

Beryllium Chemistry

Synthesis of a Boronic Acid Anhydride Based Ligand and Its Application in Beryllium Coordination

Magnus R. Buchner,^{*[a]} Matthias Müller,^[a] Onyekachi Raymond,^[b] Rebecca J. Severinsen,^[c] David J. Nixon,^[c] William Henderson,^[b] Penelope J. Brothers,^[d] Gareth J. Rowlands,^[c] and Paul G. Plieger^{*[c]}

Abstract: The synthesis of a boronic acid anhydride-based ligand containing one three- and one four-coordinated boron atom is presented. This ligand was successfully employed as a tridentate κ^1N, κ^2O -ligand in the coordination of beryllium chloride and both the ligand and the resulting complex have been structurally characterized. While the boron-element separations are within the typical range of related homo-nuclear compounds, the corresponding beryllium-element distances are rather long, suggesting unexpectedly high electron density

at the beryllium center. Incorporation of a beryllium atom in a six-membered ring causes no more distortion than the corresponding boron atom, suggesting that analogous ligand systems could be used in boron and beryllium coordination chemistry. The generated hetero-tri-nuclear complex enables the direct comparison of bond lengths and angles at beryllium and boron atoms in similar coordination environments and can act as a monomolecular model for beryllium borates.

Introduction

Organic light-emitting diodes (OLEDs) are of high industrial importance and widely employed for the manufacture of displays and light sources. Over the last decade boron-based dyes for OLEDs have gained much attention and through the use of *N,N*-chelating ligands, devices could be constructed which – depending on the ligand design – emit within the near-UV to the orange region.^[1–5] With the help of *O,O*-chelating ligands, devices with an emission in the red/near-infrared were realized,^[6] while *C,N*-chelated boron yields blue-green to red,^[7,8] and *N,O*-chelation yields blue emission respectively.^[9–12] While

an abundance of boron compounds have been investigated as potential components of OLED devices, the number of related beryllium compounds is extremely limited, even though these compounds show promise in the construction of white emitting OLEDs.^[13–17] The reason for this lies with the assumed toxicity of beryllium compounds, and the small number of simple beryllium coordination compounds, that can act as starting materials for the development of beryllium-based dyes.^[18] Hence model compounds that contain beryllium and boron atoms in similar coordination environments are necessary to develop our knowledge of the structure relationships between these species.^[19]

Recently Eu^{2+} and Ce^{3+} doped nitridoberyllsilicates^[20] and Eu^{2+} doped oxoberyllates have proven to be efficient phosphors for LED applications, exhibiting luminescence in the yellow to orange region.^[21] Furthermore, alkaline beryllium borates of the type BeB_3O_6^- and $\text{Be}_2\text{B}_3\text{O}_7^-$ show non-linear optical (NLO) properties in the UV region.^[22] Based on these compounds, LaBeB_3O_7 ^[23] and $\text{CsBe}_4(\text{BO}_3)_3$ were investigated for their applicability as NLO materials.^[24] This class of NLO crystals has more recently been extended to the beryllium fluoridoborates $\text{Be}_2\text{BO}_3\text{F}$ ^[25] and $\text{LiSr}_3\text{Be}_3\text{B}_3\text{O}_9\text{F}_4$, which operate in the deep-ultraviolet region,^[26] and the investigation of beryllium borate-based NLO materials is increasingly aided by theoretical methods.^[27] However, due to the fact that beryllium is the least investigated non-radioactive element there is only a very limited number of isolated compounds that incorporate both beryllium and boron atoms. Therefore, molecular model examples are necessary to provide a basic set of structural parameters on which theoretical models can be built upon.

Our groups are interested in all aspects of beryllium chemistry, including the design, synthesis, and characterization of strong selective ligands for beryllium coordination.^[28–32] Here

[a] *Nachwuchsgruppe Berylliumchemie Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany*
E-mail: magnus.buchner@chemie.uni-marburg.de
<http://www.uni-marburg.de/fb15/ag-buchner>

[b] *Chemistry, School of Science, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand*
E-mail: w.henderson@waikato.ac.nz
<http://sci.waikato.ac.nz/about-us/people/hende>

[c] *School of Fundamental Sciences, Massey University, Private Bag 11222, Palmerston North 4410, New Zealand*
E-mail: P.G.Plieger@massey.ac.nz
<http://www.massey.ac.nz/massey/learning/colleges/college-of-sciences/staff-list.cfm?stref=101530>

[d] *Research School of Chemistry, Australian National University, Canberra, ACT 2600, Australia*
E-mail: Penelope.Brothers@anu.edu.au

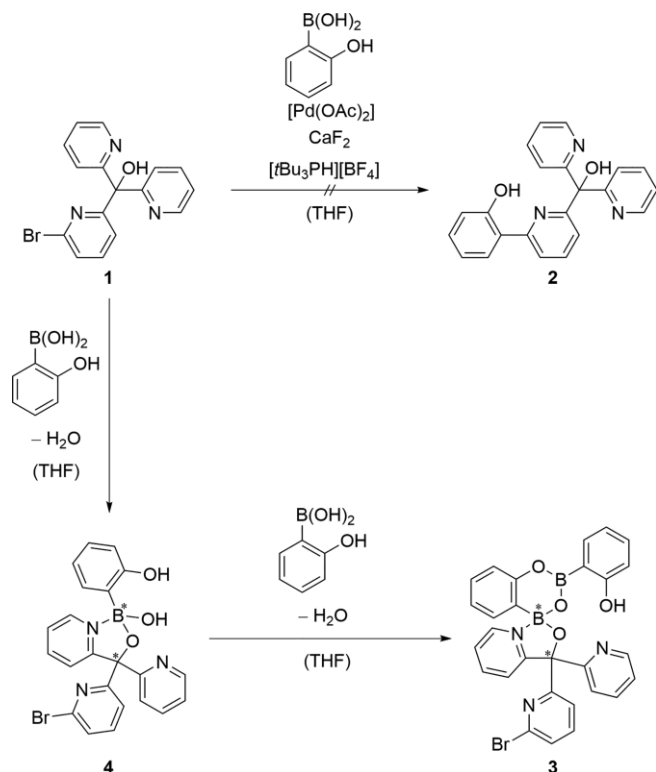
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under <https://doi.org/10.1002/ejic.201900772>.

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we present the serendipitous formation of a dinuclear boron compound, in which one boron atom is three- and the other is four-coordinated, and its use as a ligand in beryllium coordination chemistry. The isolated beryllium complex acts as a molecular model system for beryllium-based OLED materials as well as beryllium borates.

Results and Discussion

Our original goal was to synthesize the tetradentate κ^3N, κ^1O -ligand **2**^[33] by a palladium(0) catalyzed cross-coupling of (6-bromopyridin-2-yl)di(pyridin-2-yl)methanol (**1**) and *ortho*-hydroxyphenylboronic acid. However, the only compound isolated was the dinuclear boron complex **3** (Scheme 1). This compound is presumably formed through the concurrent deprotonation of the OH-group of **1** and coordination of the alkoxide to the boron atom of the *ortho*-hydroxyphenylboronic acid. Subsequent *N*-coordination of one pyridine group with concomitant H₂O elimination resulted in the formation of the boronic acid ester **4**. This compound acts as a chelating ligand for a second equivalent of *ortho*-hydroxyphenylboronic acid and condenses by water elimination to boronic acid anhydride based dinuclear complex **3**. These findings and the proposed reaction pathway are summarized in Scheme 1.



Scheme 1. Serendipitous formation of the di-nuclear boron species **3** through boron coordination and subsequent boronic acid condensation, instead of the intended formation of ligand **2** by Suzuki cross-coupling.

Due to the quadrupolar nature of the ¹¹B nucleus, the chemical shift range and line width ($\omega_{1/2}$) in ¹¹B NMR spectroscopy are indicative for the coordination environment of boron atoms.^[34] The ¹¹B NMR spectrum of compound **3** in CD₃CN re-

veals two signals at 8.4 and 28.9 ppm. The latter signal is in the typical range of three-coordinate boron nuclei and this is also supported by the broad linewidth of 415 Hz.^[34] Related three-coordinate phenylboronic acid and phenylboroxine also exhibit broad ¹¹B NMR signals around 30 ppm^[35] and derivatized boronic acids are observed from 26.9 to 32.0 ppm.^[36] The signal at 8.4 ppm with a linewidth of 113 Hz is typical for a four-coordinate boron nucleus^[34] and related 2,6-dimethanopyridine arylboronic acid esters show chemical shifts of 8.0–8.4 ppm.^[37] In the ¹³C and ¹H NMR spectra two signal sets are observed. This arises from the fact that compound **3** possesses two chiral centers as shown in Scheme 1. This leads to the formation of two diastereoisomers, which exhibit different chemical shifts. Due to the broad signals of quadrupolar ¹¹B nuclei, the peaks of both diastereoisomers are overlapping. Therefore, only one signal set is observed in the ¹¹B NMR spectrum. The O–H band in the IR spectrum at 3291 cm⁻¹ suggests a relatively strong bound proton and the typical B–O stretching mode is observed at 1314 cm⁻¹.^[38]

Compound **3** crystallizes in the monoclinic space group *P*₂₁/*c* and Table S1 contains the crystallographic details, while Figure 1 shows its molecular structure including a partial labeling scheme. In this complex boron atom B1 is coordinated tetrahedrally, while B2 is surrounded in a trigonal planar fashion. B1 is ligated by one nitrogen atom, two oxygen atoms and one carbon atom. With exception of the N2–B1–O4 angle at 96(1)[°] all angles around B1 are close to 109.47[°] (105(1)–117(1)[°]). The small N2–B1–O4 angle is caused by the incorporation of boron into a five-membered ring. The element–B2–element angles in the range 117(1)[°] to 122(1)[°] are very close to the ideal 120[°]. The O2 atom bridges the two boron atoms with a B1–O2–B2 angle of 123(1)[°]. The distance from O2 to the coordinating boron atoms decreases from B1 (1.48(2) Å) to B2 (1.33(2) Å), which is in accordance with the decreasing electron density from four- to three-coordinate boron. A similar trend is observed for the B1–O4 (1.53(2) Å) and B2–O3 (1.40(2) Å) distances. Due to the low quality of the dataset these parameters should be interpreted with caution.

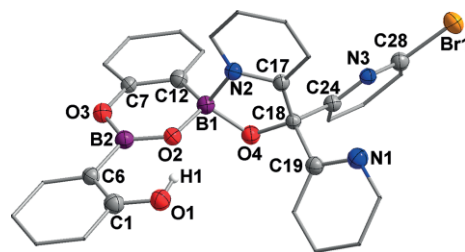
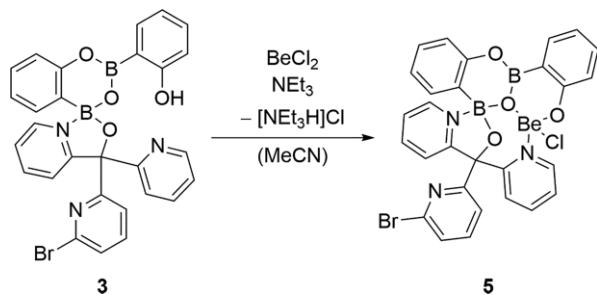


Figure 1. Molecular structure of complex **3** in the solid state, as determined by X-ray crystallography. Ellipsoids are depicted at 30 % probability at 100 K. The hydrogen atom is represented isotropically with an arbitrary radius. Non-OH hydrogen atoms are omitted, and some C atoms are shown as wire frame for clarity. Selected bond lengths [Å] and angles [°]: B1–N2 1.60(2), B1–C12 1.53(2), B1–O4 1.53(2), B1–O2 1.48(2), B2–C6 1.57(2), B2–O3 1.40(2), B2–O2 1.33(2), N1–C19 1.39(1), N2–C17 1.35(2), O1–C1 1.32(2), O3–C7 1.37(1), O4–C18 1.40(1), C1–C6 1.45(2), C7–C12 1.39(2), C18–C17 1.43(2), C18–C19 1.51(1); N2–B1–O2 105(1), N2–B1–O4 96(1), N2–B1–C12 117(1), O2–B1–O4 109(1), O2–B1–C12 112(1), O4–B1–C12 116(1), O2–B2–O3 121(1), C6–B2–O2 122(1), C6–B2–O3 117(1), B1–O2–B2 123(1).

Compound **3** has an abundance of functional groups, which can coordinate to metal atoms and form five-, six- and seven-membered rings. Since the coordination chemistry of beryllium has not been investigated to any great extent, this ligand was a promising candidate to determine the preferred chelate ring size for beryllium ions. Additionally, due to the close size relationship of beryllium and boron, a complex with beryllium and boron atoms in related coordination environments would give the opportunity to directly compare bond lengths and angles. Therefore, we deliberately prepared compound **3** through the reaction of compound **1** and *ortho*-hydroxyphenylboronic acid in the presence of CaF₂, which affords the desired di-nuclear boron species in 88 % isolated yield in a 1:1.2 mixture of both diastereoisomers. Ligand **3** was then reacted with an excess of BeCl₂ in acetonitrile (Scheme 2). Upon addition of an excess of triethylamine to the reaction solution, yellow crystals immediately formed at the glass wall of the reaction vessel. These crystals were comprised of hetero-tri-nuclear complex **5** and acetonitrile in a 1:1 ratio and crystallize in the monoclinic space group *P*2₁/*c*. The corresponding crystallographic details are given in Table S1. Compound **5** is insoluble in organic solvents that do not decompose the complex. Thus, attempts to measure the NMR spectra of this species were unsuccessful.



Scheme 2. Reaction of compound **3** with BeCl₂ in the presence of NEt₃ yields complex **5** and triethylammonium chloride.

Figure 2 shows the molecular structure of complex **5** including a partial labelling scheme. Complex **5** contains one beryllium atom, which is coordinated tetrahedrally by one nitrogen atom, two oxygen atoms and one chlorine atom. The six element–Be–element angles range from 103.3(1)° to 113.2(1)°, and are therefore close to the ideal tetrahedral angle of 109.47°. One boron atom (B1) is also coordinated tetrahedrally by one nitrogen atom, two oxygen atoms and one carbon atom. With exception of the N2–B1–O4 angle at 100.3(1)°, all angles around B1 are close to 109.47° (106.2(1)–115.3(2)°). The small N2–B1–O4 angle is caused by the incorporation of boron into a five-membered ring in accordance with compound **3**. The second boron atom (B2) is coordinated in a trigonal planar fashion by two oxygen and one carbon atom; the element–B2–element angles (117.3(2)° to 121.7(2)°) being very close to the ideal 120°. The trigonal planar O2 atom bridges the beryllium and both boron atoms with element–O2–element angles of 118.8(1)–121.1(1)°. The distance from O2 to the coordinated atoms decreases from Be1 (1.695(3) Å) via B1 (1.518(2) Å) to B2 (1.389(2) Å), which is in accordance with the increasing electronegativity – from beryllium to boron – and decreasing electron

density – from four- to three-coordinated boron. A similar trend is observed for the Be1–O1 (1.557(3) Å), B1–O4 (1.443(2) Å) and B2–O3 (1.368(2) Å) distances. This trend is consistent with that observed for compound **3**.

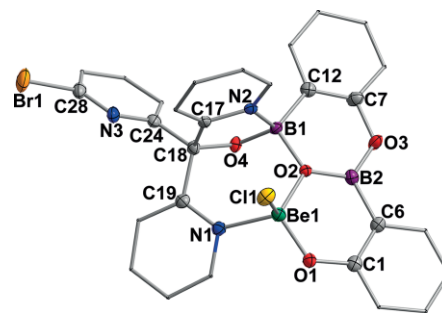


Figure 2. Molecular structure of complex **5** in the solid state, as determined by X-ray crystallography. Ellipsoids are depicted at 70 % probability at 100 K. Hydrogen atoms are omitted and some C atoms are shown as wire frame for clarity. Selected bond lengths [Å] and angles [°]: Be1–N1 1.845(3), Be1–Cl1 2.008(2), Be1–O1 1.557(3), Be1–O2 1.695(3), B1–N2 1.582(2), B1–C12 1.584(3), B1–O4 1.443(2), B1–O2 1.518(2), B2–C6 1.540(3), B2–O3 1.368(2), B2–O2 1.389(2), N1–C19 1.359(2), N2–C17 1.346(2), O1–C1 1.336(2), O3–C7 1.383(2), O4–C18 1.409(2), C1–C6 1.413(3), C7–C12 1.384(3), C18–C17 1.534(3), C18–C19 1.540(3), N1–Be1–O1 107.9(2), N1–Be1–O2 112.2(2), N1–Be1–Cl1 103.3(1), O1–Be1–O2 108.5(2), O1–Be1–Cl1 111.6(1), O2–Be1–Cl1 113.2(1), N2–B1–O2 106.2(1), N2–B1–O4 100.3(1), N2–B1–C12 113.7(2), O2–B1–O4 109.2(2), O2–B1–C12 111.3(2), O4–B1–C12 115.3(2), O2–B2–O3 121.7(2), C6–B2–O2 121.0(2), C6–B2–O3 117.3(2), Be1–O2–B1 118.8(1), Be1–O2–B2 119.6(1), B1–O2–B2 121.1(1).

The Be1–O1 atomic distance of 1.557(3) Å is within the typical range of beryllium phenolate contacts (1.481(2)–1.650(3) Å),^[39–42] while the Be–O2 distance is 1.695(3) Å, which is closer to Be–O bonds of neutral O-donor ligands like carboxylic acid esters (1.653(2)–1.668(2) Å),^[43,44] or chelating diketones (1.710(6) Å).^[45] The Be1–N1 distance (1.845(3) Å) is longer than known pyridine beryllium compounds (1.687(7)–1.758(5) Å)^[40,41,46] but is close to the Be–N bond length of nitrogen Lewis base adducts to BeCl₃[–] (1.765(6)–1.813(3) Å).^[47] The Be1–Cl1 separation at 2.008(2) Å is close to the bond lengths found in Lewis base adducts to BeCl₃[–] (2.003(3)–2.022(5) Å) and longer than in neutral coordination compounds of BeCl₂ (1.990(3) Å)^[48] or non-coordinated BeCl₃[–] (1.906(2)–1.921(2) Å).^[49] The B1–O2 distance of 1.518(2) Å is slightly longer than the B1–O4 separation (1.443(2) Å) indicating a weaker interaction with O2. This is in accordance with the fact that O2 is three-coordinate. A similar, however less pronounced trend is also observed for the B2–O2 (1.389(2) Å) and B2–O3 (1.368(2) Å) distances. Furthermore, the B1–O2/O4 and B2–O2/O3 distances are within the normal range of four- (1.463(4)–1.479(6) Å)^[37,50] and three-coordinate (1.352(3)–1.368(2) Å)^[50,51] boronic acid derivatives respectively. Also the B1–N2 (1.582(2) Å), B1–C12 (1.584(3) Å), and the B2–C6 (1.540(3) Å) atomic distances are all in the typical range for boronic acid derivatives with four-^[37] and three-coordinate^[51] boron atoms respectively.

Conclusions

The Be–N and Be–Cl distances suggest that the electron density at the beryllium atom is still rather high. This is surprising con-

sidering the fact that boron is significantly more electronegative and shows that the three-coordinate oxygen atom is still a good ligand for beryllium. Thus, a partial substitution of boron through beryllium atoms should be feasible in most borates, opening new avenues for novel NLO materials. Although the atomic and ionic radii of beryllium are both larger than the corresponding boron radii, the beryllium containing six-membered heterocyclic ring geometry closely resembles the corresponding six-membered ring containing the boron atom B1. This suggests, that in principle all ligands that have been employed successfully for the synthesis of boron-based OLED materials can also be applied to beryllium. Therefore, we encourage intrepid material chemists experienced with boron to venture more into the related field of beryllium chemistry.

Experimental Section

Caution! Beryllium and its compounds are regarded as toxic and carcinogenic. As the biochemical mechanisms that cause beryllium associated diseases are still unknown, special (safety) precautions are strongly advised.^[18]

General experimental techniques

All manipulations were performed either under solvent vapor pressure or dry argon using glovebox and Schlenk techniques if not stated otherwise. Glassware was flame-dried prior to use. Acetonitrile and CD₃CN were dried with P₄O₁₀ and distilled prior to use and THF was passed through columns of activated alumina, whereas dichloromethane and CDCl₃ were used as received. BeCl₂^[52] and compound **1**^[53] were prepared according to literature procedures, while triethylamine was purchased from VWR² 2-hydroxyphenylboronic acid from AK Scientific and CaF₂ from BDH Chemical NZ Limited and used as received. Due to the expected extreme toxicity of compound **5**, no elemental analysis or mass spectrometry could be performed.

NMR spectroscopy

¹H, ¹³C and ¹¹B NMR spectra were recorded on Bruker Avance III HD 300 and Avance 700 spectrometers. ¹H NMR (300/700 MHz) and ¹³C NMR (76/176 MHz) chemical shifts are given relative to the solvent signal for CD₃CN (1.94 and 1.32 ppm)/CDCl₃ (7.26 and 77.2 ppm) while ¹¹B (96/160 MHz) used 15 % BF₃·Et₂O in CDCl₃ as an external standard. NMR spectra were processed with the MestReNova software.^[54]

IR spectroscopy

IR spectra were recorded on a Bruker alpha FTIR spectrometer equipped with a diamond ATR unit in an argon filled glovebox and a Nicolet iS5 IR with iD7 ATR accessory. Processing of the spectra was performed with the OPUS software package^[55] and Origin-Pro8.^[56]

Single crystal X-ray diffraction

Crystals were selected under exclusion of air in perfluorinated polyether (Fomblin YR 1800, Solvey Solexis) and mounted using the MiTeGen MicroLoop system. X-ray diffraction data were collected using either the graphite monochromated Mo-K_α radiation of a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source and a CMOS Photon 100 detector or the Cu-K_α radiation of a Rigaku-Spider X-ray diffractometer, comprising a Rigaku MM007 microfocus copper rotating-anode generator, high-flux Osmic monochromating and focusing multilayer mirror optics and a

curved image-plate detector. The diffraction data were reduced with the X-Area software^[57] in case of **5**. For **3**, CrystalClear^[58] was utilized for data collection and FSPProcess in PROCESS-AUTO^[59] for cell refinement and data reduction. The structure of **5** was solved using Direct Methods (SHELXT-2018/2) and refined against F² (SHELXL-2018/3) using the ShelXle software package,^[60–62] while **3** was solved employing Direct Methods and expanded by Fourier techniques.^[63] All atoms were located by Difference Fourier synthesis and non-hydrogen atoms refined anisotropically. Hydrogen atoms were refined isotropically.

CCDC 1940858 (for **3**), and 1940860 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Mass spectrometry

Mass spectrometry was performed on a Jeol AccuTOF GCv equipped with a combined FD/FI/LIFDI source using liquid field desorption ionization (LIFDI) as ionization techniques and on a ThermoScientific Q Exactive Focus Hybrid Quadrupole-Orbitrap mass spectrometer using electrospray ionization (ESI).

Synthesis and characterization

Compound 3 (as received from the cross coupling attempt): A mixture of compound **1** (500 mg, 1.46 mmol), 2-hydroxyphenylboronic acid (243 mg, 1.75 mmol), calcium fluoride (343 mg, 4.38 mmol), tritert-butylphosphonium tetrafluoroborate (8.40 mg, 27.2 μmol) and palladium acetate (3.50 mg, 14.6 μmol) in THF (74 mL) was stirred under Ar at reflux for 5 h. The reaction mixture was filtered and the residue extracted with THF (3 × 50 mL). The combined organic fractions were washed with water (2 × 25 mL each). The organic layer was dried with anhydrous MgSO₄, filtered, and the solvents evaporated in vacuo to afford an off-white solid. Yields were not determined. ¹H NMR (300 MHz, CD₃CN) major diastereoisomer: δ = 6.61–6.68 (m, 1H, H_{A,r}), 6.83–6.90 (m, 1H, H_{A,r}), 6.91–6.95 (m, 1H, H_{A,r}), 7.08–7.17 (m, 1H, H_{A,r}), 7.27–7.34 (m, 3H, H_{A,r}), 7.49–7.57 (m, 1H, H_{A,r}), 7.62–7.86 (m, 7H, H_{A,r}), 8.10–8.19 (m, 1H, H_{A,r}), 8.23–8.36 (m, 1H, H_{A,r}), 8.47–8.55 (m, 2H, H_{A,r}) 8.78 (s, 1H, OH); minor diastereoisomer: δ = 6.95–7.05 (m, 5H, H_{A,r}), 7.32–7.38 (m, 6H, H_{A,r}), 7.42–7.48 (m, 1H, H_{A,r}), 7.58–7.65 (m, 2H, H_{A,r}), 7.89–7.97 (m, 2H, H_{A,r}), 8.54–8.60 (m, 3H, H_{A,r}), 8.63 (s, 1H, OH). ¹H NMR (300 MHz, CDCl₃) major diastereoisomer: δ = 6.71–6.77 (m, 1H, H_{A,r}), 6.84–7.07 (m, 2H, H_{A,r}), 7.10–7.16 (m, 1H, H_{A,r}), 7.20–7.35 (m, 4H, H_{A,r}), 7.40–7.45 (m, 1H, H_{A,r}), 7.49–7.61 (m, 2H, H_{A,r}), 7.63–7.85 (m, 2H, H_{A,r}), 7.87–7.94 (m, 1H, H_{A,r}), 7.97–8.03 (m, 1H, H_{A,r}), 8.11–8.23 (m, 2H, H_{A,r}), 8.54–8.62 (m, 1H, H_{A,r}), 8.65–8.75 (m, 1H, H_{A,r}), 8.91 (s, 1H, OH); minor diastereoisomer: δ = 6.71–6.77 (m, 1H, H_{A,r}), 6.84–7.07 (m, 2H, H_{A,r}), 7.10–7.16 (m, 1H, H_{A,r}), 7.20–7.35 (m, 4H, H_{A,r}), 7.40–7.45 (m, 1H, H_{A,r}), 7.49–7.61 (m, 2H, H_{A,r}), 7.63–7.85 (m, 2H, H_{A,r}), 7.87–7.94 (m, 1H, H_{A,r}), 7.97–8.03 (m, 1H, H_{A,r}), 8.11–8.23 (m, 2H, H_{A,r}), 8.54–8.62 (m, 1H, H_{A,r}), 8.65–8.75 (m, 1H, H_{A,r}), 8.81 (s, 1H, OH). ¹¹B NMR (96 MHz, CD₃CN) δ = 8.4 (ω_{1/2} = 113 Hz, B_{four-coordinate}), 28.9 (ω_{1/2} = 415 Hz, B_{three-coordinate}). ¹¹B NMR (96 MHz, CDCl₃) δ = 8.2 (ω_{1/2} = 200 Hz, B_{four-coordinate}), 28.6 (ω_{1/2} = 430 Hz, B_{three-coordinate}). ¹³C NMR (76 MHz, CD₃CN): δ = 90.3 (CC₃), 93.9 (CC₃), 116.1 (C_{A,r}), 116.1 (C_{A,r}), 117.7 (C_{A,r}), 119.9 (C_{A,r}), 120.0 (C_{A,r}), 121.8 (C_{A,r}), 121.9 (C_{A,r}), 122.6 (C_{A,r}), 122.7 (C_{A,r}), 122.7 (C_{A,r}), 123.8 (C_{A,r}), 123.8 (C_{A,r}), 123.9 (C_{A,r}), 124.1 (C_{A,r}), 124.1 (C_{A,r}), 124.2 (C_{A,r}), 126.5 (C_{A,r}), 127.0 (C_{A,r}), 127.3 (C_{A,r}), 127.3 (C_{A,r}), 127.8 (C_{A,r}), 128.2 (C_{A,r}), 128.5 (C_{A,r}), 130.7 (C_{A,r}), 134.0 (C_{A,r}), 134.1 (C_{A,r}), 136.4 (C_{A,r}), 136.4 (C_{A,r}), 137.9 (C_{A,r}), 138.4 (C_{A,r}), 141.1 (C_{A,r}), 141.1 (C_{A,r}), 141.2 (C_{A,r}), 141.2 (C_{A,r}), 141.6 (C_{A,r}), 143.2 (C_{A,r}), 143.4 (C_{A,r}), 148.3 (C_{A,r}), 149.7 (C_{A,r}), 149.8 (C_{A,r}), 162.9 (C_{A,r}), 163.3 (C_{A,r}), 163.5 (C_{A,r}), 164.9 (C_{A,r}), 165.5 (C_{A,r}), 165.7 (C_{A,r}), 165.8 (C_{A,r}). ¹³C NMR (76 MHz, CDCl₃): δ = 89.3 (CC₃), 89.4 (CC₃), 115.4 (C_{A,r}), 115.4 (C_{A,r}), 117.2 (C_{A,r}), 117.2 (C_{A,r}), 119.1 (C_{A,r}), 119.2 (C_{A,r}), 120.4 (C_{A,r}), 121.1 (C_{A,r}),

121.5 (C_{Ar}), 121.8 (C_{Ar}), 122.2 (C_{Ar}), 122.9 (C_{Ar}), 123.0 (C_{Ar}), 123.0 (C_{Ar}), 123.1 (C_{Ar}), 123.1 (C_{Ar}), 123.5 (C_{Ar}), 125.6 (C_{Ar}), 126.4 (C_{Ar}), 126.8 (C_{Ar}), 127.1 (C_{Ar}), 127.4 (C_{Ar}), 127.4 (C_{Ar}), 129.9 (C_{Ar}), 133.1 (C_{Ar}), 133.2 (C_{Ar}), 135.8 (C_{Ar}), 135.9 (C_{Ar}), 137.2 (C_{Ar}), 137.5 (C_{Ar}), 137.6 (C_{Ar}), 139.1 (C_{Ar}), 139.5 (C_{Ar}), 139.5 (C_{Ar}), 139.9 (C_{Ar}), 141.0 (C_{Ar}), 141.2 (C_{Ar}), 141.3 (C_{Ar}), 141.4 (C_{Ar}), 147.4 (C_{Ar}), 148.8 (C_{Ar}), 149.2 (C_{Ar}), 157.4 (C_{Ar}), 157.5 (C_{Ar}), 160.0 (C_{Ar}), 160.1 (C_{Ar}), 161.8 (C_{Ar}), 162.3 (C_{Ar}), 163.7 (C_{Ar}), 164.0 (C_{Ar}), 164.8 (C_{Ar}), 164.9 (C_{Ar}). FT-IR (cm⁻¹): 3291(m; OH), 1619 (m), 1606 (w), 1571 (m), 1551 (m), 1476 (m), 1462 (m), 1441 (m), 1425 (s), 1396 (m), 1376 (w), 1339 (m), 1314 (s, B-O), 1283 (s), 1225 (s), 1215 (m), 1201 (m), 1159 (m), 1151 (m), 1135 (m), 1116(m), 1104 (s), 1081(s), 1063 (s), 1030 (m), 1051 (s), 995 (w), 986 (m), 943 (m), 910 (w), 898 (w), 877 (m), 862 (m), 850 (m), 799 (s), 785 (m), 773 (m), 760 (vs), 748 (s), 733 (s), 684 (s), 675 (vs), 649 (m), 634 (s), 614 (s), 577 (m), 558 (m), 523 (s), 502 (m), 488 (m), 470 (s), 447 (m), 432 (w), 404 (m). HR-MS (FD⁺): m/z calcd. for [(C₂₈H₂₀B₂BrN₃O₄)⁺]: 563.08233, found 563.08070.

Compound 3 (directed synthesis): A mixture of compound 1 (100 mg, 0.29 mmol), 2-hydroxybenzene boronic acid (100 mg, 0.73 mmol), and calcium fluoride (68.0 mg, 0.87 mmol) in THF (10 mL) was stirred under Ar at reflux for 5 h. The mixture was extracted with DCM (150 mL) and washed with water and brine alternatively (2 × 50 mL each). The organic layer was dried with anhydrous MgSO₄, filtered, and the solvents evaporated in vacuo to afford an off-white solid (ca. 145 mg, 88 %). ¹H NMR (700 MHz, CDCl₃) major diastereoisomer: δ = 6.72–6.76 (m, 1H, H_{Ar}), 6.86–6.96 (m, 2H, H_{Ar}), 7.04 (dd, J_{HH} = 7.3, 1.8 Hz, 1H, H_{Ar}), 7.11–7.15 (m, 1H, H_{Ar}), 7.22–7.34 (m, 3H, H_{Ar}), 7.41–7.45 (m, 1H, H_{Ar}), 7.52–7.60 (m, 2H, H_{Ar}), 7.66–7.72 (m, 1H, H_{Ar}), 7.80 (td, J_{HH} = 7.8, 1.9 Hz, 1H, H_{Ar}), 7.89–7.93 (m, 1H, H_{Ar}), 7.99–8.04 (m, 1H, H_{Ar}), 8.13–8.22 (m, 2H, H_{Ar}), 8.58–8.60 (m, 1H, H_{Ar}), 8.69 (d, J_{HH} = 8.3 Hz, 1H, H_{Ar}), 8.91 (s, 1H, OH); minor diastereoisomer: δ = 6.72–6.77 (m, 1H, H_{Ar}), 6.87–6.96 (m, 2H, H_{Ar}), 7.00 (dd, J_{HH} = 7.1, 1.8 Hz, 1H, H_{Ar}), 7.11–7.15 (m, 1H, H_{Ar}), 7.22–7.34 (m, 3H, H_{Ar}), 7.44–7.45 (m, 1H, H_{Ar}), 7.52–7.60 (m, 2H, H_{Ar}), 7.66–7.72 (m, 2H, H_{Ar}), 7.89–7.93 (m, 1H, H_{Ar}), 7.99–8.04 (m, 1H, H_{Ar}), 8.13–8.22 (m, 2H, H_{Ar}), 8.58–8.60 (m, 1H, H_{Ar}), 8.71 (d, J_{HH} = 8.4 Hz, 1H, H_{Ar}), 8.81 (s, 1H, OH). ¹¹B NMR (160 MHz, CDCl₃) δ = 8.2 (ω_{1/2} = 282 Hz), 28.2 (ω_{1/2} = 821 Hz). FT-IR (cm⁻¹): 3308 (m; OH), 3064 (w), 3013 (w), 1619 (m), 1607 (w), 1575 (s), 1554 (w), 1475 (m), 1460 (m), 1444 (m), 1427 (m), 1397 (w), 1338 (m), 1316 (s, B-O), 1285 (m), 1226 (w), 1152 (w), 1134 (m), 1118 (m), 1082 (m), 1063 (m), 1033 (m), 1017 (m), 995 (w), 987 (w), 942 (w), 909 (w), 877 (w), 851 (w), 807 (w), 762 (s), 734 (m), 749 (m), 688 (w), 676 (m), 636 (w), 615 (w), 577 (w), 559 (w), 524 (w), 471 (w), 449 (w), 430 (w), 405 (w). HR-MS (ESI⁺): m/z calcd. for [(C₂₈H₂₁B₂BrN₃O₄)⁺]: 564.08961, found 564.0896.

Compound 5: Compound 3 (17.7 mg, 0.03 mmol) and BeCl₂ (4.0 mg, 0.05 mmol) were weighed into a Schlenk tube and acetonitrile was vacuum transferred into the vessel. To the colorless solution, triethylamine (14.9 μL, 10.0 mg, 0.10 mmol) was added upon which yellow crystals suitable for X-ray diffraction formed at the wall of the reaction vessel. *In situ* NMR experiments suggest quantitative formation of 5. However, isolated yields were not determined.

Acknowledgments

M. R. B. and M. M. gratefully acknowledge the Deutsche Forschungsgemeinschaft (BU2725/5–1 & BU2725/8–1) for financial support. O. R., D. N., W. H. and P. G. P. thank the Marsden Fund of the New Zealand Government (MAU1204), administered by the Royal Society of New Zealand for financial support of this

work. R. J. S. would like to acknowledge the assistance of Pat Edwards in collecting the ¹¹B NMR spectra.

Keywords: Beryllium · Boron · Coordination modes · Main group chemistry · Structure elucidation

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Received: July 16, 2019