An Alternative Method for the Preparation of Diphenylboron Chelates. The Crystal and Molecular Structures of (Pyridine-2acetyloximato)diphenylboron and (1-Phenylazo-2-naphtholato)diphenylboron

Karl E. Bessler^{a,*}, Elisabeth B. Dourado^a, Myller de S. Carvalho^a, Sebastião S. Lemos^a, and Javier Ellena^{*,b}

^a Brasília – DF / Brazil, Instituto de Química, Universidade de Brasília

^b São Carlos - SP / Brazil, Instituto de Física de São Carlos, Universidade de São Paulo

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Abstract. A convenient method for the preparation of diphenylboron chelates from ammonium tetraphenylborate is described. A variety of five- or six-membered O,O-, N,O- and N,N-chelates were obtained in yields from 60 to 90 %. The isolated compounds were characterized by elemental analysis, IR spectroscopy and multinuclear magnetic resonance spectroscopy (¹H, ¹³C, and ¹¹B). The cry-

Introduction

A large variety of tetrahedral boron chelates of the general composition X_2BL , for X = H, F, Cl, alkyl, aryl, alkoxy, aryloxy, acyloxy, etc. and a bidentate chelating anion L, have been described in the past. Among these chelates the diaryl species Ar₂BL show outstanding thermal and hydrolytic stability [1]. Diphenylborinates Ph₂BL are usually prepared from the commercially available 2-aminoethanol complex of diphenylborinic acid [2-6]. The *n*-butylester of diphenylborinic acid has been employed for the preparation of several aminoacid complexes [7]. Triphenylborane has also been used as starting material [1]. Eventually diphenylboron chelates were obtained from trimethylborate and phenylmagnesium bromide [8]. Diphenylboron complexes with aminoacids have been obtained from the commercially available sodium tetraphenylborate and aminoacid hydrochlorides [9]. We describe here the preparation of diphenylboron complexes starting from the readily available and stable ammonium tetraphenylborate.

Results and Discussion

Ammonium tetraphenylborate reacts with chelating agents LH in refluxing toluene according to equation (1):

$$[NH_4][B(C_6H_5)_4] + LH \to (C_6H_5)_2BL + NH_3 + 2 C_6H_6$$
(1)

This method was applied for the preparation of a variety of five- or six-membered O,O-, N,O- and N,N-chelates, three of them have been described earlier (LH = 2-hydroxypyri-

stal and molecular structures of (pyridine-2-acetyloximato)diphenylboron and (1-phenylazo-2-naphtholato)diphenylboron were determined by X-ray diffraction on single crystals.

Keywords: Boron; Coordination chemistry; NMR spectroscopy; Crystal structures

dine-N-oxide (1) [10], maltol (2) [3] and 1-phenylazo-2naphthol (3) [11]), four of them are presented here for the first time (LH = β -alanine (4), pyridine-2-acetyloxime (5), picolinic acid (6) and L-valine (7)).

At reaction times from 12 to 24h; the corresponding diphenylboron chelates Ph_2BL are obtained in high yields (60 – 93 %). All compounds are characterized by IR and multinuclear magnetic resonance spectroscopy (¹H, ¹³C and ¹¹B). The determination of the crystal and molecular structures by X-ray diffraction on single crystals reveals a six membered O,N chelate for **3** and a five membered N,N chelate for **5**.



^{*} Prof. Dr. Karl E. Bessler Instituto de Química Universidade de Brasília Caixa Postal 04478 70904-970 Brasília DF / Brazil E-mail: bessler@unb.br

NMR spectra

The ¹H- and ¹³C-NMR spectra of the Ph₂B fragment in all studied compounds show constant chemical shifts. In some cases, the quaternary carbon atom (ipso) was only hardly seen since it is a broad signal due to its coupling to both 10 B and 11 B isotopes. While the coordinated β -alaninate exhibits a broad signal for the NH₂ group at 6.78 ppm, the Lvalinate analog shows diastereotopic signals not only for methyl groups but also for NH₂ and Ph₂B moieties in consequence of the asymmetric center on the coordinated L-valinate. Accordingly, a pseudotriplet centered at 6.29 ppm was assigned to one hydrogen atom from NH₂, which is coupling to its geminal hydrogen atom and also to that attached to the asymmetric carbon atom. This could be unequivocally confirmed with the aid of ${}^{1}H{}^{1}H{}$ selective decoupling experiments. The other amino hydrogen signal is overlapped with those of phenyl groups. Moreover, when the spectrum was run in acetonitrile-d₃ instead of dimethylsulfoxide-d₆ a different pattern was observed. The amino hydrogen atoms have appeared as broad signals at higher magnetic fields (5.85 and 4.80 ppm) if compared to the spectrum obtained in dimethylsulfoxide-d₆. Furthermore, the hydrogen atom bound to the asymmetric carbon atom became clearly seen as a well-resolved doublet of triplet centered at 3.61 ppm.

The ¹³C NMR spectra of all studied compounds present the expected resonances. Those containing the 2-substituted pyridine derivatives (5 pyridine-2-acetyloxime and 6 picolinic acid) have the C₆-H (this numbering scheme is not in agreement with the labeling of the crystallographic structure) position easily recognizable and they resonate at higher magnetic fields (approximately 5 ppm) if compared to the respective free precursor ligand molecules. This is a consequence of the proximity of phenyl groups to C₆-H as has been pointed out for other diphenylboron chelates [4]. This interpretation is further supported by the fact that in 2-hydroxipyridine N-oxide there is almost no such change



Fig. 1 An ORTEP view of the molecular structure of **5**. The displacement ellipsoids are drawn at the 50 % probability level. H atoms have been omitted for clarity.

upon coordination to boron atom. Satisfactory NMR data for the maltolato complex 2 could only be obtained in acetonitrile-d₃ since it hydrolyses in water containing DMSO-d₆, even when an ampoule stored solvent was utilized.

The ¹¹B chemical shift (δ) in R₂B(chelate) complexes is sensitive to a number of factors pertaining the resultant heterocyclic ring including i) its size, ii) the nature of the coordinating atoms, iii) substitution on the ring. The observed ¹¹B resonances (δ) lie within the range of other reported diphenylboron chelate compounds [5, 12].

The crystal and molecular structure of (2acetylpyridineoximato)diphenylboron (5)

The molecular structure of **5** is shown in Fig. 1. Selected bond lengths and angles are summarized in Table 1.

Table 1 Selected bond lengths /Å and angles /° for 5.

B-N(2)		1.581(2)		N(1)-C(5)	1.358(2)
B-N(1)	1.589(2)	N(2)-C(6)	1.314(2)		
B-C(11)	1.607(2)	C(5)-C(6)	1.437(2)		
B-C(21)	1.615(2)	C(6)-C(7)	1.489(2)		
O-N(2)	1.295(2)				
N(2)-B-N(1)	95.54(10)	C(11)-B-C(21)	116.08(12)		
N(2)-B-C(11)	111.84(12)	C(1)-N(1)-B	128.61(14)		
N(1)-B-C(11)	110.33(11)	C(6)-N(2)-B	113.55(13)		
N(2)-B-(C(21)	109.46(11)	N(1)-C(5)-C(6)	110.33(13)		
N(1)-B-C(21)	111.75(11)	N(2)-C(6)-C(5)	109.49(13)		

The pyridine-2-acetyloximato ligand offers two chelating possibilities: a six membered N,O- and a five membered N,N-chelate, as shown below.



The crystal structure of 5 contains discrete molecules of the type (b) chelate with a distorted tetrahedral coordination on the boron atom. The same coordination mode was found in several pyrinine-2-acetyloximato transition metal complexes [13-15]. The endocyclic N-B-N angle is quite small (95.54°), whereas the exocyclic C-B-C angle is enlarged (116.08°). It is noteworthy that the two B-N bond lengths B-N(1) with 1.589(2) Å (pyridine nitrogen atom) and B-N(2) with 1.581(2) Å (oxime nitrogen atom) are similar to each other and are situated in the range of the lowest values (below 1.60 Å) found for Bsp^3 - Nsp^2 bonds [16]. The B-N(2) bond length is compatible with the corresponding C-N distance in (salicylaldoximato)diphenylboron [17]. In the diphenylboron chelate 5 the oxime C=N bond C(6)-N(2) with 1.314(2) A is slightly lengthened by 2.8% compared to the free oxime with 1.278 Å. However, the N-O bond is considerably shortened by 7.9 % from 1.406 Å in the free oxime [18] to 1.295(2) Å, similar to N-O distances

B(1)-O(1)	1 514(3)	B(2)-O(2)	1 516(3)
B(1)-C(111)	1.596(3)	B(2) - C(221)	1.596(4)
B(1)-C(121)	1.607(3)	B(2)-C(211)	1.6)4(3)
B(1)-N(2)	1.615(3)	B(2)-N(22)	1.617(3)
O(1)-C(140)	1.326(2)	O(2)-C(240)	1.325(2)
N(11)-N(12)	1.291(2)	N(21)-N(22)	1.294(2)
N(11)-C(149)	1.372(3)	N(21)-C(249)	1.364(3)
N(12)-C(131)	1.436(3)	N(22)-C(231)	1.439(3)
C(140)-C(149)	1.390(3)	C(240)-C(249)	1.392(3)
O(1)-B(1)-C(111)	107.2(2)	O(2)-B(2)-C(211)	107.8(2)
O(1)-B(1)-C(121)	108.4(2)	O(2)-B(2)-C(221)	109.8(2)
C(111)-B(1)-C(121)	117.9(2)	C(211)-B(2)-C(221)	115.5(2)
O(1)-B(1)-N(12)	102.7(2)	O(2)-B(2)-N(22)	102.0(2)
C(111)-B(1)-N(12)	111.1(2)	C(211)-B(2)-N(22)	112.4(2)
C(121)-B(1)-N(12)	108.5(28)	C(221)-B(2)-N(22)	108.5(2)
C(140)-O(1)-B(11)	116.8(2)	C(240)-O(2)-B(2)	115.6(2)
N(12)-N(11)-C(149)	117.9(2)	N(22)-N(21)-C(249)	117.5(2)
N(11)-N(12)-B(1)	121.9(2)	N(21)-N(22)-B(2)	120.5(2)
O(1)-C(140)-C(149)	120.6(2)	O(2)-C(240)-C(249)	120.1(2)
N(11)-C(149)-C(140)	121.3(2)	N(21)-C(249)-C(240)	121.3(2)

Table 2 Selected bond lengths /Å and angles $/^{\circ}$ for 3.

found in pyridine N-oxides [19]. The chelate ring is nearly planar, the boron atom being displaced by 0.098(2) Å from the C₂N₂ plane which is almost coplanar with the pyridine ring (dihedral angle between the least square planes of $3.22(5)^\circ$). Displacement of the O atom from the chelate C₂N₂ plane is 0.040(1) Å.

The crystal and molecular structure of (1-phenylazo-2-naphtholato)diphenylboron (3)

Complexes of 2-hydroxyazo compounds may have either a five membered (c) or a six membered (d) chelate structure.



The six-membered version (d) was found for bis-chelates of copper(II) [20] and nickel(II) [21]. The crystal structure of 3 confirms the coordination mode (d) of the azo ligand, which has been proposed earlier from spectroscopic data [11]. This is the first example for a crystal structure of a boron complex involving an azo ligand. Selected bond lengths and angles are summarized in Table 2. The asymmetric unit of 3 consists of two crystallographically non equivalent molecules, as shown in Figure 2. The two molecules differ mainly in the torsion angles between the Bphenyl groups and in minor conformational changes of the chelate ring. In the following discussion the indicated bond lengths and angles correspond to approximate mean values from the two independent molecules. The boron atom shows a distorted tetrahedral coordination with the exocyclic C-B-C- angle of 116.7° and the endocyclic N-B-O angle of 102.3°. The chelate ring has a considerably puckered conformation. The B and N(2) atoms are displaced by



Fig. 2 An ORTEP view of the asymmetric unit of 3. The displacement ellipsoids are drawn at the 50 % probability level. H atoms have been omitted for clarity.

0.80 and 0.23, respectively, from the OCCN(1) least square plane. The N=N-distance (1.293 Å) is slightly longer than the mean value for aromatic azo compounds (1.254 Å) [19]. The B-N distance of 1.616 Å indicates a strong B-N bond, being slightly shorter compared to B-N distances observed in boron O,N-chelates involving coordination of azine nitrogen atoms [22, 23]. On the other hand the B-O bond length of 1.515 Å is situated at the upper limit of the corresponding values found in boron chelates with phenolic B-O bonds [8, 22, 23].

In contrast to the copper or nickel bis-chelates [20, 21], the naphthalene C-N bond is by 5 % shorter compared to the phenyl C-N bond.

Experimental Section

Materials and Equipment

Solvents and reagent grade starting materials were used as received from commercial suppliers. A FISIONS CHNS micro analyser mod. EA 1108 was used for the CHN analyses. Melting points are uncorrected. The infrared spectra (KBr pellets, 4000-400 cm⁻¹) were recorded on a BOMEM BM 100 FT-IR spectrometer. UV-VIS absorption spectra were obtained with a Beckmann DU 650 equipment. All NMR spectra were recorded on a Varian MER-CURY plus (M-300) spectrometer operating at 300.07, 75.46, and 96.27 MHz for ¹H, ¹³C, and ¹¹B, respectively. The ¹H, ¹³C $\{^{1}H\}$, and ¹¹B{¹H} NMR spectra were obtained in CDCl₃, CD₃CN or DMSO- d_6 as solvents at 25 °C. Chemical shifts (δ) are given in ppm relative to SiMe₄ (internal reference for ¹H and ¹³C), and neat BF_3OEt_2 (external reference for ¹¹B). They are positive if the signal was shifted to higher frequencies than the standard. The solutions were placed in 5 mm (o.d.) NMR tubes and deuterated solvents were used as internal lock. All ¹¹B NMR spectra have been subtracted from the background signal of the NMR tube by using the VNMR 6.1C software.

Crystal structure determinations

X-ray diffraction data collections (scans and scans with κ offsets) were performed on an Enraf-Nonius Kappa-CCD diffractometer

	5	3
Empirical formula	C ₁₉ H ₁₇ BN ₂ O	$C_{28}H_{21}BN_2O$
Formula weight	300.16	412.28
Temperature /K	150(2)	293(2)
Wavelength /Å	0.71073(6)	0.71073(6)
Crystal system	monoclinic	orthorhombic
Space Group	$P2_1/n$	Pna2 ₁
Unit cell dimensions /Å, °	a = 8.4114(3)	a = 29.0810(6)
	b = 17.2554(8)	b = 10.1207(1)
	c = 10.8552(5)	c = 15.2138(3)
	$\beta = 97.890(3)$	
Z	4	8
Cell volume /Å ³	1560.6(1)	4477.7 (1)
Calculated density /(g/cm ³)	1.277	1.223
Absorption coefficient /mm ⁻¹	0.079	0.074
F(000)	632	1728
Crystal size /mm ³	0.30x0.22x0.14	0.30x0.25x0.08
Theta range for data collection /°	3.73 to 25	3.02 to 26
Index ranges	$-9 \le h \le 9$	$-35 \le h \le 35$
	$-20 \le k \le 20$	$-12 \le k \le 10$
	$-12 \le l \le 12$	$-17 \le l \le 18$
Reflections collected	7812	25363
Independent reflections	2714 [R(int) = 0.0496]	8364 [R(int) = 0.0666]
Completeness to theta 1%	$\theta = 25.00^{\circ}: 99.0$	$\theta = 26.00^{\circ}: 98.9$
Max. And min. transmission	0.998 and 0.845	0.9941 and 0.9782
Data / restraints / paramters	2714 / 0 / 209	8364 / 1 / 578
Goodness-of-fit on F ²	1.033	1.004
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0419, wR2 = 0.1038	R1 = 0.0457, wR2 = 0.0804
R indices (all data)	R1 = 0.0564, wR2 = 0.1133	R1 = 0.0974, WR2 = 0.0926
Extinction coefficient		0.0100(8)
Largest diff. Peak and hole (e/ A ³)	0.168 and -0.185	0.124 and -0.150

Table 3 Crystal data and structure refinement for 3 and 5.

(95 mm CCD camera on κ -goniostat) using graphite-monochromated MoK α radiation (0.71073 Å). Data were collected with a redundancy of 4. The final unit cell parameters were based on all reflections. Data collections were made using the *COLLECT* program [24]; integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [25]. Multiscan absorption correction was applied [26].

The structures were solved by direct methods with *SHELXS-97* [27]. The model was refined by full-matrix least squares on F^2 with *SHELXL-97* [28]. All the hydrogen atoms were stereochemically positioned and refined with the riding model [29]. Hydrogen atoms of the CH and CH₂ groups were set isotropic with a thermal parameter 20 % greater than the equivalent isotropic displacement parameter of the atom to which each one was bonded. This percentage was set to 50 % for the hydrogen atoms of the CH₃ and OH groups. Data collections and experimental details for the complexes are summarized in Table 3. The programs SHELXL-97 [28], and OR-TEP-III [29] were used within WinGX [30] to prepare materials for publication.

Syntheses

General procedure

 NH_4BPh_4 and the reactant LH (1.0 mmol respectively) are kept under reflux at 135–140 °C in 25 mL toluene until the evolution of ammonia has ceased (controlled with a pH-strip in the gas phase).

(2-Pyridinolato-N-oxide) diphenylboron (1)

Reaction time 15 h. The resulting cold solution is filtered and the filtrate evaporated to dryness. Yield 93 %. Recryst. from ethanol.

Colorless prismatic crystals; soluble in acetone, acetonitrile, chloroform and toluene. Mp 125-127 °C. Calc. for $C_{17}H_{14}BNO_2$ (275.11): C 74.22; H 5.13; N 5.09 %. Found: C 75.12; H 4.98; N 5.28 %.

NMR spectra (CDCl₃, δ /ppm): ¹**H** 6.75 (ddd, **J** = 7.8, 6.6, 1.1 Hz, 1H), 7.01 (dd, **J** = 8.7, 1.1 Hz, 1H), 7.19-7.33 (m, 6H), 7.50-7.56 (m, 5H), 8.02 (dd, **J** = 6.5, 1.1 Hz, 1H). ¹³**C** 111.01, 113.60, 126.92, 127.28, 130.93, 131.66, 138.44, 145.2, 156.60. ¹¹**B** 15.5. **IR** (KBr, cm⁻¹): 3093 ms, 3057 ms, 3005 m, 1630 vs, 1567 ms, 1519 vs, 1453 ms, 1432 ms, 1361 ms, 1263 ms, 1213 s, 1189 ms, 1150 s, 930 ms, 903 s,881 s, 758 s, 738 s, 704 vs, 613 ms, 582 m, 421 m.

(Maltolato)diphenylboron (2)

Reaction time 12 h. The resulting solution is hot filtered and cooled on ice. The crystallized product is filtered off and air-dried. Yield 62 %. Colorless crystal leaflets, soluble in acetonitrile and DMSO. Mp 200-202 °C. Calc. for $C_{18}H_{15}BO_3$ (290.13): C 74.52; H 5.21 %. Found: C 74.52; H 5.46 %.

NMR spectra (CD₃CN, δ /ppm): ¹H 2.52 (s, 3H, CH₃), 6.99 (d, J = 5.1 Hz, 1H), 7.14-07.27 (m, 6H, CH_{arom}), 7.39-7.44 (m, 4H, CH_{arom}), 8.31 (d, J = 5.1 Hz, 1H). ¹³C 14.97, 107.15, 127.43, 128.13, 132.47, 151.68, 153.04, 161.29, 176.16. ¹¹B 17.6. **IR** (KBr, cm⁻¹): 1638 s, 1572 vs, 1560 vs, 1468 vs, 1432 ms, 1298 s, 1270 m, 1251 m, 1209 s, 1105 m, 942 ms, 904 ms, 881 s, 859 ms, 828 ms, 754 s, 744 s, 708 s, 647 ms, 616 ms, 588 m, 537 m.

(1-Phenylazo-2-naphtholato) diphenylboron (3)

Reaction time 20 h. The resulting deep red solution is filtered and the filtrate evaporated to dryness. Yield 92 %. Red prismatic crystals; soluble in usual organic solvents. Recryst. from methanol. Mp 195 °C. Calc. for $C_{28}H_{21}BN_2O$ (412.30): C 81.57; H 5.13; N 6.79 %. Found: C 81.72; H 4.96; N 6.81 %.

NMR spectra (CDCl₃, δ/ppm): ¹H 7.11-7.30 (m), 7.39-7.47 (m), 7.56-7.62 (m), 7.67 (dd, J = 8.1, 0.6 Hz), 7.91 (d, J = 9.0 Hz), 8.42 (dd, J = 8.1, 0.5 Hz). ¹³C 120.58, 121.33, 124.47, 125.74, 126.86, 127.21, 128.24, 128.93, 129.53, 129.58, 129.74, 132.49, 142.48, 148.08, 154.79. ¹¹B 1.2. IR (KBr; cm⁻¹): 1617 m, 1589 m, 1556 m, 1508 s, 1489 m, 1456 m, 1443 m, 1432 m, 1384/1357 vs, 1294 ms, 1280 ms, 1212 s, 1191 ms, 1146 s, 1007 ms, 963 m, 919 m, 887 ms, 838 ms, 751 vs, 720 m, 702 s, 689 s, 662 m, 563 m, 489 m. UV-VIS (CHCl₃, λ_{max} nm/logε) 330/3.879, 414/4.008, 498/4.177.

$(\beta$ -Alaninato) diphenylboron (4)

Reaction time 20 h. The solid product is filtered off, air-dried and washed with water. Yield 93 %. Colorless crystal needles; soluble in DMSO. Recryst from methanol. Mp 255 °C (dec.). Calc. for $C_{15}H_{16}BNO_2$ (253.11): C 71.18; H 6.37; N 5.53 %. Found: C 71.20; H 6.06; N 5.78 %.

NMR spectra (DMSO- d_6 , δ /ppm): ¹**H** 2.46 (t, **J** = 6.4 Hz, 2H, CH₂), 2.84 (t, br, 2H, NCH₂), 6.78 (s, br, 2H, NH₂), 7.06-7.12 (m, 2H, p-C₆H₅), 7.15-7.22 (m, 4H, m-C₆H₅), 7.38-7.44 (m, 4H, o-C₆H₅). ¹³**C** 30.03 (CH₂), 35.50 (CH₂), 125.67, 127.07, 130.81, 149.30, 169.41 (COO). ¹¹**B** 3.0. **IR** (KBr, cm⁻¹): 3171 vs, br, 3101 vs, br, 3001 ms, 2910 m, 1643 vs, 1607 s, 1432 ms, 1418 m, 1361 vs, 1313 ms, 1268 m, 1228 m, 1206 m, 1178 m, 1158 s, 1050 m, 998 ms, 917 ms, 893 m, 841 m, 738 s, 703 s.

(Pyridine-2-acetyloximato)diphenylboron (5)

Reaction time 6 h. Yield 88 %. Colorless prismatic plates, insoluble in toluene. Mp 249-250 °C. Calc. for $C_{19}H_{17}BN_2O$ (300.17): C 76.03; H 5.71; N 9.33 %. Found: C 74.38; H 5.44; N 9.08 %.

NMR spectra (CDCl₃, δ /ppm): ¹H 2.35 (s, 3H, CH₃), 7.21-7.32 (m, 10H, CH_{arom}), 7.34 (ddd, J = 7.5, 5.7, 1.0 Hz, 1H), 7.53 (ddd, J = 8.1, 1.0 Hz, 1H), 8.01 (ddd, J = 8.1, 7.5, 1.5 Hz, 1H), 8.30 (ddd, J = 5.7, 1.5, 1.0 Hz, 1H). ¹³C 8.21 (CH₃), 117.02, 120.84, 127.30, 127.76, 132.44, 140.24, 141.62, 142.35, 153.03. ¹¹B 5.9. **IR** (KBr, cm⁻¹): 3069 m, 3053 m, 1621 vs, 1530 m, 1467 vs, 1396 s, 1329 ms, 1244 s, 1193 ms, 1135 ms, 890 ms, 834 m, 777 s, 748 s, 736 s, 709 s, 699 s, 652 m, 631 m, 514 m, 468 ms.

(*Picolinato*) diphenylboron (6)

Reaction time 20 h. The resulting solution is cooled on ice and the crystalline solid product filtered and air dried. Yield 80 %. Colorless prismatic crystals. Soluble in acetone and Chloroform, slightly soluble in methanol. Mp 158-159 °C. Calc. for $C_{18}H_{14}BNO_2$ (287.12): C 75.30; H 4.91; N 4.88 %. Found: C 77.08; H 4.76; N 5.02 %.

NMR spectra (DMSO- d_6 , δ /ppm): ¹H 7.18-7.24 (m, 10H), 8.18 (ddd, J = 7.8, 5.7, 1.2 Hz, 1H), 8.46 (ddd, J = 7.8, 1.2 Hz, 1H), 8.64 (ddd, J = 7.8, 1.1 Hz, 1H), 9.19 (ddd, J = 5.7, 1.1 Hz, 1H). ¹³C 123.97, 127.03, 127.46, 130.36, 131.75, 141.53, 142.89, 144.82, 163.26. ¹¹B 9.3. **IR** (KBr, cm⁻¹): 3067 w, 3004 w, 1741 vs, 1626 m, 1483 m, 1455 m, 1430 m, 1337 ms, 1288 ms, 1272 ms, 1206 ms, 1162 ms, 1146 ms, 938 ms, 851 m, 777 ms, 747 s, 705 s, 688 ms, 655 m, 616 m.

(L-Valinato) diphenylboron (7)

Reaction time 24 h. The solid product is filtered off, air-dried and washed with water. Yield 86 %. Recryst. from hot toluene. Color-less crystal needles, soluble in acetone, methanol and DMSO, insoluble in water and non-polar solvents. Mp 219 – 228 °C (dec.). Calc. for $C_{17}H_{20}BNO_2$ (281.16): C 72.62; H 7.17; N 4.98 %. Found: C 70.90; H 7.16; N 5.21 %.

NMR spectra (DMSO- d_6 , δ /ppm): ¹H 0.91 (d, J = 6.7 Hz, 3H, CH₃); 1.00 (d, 6.7 Hz, 3H, CH₃); 2.08 (m, 1H, CH(CH₃)₂), 3.3 (CHCOO + residual water peak),6.29 (dd, J = 10.5, 1H, NH), 7.09-7.16 (m, 2H, *p*-C₆H₅), 7.17-7.25 (m, 5H, *m*-C₆H₅ + NH), 7.38-7.45 (m, 4H, *o*-C₆H₅). ¹³C 18.54/18.98 (CH₃); 26.65 (CH); 60.57 (NCH); 126.15/126.18, 127.16/127.24, 131.38/

131.42, 148.0 (C_{arom}); 173.60 (COO). ¹¹B 6.3. IR (KBr, cm⁻¹): 3270 ms, 3206 m, 3099 s, br, 1702 vs, 1603 s, 1434 ms, 1339 ms, 1316 ms, 1276 s, 1246 s, 1170 m, 1008 m, 954 ms, 868 m, 762 m, 740/734 m, 711 s, 680 m, 643 m, 593 m, 503 m.

Supplementary Information – Supplementary Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 265848 & 265849 for compound 5 and 3, respectively.. Copies of available material can be obtained, free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CH2 1EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk).

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