepared by the same method refluxing for 6 h instead of 30 min.

*2.2.3.1. Bis[μ-[2-[[[3-(5-hydroxy-$_k$O)aza] pentyl] imine-$_k$N] ethylphenolate (2-)-$_k$O]] diboron (**4a**).* Compound **4a** was prepared from 0.20 g (0.89 mmol) of **3a** and 0.10 g (0.89 mmol) of phenylboronic acid. A yellow solid was obtained with yield of 75% (0.21 g, 0.34 mmol). M.p.$_{(decomp)}$ = 120–123 °C. IR (KBr)ν = 3046, 3006, 1616 (C=N), 1456, 1276, 750, 706 cm^{-1}. MS (EI, 15 eV, DIP) m/z (%): 539 (M^+–C_6H_5, 34), 435 (50), 407 (35), 313 (24), 308 (81), 256 (15), 257 (17), 231 (100), 213 (11), 172 (21), 160 (42), 77 (35). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 7.52 (1H, dd, $J = 7.7$, 1.5 Hz, H-3), 7.43 (1H, dt, $J = 7.7$, 1.5 Hz, H-5), 7.36–7.42 (2H, m, H-*o*), 7.16–7.22 (2H, m, H-*m, H-p*), 7.01 (1H, d, $J = 7.7$ Hz, H-6), 6.83 (1H, t, $J = 7.7$ Hz, H-4), 4.11 (1H, ddd, $J = 14.3$, 7.6, 4.0 Hz, H-8a), 3.95 (1H, ddd, $J = 12.5$, 7.3, 2.9 Hz, H-11a), 3.76 (1H, ddd, $J = 14.3$, 10.8, 4.3 Hz, H-11b), 3.66 (1H, dt, $J = 14.3$, 6.0, 3.1 Hz, H-8b), 3.27 (1H, dt, $J = 12.5$, 7.3, 2.9 Hz, H-10a), 3.05 (1H, ddd, $J = 14.3$, 10.8, 4.3 Hz, H-10b), 2.98 (1H, ddd, $J = 14.3$, 7.6, 4.0 Hz, H-9a), 2.82 (1H, ddd, $J = 14.3$, 6.0, 3.2 Hz, H-9b), 2.54 (3H, s, H-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.6 (C-7), 160.5 (C-1), 130.9 (C-5), 128.2 (C-3), 127.5 (C-*o*), 127.3 (C-*m*), 126.9 (C-*p*), 120.5 (C-6),118.9 (C-2), 118.4 (C-4), 67.9 (C-11), 62.8 (C-9), 51.0 (C-8), 49.6 (C-10), 16.5 (C–Me) ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: +7.9 ppm ($h_{1/2}$ = 1032 Hz).

*2.2.3.2. Bis[μ-[2-[[[3-(5-hydroxy-$_k$O)oxa] pentyl] imine-$_k$N] ethylphenolate(2-)-$_k$O]] diboron (**4b**).* Compound **4b** was prepared from 0.20 g (0.89 mmol) of **3b** and 0.11 g (0.89 mmol) of phenylboronic acid. A yellow solid was obtained with yield of 89% (0.24 g, 0.38 mmol). M.p.$_{(decomp)}$ = 110–115 °C. MS (EI, 15 eV, DIP) m/z (%): 541 (M^+–C_6H_5, 34), 309 (78), 232(100), 77 (27). IR (KBr)ν = 3004, 2918, 1622 (C=N), 1558, 1456, 1380, 1350, 1278, 1188, 1140, 750, 704 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (3H, d, $J = 7.7$ Hz, H-3, H-*o*), 7.44 (1H, t, $J = 7.7$ Hz, H-5), 7.20–7.26 (3H, m, H-*m*, -*p*), 7.04 (1H, d, $J = 7.7$ Hz, H-6), 6.84 (1H, t, $J = 7.7$ Hz, H-4), 4.29 (1H, ddd, $J = 14.4$, 8.7, 4.6 Hz, H-8a), 4.09 (1H, ddd, $J = 14.3$, 9.7, 4.8 Hz, H-10a), 4.00 (1H, ddd, $J = 14.3$, 9.7, 4.8 Hz, H-11a), 3.76–3.88 (3H, m, H-9b, H-10b, H-11b), 3.63 (1H, ddd, $J = 14.4$, 8.7, 4.6 Hz, H-9a), 3.57 (1H, ddd, $J = 14.4$, 9.7, 4.6 Hz, H-8b), 2.47 (3H, s, H-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.3 (C-7), 160.6 (C-1), 136.6 (C-5), 131.2 (C-*o*), 128.4 (C-3), 127.5 (C-*m*), 126.9 (C-*p*), 120.3 (C-6), 118.4 (C-4), 117.7 (C-2), 74.0 (C-9), 68.5(C-11), 62.8 (C-10), 48.1 (C-8), 16.6 (Me) ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ: +7.7 ppm ($h_{1/2}$ = 254 Hz).

*2.2.3.3. 2-Phenylbenzo[k]-9-aza-1,3,6-trioxa-2-boracyclodoceca-9-ene (**5a**).* Compound **5a** was prepared from 0.50 g (2.22 mmol) of **3b** and 0.27 g (2.22 mmol) of phenylboronic acid. A yellow solid was obtained with yield of 61% (0.42 g, 1.36 mmol). M.p.$_{(decomp)}$ = 250–252 °C, IR (KBr)ν = 3408, 3172, 2918, 1622 (C=N), 1526, 1136, 1128, 1066, 800, 568 cm^{-1}. MS (EI, 15 eV, DIP) m/z (%): 232 ([M–C_6H_5]$^+$, 20), 188 (6), 129 (8), 114 (15), 110 (10), 97 (15), 73(12), 44 (22), 30 (100). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54 (1H, d, $J = 8.1$, 1.2 Hz, H-3), 7.45 (1H, td, $J = 8.1$, 1.2 Hz, H-5), 7.40 (2H, dd, $J = 7.3$, 1.7 Hz, H-*o*), 7.20 (3H, m, H-*m*, -*p*), 7.01 (1H, dd, $J = 8.1$, 1.2 Hz, H-6), 6.84 (1H, td, $J = 8.1$, 1.2 Hz, H-4), 4.31 (1H, ddd, $J = 9.9$, 5.8, 4.0 Hz, H-8a), 4.07 (1H, ddd, $J = 10.2$, 5.8, 2.8 Hz, H-10a), 4.05 (1H, ddd, $J = 9.9$, 5.8, 4.0 Hz, H-9a), 3.90 (1H, ddd, $J = 13.2$, 9.9, 4.0 Hz, H-9b), 3.87(1H, ddd, $J = 15.1$, 10.2, 2.8 Hz, H-11a), 3.78(1H, ddd, $J = 15.1$, 10.2, 5.8 Hz, H-10b), 3.66 (1H, ddd, $J = 10.2$, 5.8, 2.8 Hz, H-11b), 3.62 (1H, ddd, $J = 13.2$, 9.9, 5.8 Hz, H-8b), 2.58 (3H, s, H–Me) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.6 (C-7), 160.9 (C-1), 137.0 (C-5), 131.4 (C-*o*), 128.7 (C-6), 127.7 (C-*m*), 127.3 (C-*p*), 120.7 (C-6), 118.7 (C-4), 118.0 (C-2), 74.4 (C-9), 68.8(C-11), 63.1 (C-10), 48.1 (C-8), 17.0 (Me) ppm. ^{11}B NMR (96 MHz, DMSO-d_6) δ: +7.5 ppm ($h_{1/2} = 192$ Hz). Elemental *Anal*. Calc.: C, 69.90; H, 6.47; N, 4.53%. Found: C, 69.66; H, 6.54; N, 4.38%.

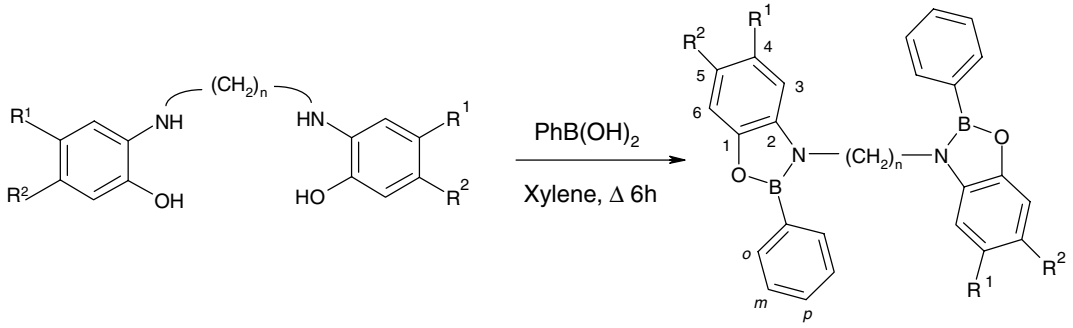
*2.2.3.4. 2-(4-Acetyl)phenyl-10-methylbenzo[k]-9-aza-1,3,6-trioxa-2-boracyclododeca-9-ene (**5b**)*. Compound **5b** was prepared from 0.50 g (2.22 mmol) of **3b** and 0.36 g (2.22 mmol) of 4-acetylphenylboronic acid. A pale yellow solid was obtained with yield of 71% (0.56 g, 1.59 mmol). M.p. = 211–213 °C. IR (KBr)ν = 3568, 2944, 2860, 1674 (C=O), 1624 (C=N), 1560, 1290, 1268, 1178, 1152, 1134, 1114, 1004, 952, 804, 762. MS (EI, 15 eV, DIP) *m*/*z* (%): 351 (M^+, 6), 308 (10), 232 ([M–$C_6H_4COCH_3$]$^+$, 100), 202 (25), 188 (70), 175 (15), 146 (11). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.78 (2H, d, $J = 8.1$ Hz, H-*m*), 7.52 (3H, d, $J = 8.1$ Hz, H-3, H-*o*), 7.44 (1H, td, $J = 8.1$, 1.5 Hz, H-5), 7.00 (1H, dd, $J = 8.1$, 1.5 Hz, H-6), 6.84 (1H, td, $J = 8.1$, 1.5 Hz, H-4), 4.24 (1H, ddd, $J = 13.1$, 10.1, 5.3 Hz, H-8a), 4.00–4.10 (2H, m, H-10a, 11a), 3.80 (1H, ddd, $J = 13.1$, 10.1, 2.8 Hz, H-9a), 3.67 (1H, ddd, $J = 13.1$, 5.3, 2.8 Hz, H-8b), 3.62 (1H, dd, $J = 13.1$, 5.3 Hz, H-9b), 3.20– 3.35 (2H, m, H-10b, 11b), 2.59 (3H, s, Me–C=N), 2.52 (3H, s, Me–C=O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 198.0 (CO), 171.8 (C-7), 160.4 (C-1), 137.0 (C-5), 135.9 (C-*p*), 131.4 (C-*m*), 128.5 (C-3), 127.4 (C-*o*), 120.4 (C-6), 118.8 (C-4), 117.7 (C-2), 74.1 (C-9), 68.5 (C-11), 62.9 (C-10), 48.1 (C-8), 26.7 (Me–CO), 17.0 (Me–C=N) ppm. ^{11}B NMR (96 MHz, $CDCl_3$) δ: +7.2 ppm ($h_{1/2} = 192$ Hz). Elemental *Anal*. Calc.: C, 68.38; H, 6.27; N, 3.99%. Found: C, 68.66; H, 6.12; N, 4.08%.

3. Results and discussion

Ligands **1a**–**1d** were prepared by reaction of *o*-aminophenol with glyoxal derivatives using the methodology described in the literature [11]. Compounds **1e**–**1g** were synthesized from one equivalent of 1,3-dibromopropane and two equivalents of the corresponding *ortho*-aminophenol as described in detail in the experimental part. The reactions of ligands **1a**–**1g** with two equivalents of phenylboronic acid were carried out under reflux in xylene. After 6 h, the reaction mixture was cooled down to room temperature and the solvent was removed under high vacuum. The product was washed with several portions of a hexane:chloroform (9:1) mixture, to give the oxazaborolidines **2a**–**2g** as gray or white solids, which were fully characterized by spectroscopic methods (Scheme 1).

The formation of this type of compounds requires the use of a solvent with a high boiling point (e.g. xylene), in order to replace the amine hydrogen atom during the reaction of the ligand with phenylboronic acid, and to form a covalent boron–nitrogen bond after water elimination [28,29].

The structures of oxazaborolidines **2a**–**2g** were first established by mass spectrometry, which in all seven cases showed the molecular ion as the base peak. The NMR spectra showed the symmetric nature of these compounds, since only one set of signals was observed, due to the presence of a C_2 fold axis. The ^{11}B NMR spectra of compounds **2a**–**2g** showed a single broad



1a-1g		R^1	R^2	n	2a-2g
	a:	H	H	2	
	b:	Me	H	2	
	c:	H	Me	2	
	d:	*t*-Bu	H	2	
	e:	H	H	3	
	f:	Me	H	3	
	g:	H	Me	3	

Scheme 1. Synthesis of the bisoxazaborolidines **2a**–**2g**.

signal in the range from 32.0 to 34.4 ppm, characteristic for tricoordinated species having two donor atoms coupled to an aromatic system [30].

The ^{1}H NMR spectra of compounds **2a**–**2d** show a singlet in the range between 4.20 and 4.34 ppm. Methylene groups attached to the nitrogen atom (NCH_2) in compounds **2e**–**2g** were observed as triplets between 4.00 and 4.05 ppm, while the adjacent NCH_2CH_2 groups appear as a quintuplet at 2.37–2.42 ppm (H-11). The aromatic protons appear in the range of 6.75–7.36 ppm in all compounds. In general, the signals are shifted to higher field in comparison to those of the free ligands due to the presence of a boron atom.

The ^{13}C NMR data also support this trend and 2D NMR experiments were carried out to obtain the complete assignment of the compounds. The signals for the boron derivatives are shifted to higher field with respect to the starting materials.

The structure of **2e** was established by X-ray crystallography. From the structure shown in Fig. 1, it can be noticed that the symmetry of the molecule observed in solution is not present in the solid state. The phenyl groups attached to the boron atoms are in a *trans* disposition with respect to each other to give a *pseudo*-C_2-symmetry. The average values for the O(1)–B(1)–C(16)–C(17) and N(1)–B(1)–C(16)–C(21) torsion angles are 30.15° and 34.20°, respectively, indicating that the phenyl groups are not coplanar to the five-membered heterocycle, most probably because of a steric effect between the hydrogen atoms of the phenyl group and those of the CH_2 group from the backbone. The five-membered ring is almost planar. The maximum deviation from the mean plane is 0.051 Å for boron atom. This is in accordance with a delocalization of the π electron density within the heterocycle. The B–N distances are 1.397(6) and 1.415(6) Å, and the B–O distances are 1.400(5) and 1.394(6) Å. Both are shorter than the corresponding distances in aliphatic derivatives [28,31], due to B–N and B–O π interactions. Based on the trigonal environment of the boron atom, one would expect angles close to 120°, however, due to the high annular tension in the five-membered heterocycle, the O(1)–B(1)–N(1) and O(2)–B(2)–N(2) angles are smaller, 108.3(4)° and 109.2(4)°, respectively, while the N(1)–B(1)–C(16) and N(2)–B(2)–C(22) angles are larger, 131.2° and 132.5°, respectively.

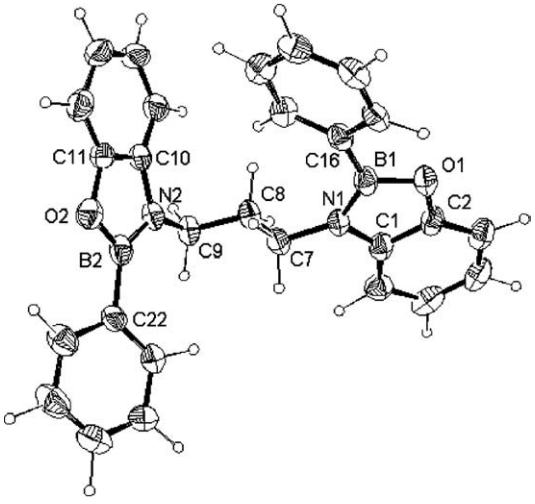
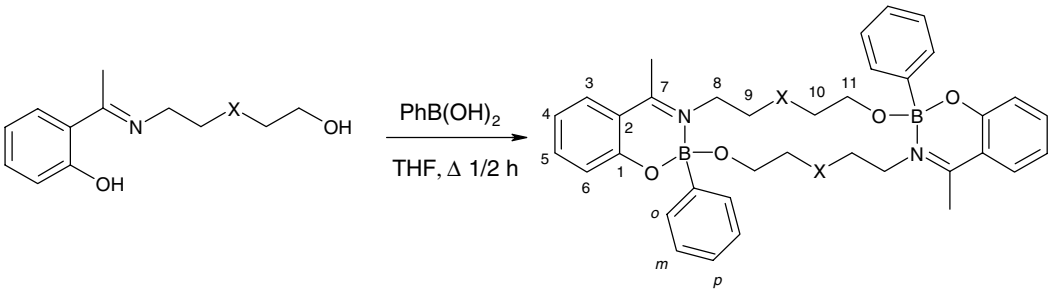


Fig. 1. Crystal structure view of **2e**. Selected bond lengths (Å) and angles (°): B(1)–N(1) 1.415(6), B(1)–O(1) 1.400(5), B(1)–C(16) 1.530(7), O(1)–C(2) 1.374(5), N(1)–C(1) 1.410(5), N(1)–C(7) 1.465(5), O(1)–B(1)–C(16) 120.5(4), O(1)–B(1)–N(1) 108.3(4), N(1)–B(1)–C(16) 131.2(4).

The tetradentate ligands **3a** and **3b** were also prepared for comparison and their reaction with phenylboronic acid was carried out, since it was anticipated that, in this case, the iminic group would lead to a different structure. The reaction mixture was refluxed for 30 min under THF (Scheme 2). Then, the solvent was removed under high vacuum to give a yellow solid, which corresponded to the dimeric compounds **4a**–**4b**, as confirmed by mass spectrometry. In both cases a peak corresponding to the loss of a phenyl group from the molecular ion was observed, in analogy to dimeric compounds previously described [32]. The compounds are hygroscopic and decompose at room temperature to give a highly viscous liquid (polymeric compound). Nevertheless, it can be stored at −20° without apparent decomposition.

The ^{1}H NMR spectra allowed to establish the symmetry (C_i) of the molecule, since only one set of signals was observed, in agreement with similar dimeric structures [20,32]. The methylene protons are diastereotopic owing to ring closure and a change in hybridization of the boron atom from sp^2 to sp^3, which leads to a new stereogenic center in the molecule. The ^{13}C NMR spectra also confirm the symmetric nature of the molecules showing signals for half of the molecule. Two dimensional NMR techniques allowed full characterization of the complexes. The carbon signals for the C=N groups are shifted to higher field with respect to the ligands. The ^{11}B NMR spectra confirm the tetrahedral geometry of the boron atoms, giving signals at 7.9 and 7.7 ppm for **4a** and **4b,** respectively. The large cavity (16 membered central ring) of the dimeric compounds makes them interesting candidates for application in host-guest chemistry, unfortunately we were unable to grow crystals suitable for X-ray analysis, so the dimensions of this cavity are unknown.

When the reaction time between ligand **3b** and phenylboronic acid was enhanced from 30 min to 6 h, the monomeric structure **5a** was isolated in good yields rather than compound **4b** (Scheme 3). This compound was fully characterized by spectroscopic methods and it is stable at room temperature. Also, the monomeric compound **5b** was obtained from 4-acetylboronic acid and the ligand **3b** (Scheme 3), using the same reaction conditions as in the case of **4b** formation, the product is a yellow solid stable at room temperature. In the last case, the dimeric compound was not observed which seems to



Scheme 2. Synthesis of the dimeric boron complexes **4a** and **4b**.

be the kinetic product, while the monomeric specie is the thermodynamic favorable specie. A similar observation was made previously for a related boronate derivative [33]. The reaction of ligand **3a** under the same conditions failed to provide a monomeric structure, even when different reaction conditions were used.

The base peak in the mass spectrum of **5a** corresponds to the $[M^+–C_6H_5]$ ion and confirms the monomeric structure for this compound. For compound **5b**, the molecular ion was observed at $m/z = 351$ and the base peak was detected also at $m/z = 232$, indicating again the loss of one of the aryl groups attached to the boron atoms. The NMR data for **5a** and **5b** are quite similar to **4b**, proton signals were unambiguously assigned by using 2D ^{1}H NMR techniques. In the ^{1}H NMR spectrum, the signals for the CH_2 groups are diastereotopic due to the formation of the eight-membered ring. The ^{11}B NMR shifts ($\delta = 7.5$ and 7.2 ppm) are quite similar to those observed in analogous dimeric compounds [32,33].

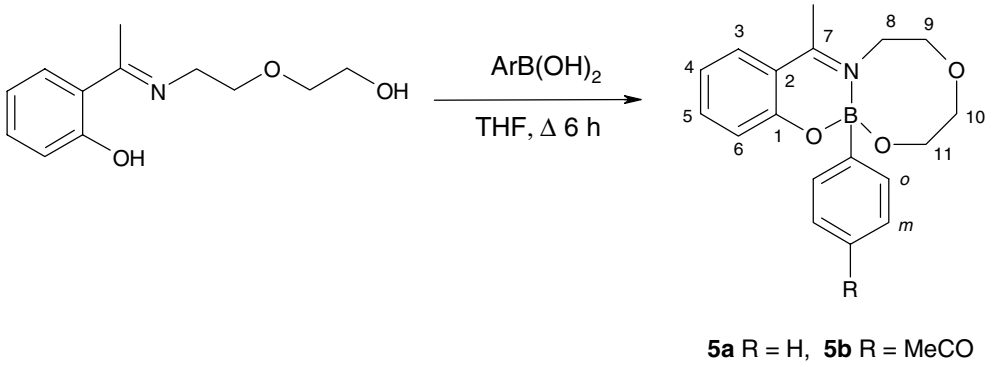
The IR spectra of compounds **4b** and **5a** show a strong band at 1622 cm^{-1}, attributable to the stretching band for the C=N group. This band is shifted to higher wavenumbers by 2 cm^{-1} compared to the same band in the ligand **3b** (1620 cm^{-1}) due to the coordination of the nitrogen atom to boron. In compound **5b**, this band was shifted to higher wavenumbers (1624 cm^{-1}) due to the presence of an electron withdrawing group (COMe) in *para* position. In analogy, the band observed for the C=N group in **4a** (1616 cm^{-1}) is also shifted to higher wavenumbers compared with the ligand **3a** (1614 cm^{-1}).

An X-ray crystallographic analysis confirmed the molecular structure of **5b** (Fig. 2). Crystallographic data are listed in Table 1. The structure has one six-membered and one eight-membered heterocyclic ring. Both heterocycles are linked by a dative N–B bond. The boron atom is deviated from the mean plane of the six-membered ring by 0.54 Å, therefore the ring is not planar, and an *envelope* conformation was observed. In the eight-membered ring, a *twist boat* conformation was observed. A distorted tetrahedral geometry of the boron atoms is evident from the bond angles around the boron atom, which are in the range from 105.76(14)° to 111.99(15)°.

The B–N distance is 1.633(2) Å and is quite similar to analogous systems [18–20,32,33]. The C–B distance (1.625(3) Å) is slightly longer compared to related compounds that have an aryl moiety attached to the boron atom. This is attributed to the presence of an electron withdrawing group (COMe) [20]. The two B–O bonds are different, the one in the six-membered ring has a distance of 1.475(2) Å, while the one in the eight-membered ring is 1.431(2) Å.

3.1. Conclusions

The reactivity of different tetradentate ligands with arylboronic acids has been described. It has been noticed



Scheme 3. Synthesis of the monomeric boron complexes **5a** and **5b**.

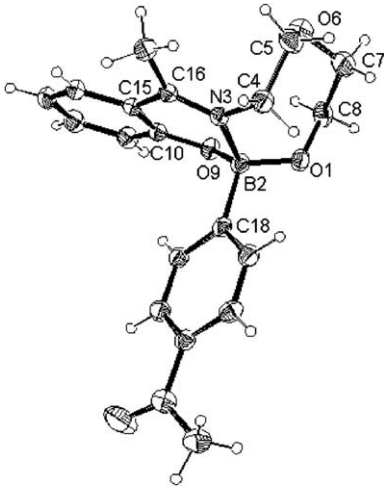


Fig. 2. Crystal structure view of **5b**. Selected bond lengths (Å) and angles (°): B(2)–O(9) 1.475(2), B(2)–O(1) 1.431(2), B(2)–N(3) 1.633(2), B(2)–C(18) 1.625(3), O(9)–C(10) 1.341(2), O(1)–C(8) 1.425(2), N(3)–C(16) 1.295(2), N(3)–C(4) 1.470(2), O(9)–B(2)–O(1) 111.13(16), O(9)–B(2)–N(3) 105.76(14), O(1)–B(2)–N(3) 109.76(15), O(1)–B(2)–C(18) 110.61(15), O(9)–B(2)–C(18) 111.99(15), N(3)–B(2)–C(18) 107.18(14), C(10)–O(9)–B(2) 120.24(14), B(2)–O(1)–C(8) 120.19(15).

that bisoxazaborolidine complexes are favored when a NH group is present in the ligand, because it can be deprotonated to form an N–B covalent bond. Nevertheless, when the ligand is a Schiff base, only an N–B coordinative bond is formed to give tetrahedral boron complexes, where the presence of a large backbone can lead to both monomeric and dimeric compounds. Monomeric compounds are relatively more stable than the dimerics, so, monomeric species are the thermodynamic products and dimeric species the kinetic ones. The presence of two Lewis acid sites in oxazaborolidines makes them interesting subjects for dinuclear catalysis.

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