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Investigations on the reactivity of arylboronic acid with phenolic pyrazole

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ABSTRACT

Reaction of phenylboronic acid with phenolic pyrazole was carried out in 1:1 stochiometry using toluene as a solvent. Depending on the steric bulk of the group present on the pyrazole ring, PhB (HPhPzPh)(OEt) **1**, [(PhB)(PhPzHt-Bu)(OH)][$(PhB)_2$(PhPzt-Bu)$_2$(O)] **2** and $(PhBPhPz)_2$ **3** were isolated. Compound **3** is an example of *cis*-isomer of pyrazabole crystallized in a boat conformation for the B_2N_4 heterocycle.

1. Introduction

Organoboron compounds have been an area of active research for several decades now due to the innumerable applications of organoboron compounds in the fields ranging from organic synthesis [1], organometallic and inorganic coordination chemistry [2–9] to materials chemistry [10]. The coordination chemistry of poly(pyrazolyl)borates have been investigated in detail and several reviews have appeared describing the rich coordination chemistry arising out of these systems [2,11–18]. The ease with which boron forms coordinate bonds with donor atoms like N and O have been exploited and a series of interesting organoboron complexes and macrocycles have been isolated by reaction of arylboronic acids with salen-type ligands and aminophenols [19–26]. Another interesting class of boron compound is the pyrazabole, a boron nitrogen containing heterocycle [27,28]. Ever since the isolation of pyrazabole was reported in 1966 by Trofimenko along with the poly(pyrazolyl)borate ion and their free acids, several pyrazaboles with substitution both at the boron atoms and the carbon atoms have been reported [28–34]. Pyrazaboles are relatively more air and moisture stable compared to other boron-nitrogen heterocycle and hence a variety of organic transformations have been carried out resulting in a large number of derivatives bearing various functional groups. Importantly, pyrazaboles have been shown to be useful as building block for discotic liquid crystals [35], linkers of *ansa* ferrocenes to form active container molecules for supramolecular applications [36,37] and for synthesizing luminescent polymers [38,39,10]. Though pyrazaboles mainly crystallize with the boat conformation for the B_2N_4 ring, planar and chair like conformers have also been reported [30,32,40,41]. In general, pyrazaboles with symmetrical 4,8-disubstitutions at the boron atom have been synthesized by the reaction of amine complexes of borane or organoborane reagents with pyrazole under reflux conditions in toluene [27,28]. The other synthetic route employed is by functionalizing the hydrogen coordinated to boron of pyrazabole by other groups [42,43]. In the case of *gem* boron disubstituted or asymmetrically boron monosubstituted materials, the synthesis is challenging due to unpredictable reaction of the bis(pyrazolyl)borate salt with the amine complexes of the boranes bearing good leaving group [44,45].

On the other hand, phenolic pyrazoles (N_2O-type ligand) have been used as ligands for synthesizing multinuclear transition metal clusters; some of which possess interesting magnetic properties [46–51]. But the ligating ability of phenolic pyrazoles (O,N,N-donors) towards main group metals were not known. Recently we have shown the utility of phenolic pyrazoles as ligands for synthesizing organoantimony oxo clusters by carrying out reactions with organostibonic acids [52]. Depending on the steric bulk of the group present in the pyrazole ring, either one or two nitrogen atoms coordinate to the antimony metal leading to the formation of novel tetranuclear clusters. Considering the various applications of organoboron complexes the complexing ability of phenolic pyrazoles towards organoboronic acids have been investigated. The syntheses and structural elucidation of the products are presented in this manuscript.

2. Experimental

2.1. Reagents and general procedure

Phenylboronic acid, solvents and other common reagents were purchased from commercial sources. Ligands were synthesized using literature procedures [53,54].

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2.2. Instrumentation

Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. The ^{1}H, ^{13}C, and ^{11}B solution NMR spectra were recorded on a Bruker DRX 400 instrument. Elemental analysis were performed on a Flash EA series 1112 CHNS analyzer. Single crystal X-ray data collection was carried at 100 k on a Bruker smart Apex CCD area detector system (λ(Mo Kα) = 0.71073 Å), with a graphite monochromotor. The data was reduced using SAINT PLUS and the structure was solved using SHELXS-97 [55] and refined SHELXL-97 [56]. All non-hydrogens are refined anisotopically.

2.3. Synthesis

2.3.1. Synthesis of *1*

Phenylboronic acid (0.15 g, 1.26 mmol), H_2PhPzPh (0.30 g, 1.26 mmol) were taken in 50 ml of toluene and the solution was stirred for 6 h. The white solid which precipitated was filtered and dissolved in ethanol for crystallization. White crystals suitable for X-ray studies were grown over night by slow evaporation. (Yield: 0.40 g, 44%, based on weight of phenylboronic acid). m.p: 260 °C. *Anal.* Calc. for **1**: $C_{23}H_{21}O_2BN_2$: C, 75.01; H, 5.74; N, 7.60. Found C, 75.12; H, 5.89; N, 7.75%. IR (KBr, cm^{-1}) 2964(w), 1614(s), 1574(s), 1485(m), 1460(w), 1431(w), 1319(s), 1267(m), 1167(w), 1107(s), 974(w), 835(w), 748(m), 692(m). ^{1}H NMR ($CDCl_3$): δ 7.65 (t, 3H); 7.39 (q, 6H); 6.9 (d, 5H); 6.86 (d, 2H); 3.68 (q, 2H); 1.14 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 146.89; 145.82; 133.23; 131.74; 131.40; 130.72; 130.06; 129.49; 128.98; 127.87; 127.38; 126.73; 125.73; 125.15; 119.44; 118.78; 97.54 .^{11}B NMR (DMSO): δ 5.0 ppm.

2.3.2. Synthesis of *2*

Phenylboronic acid (0.20 g, 1.64 mmol), H_2PhPztBu (0.35 g, 1.64 mmol) were taken in toluene (50 ml). The solution was refluxed for 6 h using a Dean stark apparatus to remove the water eliminated in the reaction as an azeotropic mixture. The clear solution then formed was cooled to room temperature, filtered and evaporated under reduced pressure to yield a colorless solid. Crystals suitable for X-ray studies were grown from chloroform solution by direct evaporation after a week time. (Yield: 0.45 g, 29.6%, based on the weight of phenylboronic acid). m.p: 192 °C. *Anal.* Calc. for **2**: $C_{57}H_{61}N_6B_3O_5$: C, 72.63; H, 6.52; N, 8.91. Found C, 72.45; H, 6.59; N, 9.03%. IR (KBr, cm^{-1}): 3460(w), 3136(w), 2964(w), 1616(s), 1564(m), 1491(s), 1369(m), 1311(m), 1259(w), 1192(m), 1105(m), 951(m), 856(w), 810(w), 754(s), 704(s), 667(w), 553(w). ^{1}H NMR ($CDCl_3$): δ 7.32 (d, 1H); 7.17 (d, 5H); 7.06 (d, 2H); 6.98 (d, 1H); 6.73 (t, 3H); 0.92 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 157.60; 155.95; 144.86; 134.22; 132.21; 130.95; 127.58; 126.96; 126.70; 125.00; 119.72; 118.59; 114.31; 96.64; 31.48, 30.94, 29.47. ^{11}B NMR ($CDCl_3$): δ 4.8 ppm.

2.3.3. Synthesis of *3*

Synthetic procedure is similar to 2. Amount and stochiometry of the reactants taken are phenylboronic acid (0.15 g, 1.24 mmol), H_2PhPzH (0.20 g, 1.24 mmol). (Yield: 0.25 g 41%, based on the weight of phenylboronic acid). m.p: 270 °C. *Anal.* Calc. for **3**: $C_{30}H_{22}N_4B_2O_2$: C, 73.21; H, 4.50; N, 11.38. Found: C, 73.11; H, 4.55; N, 11.45%. IR (KBr, cm^{-1}): 3117(w), 3067(w), 2964(w), 1614(s), 1574(s), 1537(m), 1502(m), 1448(m), 1412(m), 1365(w), 1313(s), 1249(s), 1205(m), 1124(w), 1051(m), 908(w), 856(w), 835(w), 744(m), 692(m), 646(m), 488(w). ^{1}H NMR ($CDCl_3$): δ 8.28 (d, 2H); 7.60 (d, 2H); 7.27 (t, 2H); 7.02 (d, 2H); 6.92 (m, 4H); 6.78 (d, 6H); 6.70 (d, 2H). ^{13}C NMR ($CDCl_3$): δ 153.65; 143.39; 134.58; 131.73; 130.79; 126.87; 126.81; 125.27; 120.06; 119.65; 115.69; 101.19. ^{11}B NMR ($CDCl_3$): δ 3.6 ppm.

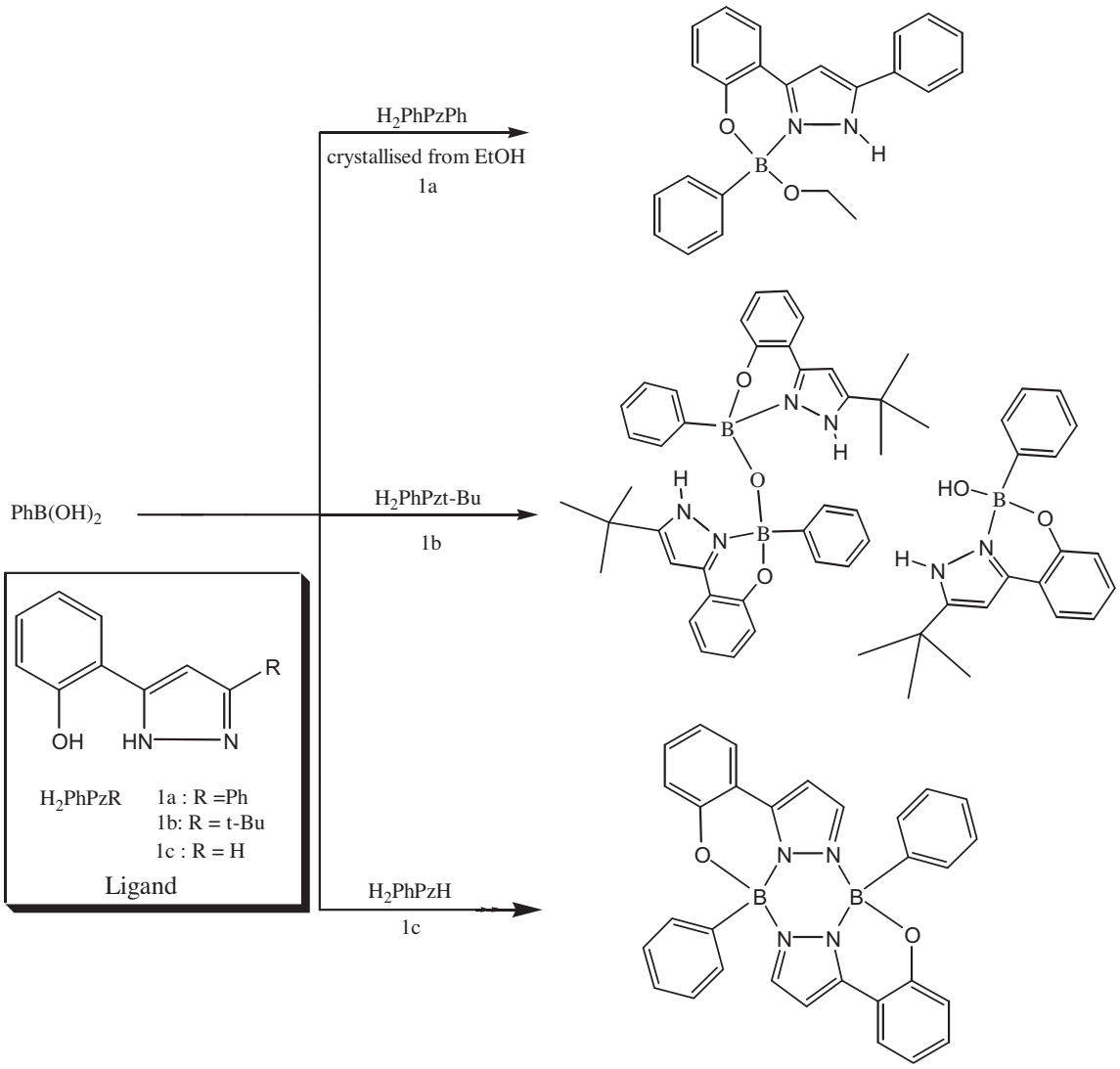
3. Results and discussion

General synthetic method used is as follows. Phenylboronic acid and phenolic pyrazole (H_2PhPzR, where R = Ph **1**, t-Bu **2**, H **3**) were either stirred at room temperature (for **1**) or refluxed in toluene for 6 h (**2** and **3**) until a clear solution was obtained. When reflux condition was employed, the water formed during the reaction was removed as an azeotropic mixture using a Dean Stark apparatus. Compound **1** dissolved in high polar solvents like ethanol and methanol whereas **2** and **3** dissolved in a wide range of solvents like dichloromethane, chloroform and toluene. Compounds **1**–**3** were characterized using standard spectroscopic and analytical techniques. IR spectrum of **2** shows the presence of a broad peak around 3067 cm^{-1} which can be attributed to the presence of OH group. ^{11}B NMR for **1**–**3** (in DMSO for **1**, $CDCl_3$ for **2** and **3**) shows single resonance at 5.0, 4.8 and 3.6 ppm, respectively, which is in similar range as reported in literature for analogous organoboron compounds. The products were crystallized in ethanol (**1**) and chloroform (**2** and **3**) to isolate crystals suitable for single crystal X-ray diffraction analysis. Crystallographic data and refinement details for **1**, **2** and **3** are provided in Table 1. Structural elucidation revealed the formation of PhB(HPhPzPh)(OEt) **1**, [(PhB)(PhPzHt-Bu)(OH)][(PhB)$_2$(PhPzt-Bu)$_2$(O)] **2** and (PhBPhPz)$_2$ **3** (Scheme 1).

Compound **1** crystallizes in monoclinic space group *P*2(1)/*n* (Fig. 1). The ligand H_2PhPzPh binds to the boron atom through

Table 1
Crystal data and structure refinement details for 1, 2 and 3.

	1	2	3
Formula	$C_{23}H_{21}BN_2O_2$	$C_{59}H_{63}B_3Cl_6N_6O_5$	$C_{30}H_{22}B_2N_4O_2$
Formula weight	368.23	1181.28	492.14
Crystal system	monoclinic	orthorhombic	monoclinic
Crystal size (mm)	0.22 × 0.16 × 0.10	0.26 × 0.18 × 0.14	0.24 × 0.18 × 0.12
Space group	*P*2(1)/n	pbca	*P*2(1)/*n*
a (Å)	12.248(9)	17.970(17)	12.302(7)
b (Å)	11.880(9)	24.943(2)	10.243(6)
c (Å)	12.844(9)	26.735(2)	19.898(12)
α (°)	90	90	90
β (°)	95.452(10)	90	104.812(10)
γ (°)	90	90	90
V (Å^3)	1860.6(2)	11983.5(17)	2424.1(2)
Z	4	8	4
D_{calc} (mg m^{-3})	1.315	1.310	1.348
T (K)	100(2)	100(2)	100(2)
μ (mm^{-1})	0.084	0.340	0.085
F(0 0 0)	776	4928	1024
θ (°)	2.20–24.99	1.52–25.03	1.77–25.09
Index ranges	$-14 \leqslant h \leqslant 14$ $-14 \leqslant k \leqslant 14$ $-15 \leqslant l \leqslant 15$	$-21 \leqslant h \leqslant 21$ $-29 \leqslant k \leqslant 29$ $-31 \leqslant l \leqslant 31$	$-14 \leqslant h \leqslant 14$ $-12 \leqslant k \leqslant 12$ $-23 \leqslant l \leqslant 23$
Number of reflections collected	16 900	108 902	22 718
Completeness to θ_{max} (%)	99.9	99.2	99.8
Number of independent reflections	3266	10 513	4308
Goodness-of-fit (GOF)	1.076	1.112	1.004
R_1 (*F*) ($I > 2\sigma(I)$)	0.0556	0.0984	0.0364
wR_2	0.1211	0.1971	0.0912
Largest difference in peak and hole (e Å^{-3})	0.228 and −0.202	0.731 and −0.553	0. 247 and −0.239



Scheme 1.

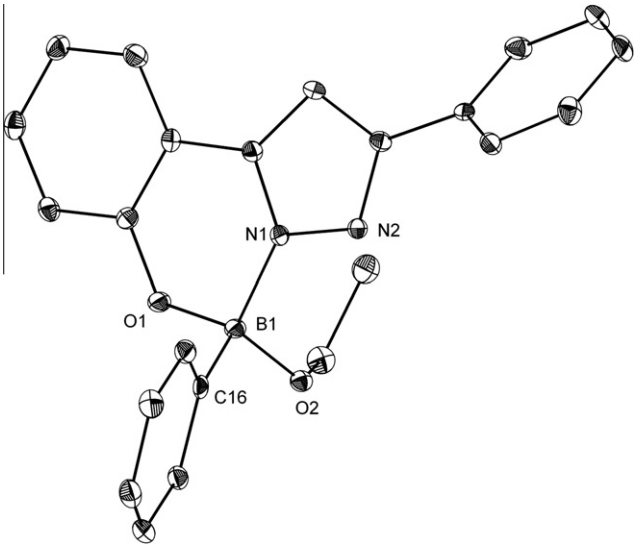


Fig. 1. ORTEP view of **1**. Thermal ellipsoids have been set at the 30% probability level. Selected bond lengths (in Å) and bond angles (in deg) in 1: B1–O1 = 1.477(3), B1–O2 = 1.459(3), B1–N1 = 1.590(3), B1–C16 = 1.600(4), N1–N2 = 1.348(2), O1–B1–C16 = 111.42(19), O1–B1–N1 = 104.76(18), O2–B1–N1 = 109.40(18), O1–B1–O2 = 110.05(19), O2–B1–C16 = 109.27(18), B1–N1–N2 = 124.40(17).

the pyrazole N atom and the phenolic oxygen while the other nitrogen of the pyrazole group bearing the hydrogen atom remains a spectator. The remaining two coordinations of the tetrahedral boron atom come from the phenyl carbon and oxygen of ethoxy group. Since ethanol was used for crystallization, the unreacted OH group from the phenylboronic acid is present as the ethoxy derivative in **1**. The crude product was not characterized by ^{1}H NMR as they were not isolated, but the crystals formed from ethanol shows the peaks corresponding to the ethyl groups present in **1** (Section 2). Selected bond lengths (Å) and angles (deg) for **1** are given in the figure caption 1. The B–O bond distances in **1** are 1.477(3) Å (B1–O1) and 1.459(3) Å (B1–O2). The phenolic oxygen to boron is slightly longer than the B–O_{ethoxy} group. The B–N bond distance is 1.590(3) Å, which falls in the range as reported in literature for tetrahedral boron atoms containing B–N bonds [57]. The % THC [58] of boron in **1** was found to be 99.73 which confirms that the boron atom is in a perfect tetrahedral site. It is of interest to mention here that monometallic boron compounds are a rarity when compared to the other elements of group 13 like aluminum, gallium and indium which readily forms monometallic complexes even with flexible salen-type N_2O_2 ligands. The isolation of a monometallic near perfect tetrahedral organoboron complex is probably due to the chelating O,N-donor atoms of the phenolic pyrazole.

Organoboron compound **2** crystallizes in orthorhombic space group pbca (Fig. 2). Despite several attempts the structure refinement for **2** was poor due to the inferior quality of the crystals obtained. However the data was sufficiently good to arrive at the core structure. The asymmetric unit consists of an oxo bridged boron dimer and a organoboron monomer. The mode of binding of the ligand H_2PhPzt-Bu in **2** is similar to that of H_2PhPzPh in **1**. The only difference observed is that the fourth coordination of boron in **1** was from an ethoxy group whereas in **2** it is from a μ_2-bridging oxo group. Since the compound was crystallized from chloroform, the B–OH group combines with a similar moiety of a neighboring boron atom forming an oxo bridged dimer eliminating a water molecule in the process. Similar observations have been reported earlier for organoboron compounds involving other ligand systems wherein crystallization from chlorinated solvents or acetonitrile have led to the formation of oxo-bridged dimers. Moreover, in the crystal lattice of **2**, a organoboron phenolic pyrazolyl complex similar to **1** co-crystallizes with the dimer. Hence we propose that a monometallic compound is formed initially which subsequently dimerises by water elimination leading to the formation of an oxo bridged dimer. The dimer and monomer are held together by hydrogen bonds. Selected bond lengths and angles for **2** are given in the figure caption 2. The B–O distances are similar to that of **1**. The phenolic oxygen to the boron atom bond distances are slightly longer than the boron to oxygen atoms of the μ_2-bridging oxo and the terminal OH groups. The B–O (phenolic) distances fall in the range 1.493(6) to 1.504(6) Å; the B–O (μ_2-bridging) being 1.427(6) and 1.446(6) Å and B–O (terminal OH) distance being 1.439(6) Å, respectively. The B–N bond distances fall in the range 1.591(6) to 1.612(7) Å, which is in the range as reported in literature for monometallic tetrahedral organoboron compounds containing B–N bonds indicating the coordinative nature of the bond [57]. The % THC of boron in **2** are 99.11 (B1), 98.67 (B2) and 99.50 (B3) which confirms that the boron atoms in **2** are also in a near perfect tetrahedral site. The B2–O2–B3 bond angle is 128.6(4)° which again falls in the range as reported earlier in literature for oxo-bridged boron dimmers [23].

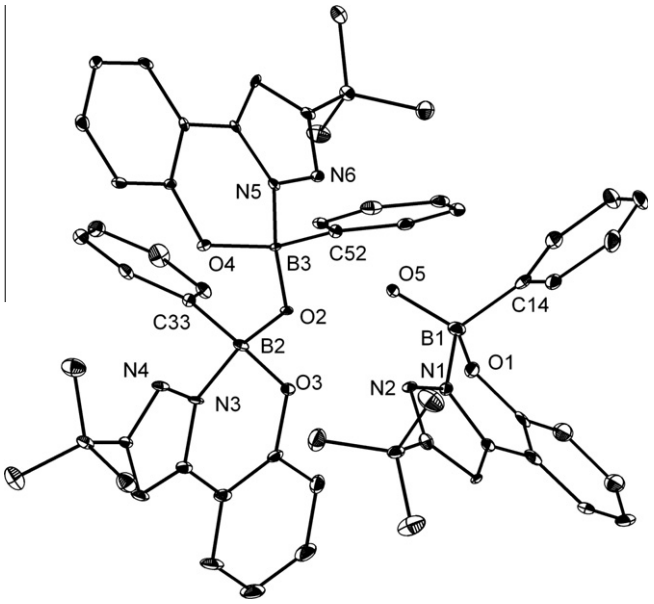


Fig. 2. ORTEP view of **2**. Thermal ellipsoids have been set at the 30% probability level. Selected bond lengths (in Å) and bond angles (in deg) in 2: B1–O1 = 1.493(6), B1–O5 = 1.439(6), B1–N1 = 1.612(7), B1–C14 = 1.615(7), B2–O2 = 1.446(6), B2–O3 = 1.495(6), B2–N3 = 1.591(6), B2–C33 = 1.622(7), B3–O2 = 1.427(6), B3–O4 = 1.504(6), B3–N5 = 1.591(6), B3–C52 = 1.628(7), O1–B1–N1 = 102.2(4), O5–B1–N1 = 110.6(4), O5–B1–C14 = 114.2(4), O1–B1–C14 = 110.6(4), O1–B1–O5 = 109.3(4), O2–B2–O3 = 105.2(4), O3–B2–N3 = 103.6(3), N3–B2–C33 = 108.9(4), O2–B2–C33 = 110.5(4), C33–B2–O3 = 110.5(4), O2–B3–O4 = 110.9(4), O4–B3–N5 = 104.0(3), N5–B3–C52 = 108.5(3), O2–B3–C52 = 112.5(4), N5–B3–O2 = 109.6(4), B2–O2–B3 = 128.6(4).

Compound **3** crystallizes in monoclinic space group *P*2(1)/*n* (Fig. 3). Structural elucidation reveals the stabilization of the B_2N_4 heterocycle, pyrazabole. The ligand chelates to the boron atom through the O,N-end while the other nitrogen of the pyrazole coordinates to the second boron atom and subsequent dimerization leads to the formation of the *cis*-pyrabazole with the boat conformation for the B_2N_4 ring. The B–O distances for B1–O1 and B2–O2 are 1.458(2) and 1.449(2) Å, respectively, and the B–N distances fall in the range 1.570(1) to 1.575(2) Å. Selected bond lengths and angles for **3** are given in the figure caption 3. The isolation of pyrazabole by reaction of arylboronic acid with phenolic pyrazole is interesting since it provides an easy access to this heterocycle bearing substitutions at both the boron and carbon atoms. Compared to earlier reports where pyrazabole has been synthesized either by reactions of the highly reactive amine complexes

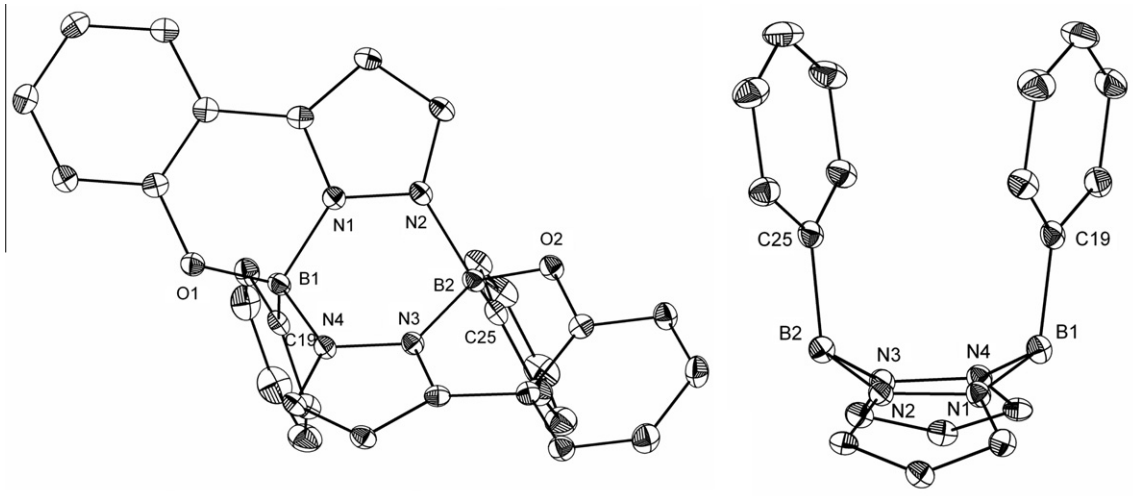


Fig. 3. ORTEP view of **3**. Thermal ellipsoids have been set at the 30% probability level. Selected bond lengths (in Å) and bond angles (in deg) in 3a and 3b are O1–B1 = 1.458(18), B1–N1 = 1.575(18), B1–N4 = 1.570(18), B1–C19 = 1.609(2), O2–B2 = 1.449(17), B2–N2 = 1.570(18), B2–N3 = 1.571(17), B2–C25 = 1.607(2), O1–B1–N4 = 108.06(11), N4–B1–C19 = 112.11(11), O1–B1–C19 = 113.54(11), O1–B1–N4 = 108.06(11), O2–B2–N2 = 108.51(11), O2–B2–N3 = 107.23(10), N2–B2–N3 = 102.51(10), O2–B2–C25 = 112.52(11), N2–B2–C25 = 111.31(11), N3–B2–C25 = 114.15(11), N1–B1–C19 = 113.16(11).

of borane or air and moisture sensitive organoborane reagents with pyrazole, our method of assembling this B_2N_4 heterocycle is more facile. Moreover, in the present case we exclusively get the *cis*-isomer probably due to the nature of the substituents present on both boron and carbon atoms. By varying the groups on boron and carbon atoms isolation of the *trans* isomer could be possible and work in that direction is currently under progress.

Recently, we have investigated the reactions of phenolic pyrazoles with organostibonic acids wherein the presence of phenyl or tert-butyl groups on the 5-position of the pyrazole ring led to the formation of isostructural tetranuclear organoantimony oxo clusters wherein the pyrazoles chelated to the metal atoms through the O,N-end while the other N atom of the pyrazole is noncoordinating [52]. But when arylstibonic acids were reacted with phenolic pyrazoles with hydrogen on the 5-position of the pyrazole ring the ligand bound to the Sb atoms through both chelating (O,N-) and bridging (N,N-) mode. Herein, when phenolic pyrazole is reacted with phenylboronic acid the substitution on the pyrazole ring directs the structure of the products. When phenyl or tert-butyl substituents are present the ligand binding mode is purely chelating (O,N-atoms) while the presence of hydrogen on the 5th position of the pyrazole encourages both the chelating (O,N-) and bridging (N,N-) mode. In the case of organoantimony oxo clusters both phenyl and tert-butyl substituents on the pyrazole led to the isolation of isostructural compounds whereas in the present case it varies due to the difference in the solvent of crystallization employed for **1** and **2**. Earlier reports [59] on organoboron complexes suggest that crystallization in chlorinated solvents or acetonitrile may lead to isolation of oxo bridged boron dimers which is probably the reason why despite similar mode of ligand binding in **1** and **2**, products with different nuclearity have been isolated. When the 5-position of the pyrazole ring bears a less bulky group like hydrogen, the phenolic pyrazolyl ligand binds to the metal centre through both the O,N-mode and N,N-bridging mode and subsequent dimerization leads to the formation of pyrazabole.

4. Conclusion

To summarize, the reactions of phenylboronic acid with phenolic pyrazoles (H_2PhPzR, where R = Ph **1**, t-Bu **2**, H **3**) have been investigated. Single crystal X-ray analysis shows the formation of a monometallic organoboron complex, an oxo bridged dimer and pyrazabole, a B_2N_4 heterocycle. It is of interest to mention that by modifying the groups present on the pyrazole ring interesting organoboron compounds have been isolated in good yield. In particular, the formation of a rare monometallic organoboron monomer and pyrazabole by this simple and straight forward reaction methodology is significant considering the recent interest in the applications of organoboron reagents and pyrazabole.

Acknowledgements

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Appendix A. Supplementary material

CCDC 798198, 798200 and 798199 contain the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.01.104.

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