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O,*N*-Chelated boron aminophenolate complexes. Crystal structure of $BPh_2(OC_6H_4(CH_2NMe_2)\text{-}2)$

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Abstract

Two diphenylboron *ortho*-aminophenolate complexes, $[BPh_2(OC_6H_4(CH_2NMe_2)\text{-}2)]$ (**2**) and $[BPh_2(OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4)]$ (**6**), have been prepared in a one-pot procedure approach starting from $B(OMe)_3$. The starting material was reacted with two equivalents of phenylmagnesium bromide, followed by hydrolysis with HCl. The resulting borinic acid, $BPh_2(OH)$, was reacted with either $HOC_6H_4(CH_2NMe_2)\text{-}2$ or $HOC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4$ to give **2** or **6**, respectively. An X-ray structure determination of **2** showed it to be a four-coordinate boron compound with a tetrahedral coordination geometry. The six-membered chelate ring in **2** is puckered. Variable temperature ^1H-NMR analysis of **6** showed the existence of two dynamic processes in solution, i.e. one process involving flipping of the puckered chelate ring conformation ($\Delta G^\ddagger = 41$ kJ mol^{-1}) and a second, higher energy, process ($\Delta G^\ddagger = 65$ kJ mol^{-1}) in which exchange of coordinated and non-coordinated amine functions occurs. The exchange is (at least partly) assisted intermolecularly.

Keywords: Boron; Phenolate; Polymorph; Fluxional processes

1. Introduction

Recent studies on the use of *ortho*-aminophenolates ($ON = [OC_6H_4(CH_2NMe_2)\text{-}2]^-$) as ancillary ligands in vanadium-based catalysts for the polymerization of α-olefins have given promising results [1]. Treatment of the vanadium(IV) oxo (bis)phenolate $[VO(OC_6H_4(CH_2NMe_2)\text{-}2)_2]$, with thionyl chloride yields $[VCl_2(OC_6H_4(CH_2NMe_2)\text{-}2)_2]$ (**1**), which shows high activity in ethene polymerization with Et_2AlCl as cocatalyst. While investigating the halide displacement reaction of **1** with several non-coordinating, non-nucleophilic anions, we performed a reaction with two equivalents of $NaBPh_4$. After crystallization of the reaction mixture from a THF–dioxane solution over a period of several months a crystalline compound was obtained, which, according to the crystal structure determination, was a neutral boron compound, $[BPh_2(OC_6H_4(CH_2NMe_2)\text{-}2)]$ (**2**). This is an interesting observation, as it points out that the *ortho*-aminophenolate ligands used as ancillary ligands are transferable under certain conditions. Accordingly, when these ligands are used in vanadium-based Ziegler–Natta type polymerizations of α-olefins with alkylaluminium compounds as cocatalysts, it is not unlikely that the *ortho*-aminophenolate ligands either form μ^2-*O* bridges between vanadium and aluminium centers or even are completely transferred to aluminium.

We set out to synthesize **2** and thus obtain its spectroscopic data in order to monitor the formation of **2** in the above-mentioned reaction between **1** and $NaBPh_4$.

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2. Experimental

All reactions were performed in an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were carefully dried and distilled prior to use. The phenols $HOC_6H_4(CH_2NMe_2)$-2 and $HOC_6H_3(CH_2NMe_2)_2$-2,6-Me-4 were prepared according to literature procedures [2]. Et_3N was distilled from CaH_2. $B(OMe)_3$ was distilled from sodium sand. All other chemicals were obtained from commercial sources and used as received. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim, Germany. ^1H and ^{13}C-NMR spectra were recorded on a Bruker AC300 or a Varian Unity Inova 300 spectrometer. ^{11}B-NMR and ^{19}F-NMR spectra were recorded on a Varian Unity Inova 300 spectrometer both relative to an external standard, ($BF_3 \cdot Et_2O$/$CDCl_3$ 15/85 v/v) and $CFCl_3$/C_6D_6. NMR spectra were recorded at 25°C and chemical shifts are in ppm.

2.1. Synthesis of [$BPh_2(OC_6H_4(CH_2NMe_2)$-2)] (**2**)

PhMgBr (1 M in Et_2O, 18 ml, 18 mmol) was added to a solution of $B(OMe)_3$ (1 ml, 8.8 mmol) in Et_2O (40 ml) at −75°C. The resulting suspension was stirred at −75°C for 4 h after which it was allowed to warm to room temperature. After stirring for an additional 48 h the precipitate formed was removed by centrifugation and subsequent decantation. Hydrochloric acid (1 M, 50 ml) was added to the decanted ethereal solution and the biphasic system was stirred vigorously for 2 h. After separation of the layers a solution of $HOC_6H_4(CH_2NMe_2)$-2 (1.33 g, 8.8 mmol) in Et_2O (100 ml) was added to the ethereal layer. A white precipitate was formed and the resulting suspension was stirred for 24 h. Removal of the solvent in vacuo and washing of the residue with pentane (40 ml) gave a white solid. This solid was dissolved in THF (20 ml) and subsequent cooling of the solution to −20°C gave white crystals of **2** (0.39 g, 14%). M.p.: 182°C.

Anal. Calc. for $C_{21}H_{22}NOB$: C, 80.02; H, 7.04; N, 4.44; Found: C, 79.84; H, 6.95; N, 4.36%.

^1H-NMR (300 MHz, $CDCl_3$): δ 2.69 (s, 6H, NMe_2), 3.77 (s, 2H, CH_2), 6.8 (m, 2H, Ar–H), 7.3 (m, 8H, Ar–H), 7.9 (m, 4H, Ar–H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 47.3 (NMe_2), 62.1 (CH_2), 117.2 (OAr–C^2), 118.2 and 119.0 (OAr–C), 126.5 (Ar–C^4), 127.1 (OAr–C), 127.3 (Ar–C), 129.6 (OAr–C), 133.5 (Ar–C), 156.0 (OAr–C^1), Ar–C^1 not observed.

^{11}B-NMR (96.3 MHz, $CDCl_3$): δ 5.41 (br, $\Delta v_{1/2} = 92$ Hz).

2.2. Synthesis of $Me_3SiOC_6H_4(CH_2NMe_2)$-2 (**3**)

$HOC_6H_4(CH_2NMe_2)$-2 (9.29 g, 61 mmol) was added dropwise to a solution of Me_3SiCl (10.1 ml, 80 mmol) and Et_3N (11 ml, 80 mmol) in Et_2O (200 ml). Immediately a white precipitate was formed and the resulting suspension was stirred for 24 h. After removing the precipitate by filtration, the solvent was removed in vacuo. Flash distillation of the residue gave a colorless oil (16.1 g, 45%).

^1H-NMR (300 MHz, $CDCl_3$): δ 0.28 (s, 9H, $SiMe_3$), 2.25 (s, 6H, NMe_2), 3.49 (s, 2H, CH_2), 6.80 (dd, 1H, $^3J_{H,H} = 8$, $^4J_{H,H} = 1$ Hz, Ar–H), 6.94 (dt, 1H, $^3J_{H,H} = 7$, $^4J_{H,H} = 1$ Hz, Ar–H), 7.13 (dt, 1H, $^3J_{H,H} = 8$, $^4J_{H,H} = 2$ Hz, Ar–H), 7.31 (dd, 1H, $^3J_{H,H} = 7$, $^4J_{H,H} = 2$ Hz, Ar–H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 0.5 ($SiMe_3$), 45.4 (NMe_2), 58.0 (CH_2), 119.0, 121.1, 127.8, 129.4 and 131.0 (Ar–C), 153.9 (Ar–C^1).

2.3. Synthesis of [$BF_2(OC_6H_4(CH_2NMe_2)$-2)] (**4**)

$Me_3SiOC_6H_4(CH_2NMe_2)$-2 (5.55 g, 24.8 mmol) was added to a solution of $BF_3 \cdot Et_2O$ (16.5 ml, 24.8 mmol) in Et_2O (100 ml). The resulting mixture was stirred for 7 h after which the solvents were removed in vacuo leaving a white solid. This solid was dissolved in CH_2Cl_2 (20 ml) and subsequently cooled to −20°C, which yielded white crystals of **4** (2.47 g, 50%). M.p.: 143°C.

Anal. Calc. for $C_9H_{12}NOBF_2$: C, 54.32; H, 6.08; N, 7.04; Found: C, 54.26; H, 6.19; N, 6.96%.

^1H-NMR (300 MHz, $CDCl_3$): δ 2.71 (s, 6H, NMe_2), 4.05 (s, 2H, CH_2), 6.86 (dt, 1H, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 1$ Hz, Ar–H), 6.95 (m, 2H, Ar–H), 7.23 (dt, 1H, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 2$ Hz, Ar–H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 45.0 (NMe_2), 60.9 (CH_2), 116.0 (Ar–C^2), 119.0, 120.0, 126.7 and 129.8 (Ar–C), 153.3 (Ar–C^1).

^{11}B-NMR (96.3 MHz, $CDCl_3$): δ 0.76 (t, $^1J_{^{19}F,^{11}B} = 17$ Hz).

^{19}F-NMR (282 MHz, $CDCl_3$): δ −164.19 (1:1:1:1 q, $^1J_{^{11}B,^{19}F} = 17$ Hz).

2.4. Attempted synthesis of [$B(OMe)_2(OC_6H_4(CH_2NMe_2)$-2)] (**5**)

A mixture of $B(OMe)_3$ (8 ml, 70.4 mmol) and $HOC_6H_4(CH_2NMe_2)$-2 (10.6 g, 70 mmol) in Et_2O (300 ml) was refluxed for 10 h. After removal of the solvent in vacuo ^1H-NMR analysis showed the product to be a mixture of $HOC_6H_4(CH_2NMe_2)$-2 and $B(OMe)_2(OC_6H_4(CH_2NMe_2)$-2) in a molar ratio of 1:2.

2.5. Synthesis of [$BPh_2(OC_6H_2(CH_2NMe_2)_2$-2,6-Me-4)] (**6**)

An ethereal solution of PhMgBr (36 ml, 1 M, 36 mmol) was added to $B(OMe)_3$ (2 ml, 17.6 mmol) in Et_2O (80 ml) at −75°C. A white precipitate was formed and the mixture was stirred at −75°C over a period of 1 h after which it was allowed to warm to room temperature. The precipitate was removed by centrifugation and decantation of the upper layer and was extracted with Et_2O (30 ml). An aqueous HCl solution (100 ml, 4 M) was added to the combined ethereal fractions and the resulting biphasic system was stirred vigorously for 1 h. After separation of the layers a solution of $HOC_6H_3(CH_2NMe_2)_2$-2,6-Me-4 (3.98 g, 17.9 mmol) in Et_2O (20 ml) was added to the ethereal fraction. A white precipitate was formed and the resulting mixture was stirred for 16 h. The solution was removed by centrifugation and decantation and the residue was dried in vacuo leaving a white solid (1.98 g). Crystallization from THF at −20°C gave colorless crystals (0.8 g, 12%). ^{1}H-NMR analysis showed these crystals to be a 9:1 mixture of the diphenylboron monophenolate [$BPh_2(OC_6H_2(CH_2NMe_2)_2$-2,6-Me-4)] (**6**) and the phenylboron (bis)phenolate [$BPh(OC_6H_2$-$(CH_2NMe_2)_2$-2,6-Me-4$)_2$] (**7**).

^{1}H-NMR (300 MHz, $CDCl_3$) (**6**): δ 2.28 (s, 3H, Me), 2.44 (br, 6H, NMe_2), 2.69 (br, 6H, NMe_2), 3.78 (br, 2H, CH_2), 3.81 (br, 2H, CH_2), 6.56 (s, 1H, O–Ar–$H^{3,5}$), 7.23 (m, 7H, Ar–H), 7.85 (dd, 4H, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 1$ Hz, B–Ar–$H^{2,6}$), (**7**): δ 2.23 (s, 6H, Me), 2.30 (s, 24H, NMe_2), 3.53 (s, 8H, CH_2), 6.84 (s, 4H, O–Ar–H), 7.1–7.3 (m, 3H, Ar–H), 7.82 (dd, 2H, $^3J_{H,H} = 8.0$ Hz, $^4J_{H,H} = 1.4$ Hz, B–Ar–$H^{2,6}$).

^{11}B-NMR (96.3 MHz, $CDCl_3$) (**6**): δ 4.97.

2.6. X-ray crystallographic structure determination and refinements

Colorless crystals of **2** suitable for X-ray diffraction were grown from a saturated THF solution at −20°C. A crystal suitable for X-ray structure analysis was glued onto the tip of a glass fiber, and transferred into the cold nitrogen stream of a Enraf–Nonius CAD4-T diffractometer. Reduced-cell calculations did not indicate higher lattice symmetry [3]. Crystal data and details on data collection are collected in Table 1. Data were collected at 150 K, using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Absorption corrections (PLATON/DELABS [4]) were applied and the structure was solved using direct methods and subsequent difference Fourier techniques (SHELXS-97 [5]). The structure was refined on F^2 using full-matrix least-square techniques (SHELXL-97 [6]); no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Weights were introduced in the last refinement cycles. Neutral atomic scattering factors and anomalous dispersion corrections were taken from the International Tables of Crystallography [7]. Geometrical calculations and illustrations were performed with PLATON [4].

Table 1
Crystallographic data for **2**

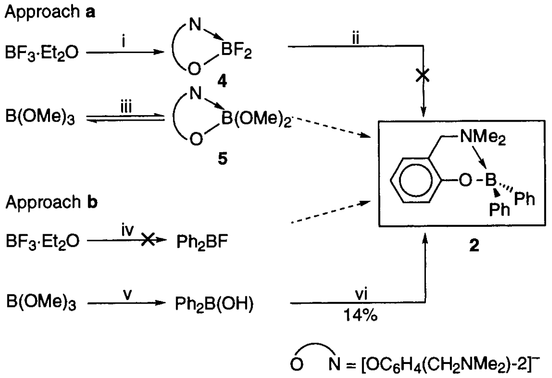
Empirical formula	$C_{21}H_{22}BNO$
Formula weight	315.21
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
a (Å)	10.2595(6)
b (Å)	12.6171(6)
c (Å)	12.7453(8)
V (Å^3)	1649.82(16)
Z	4
D_{calc} (g cm^{-3})	1.269
μ(Mo–K_α) (cm^{-1})	0.8
F(000)	672
T, K	150
Final $R1$ [a]	0.0594
Final $wR2$ [b]	0.1129
Goodness-of-fit	1.02

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, for all $I > 2\sigma(I)$.

[b] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

3. Results and discussion

Two different reaction routes were explored for the synthesis of the diphenylboron *ortho*-aminophenolate **2** (see Scheme 1). In the first one (approach a), the chelating phenolate ligand was introduced followed by phenylation. In the second (approach b), a diphenylboron compound was synthesized first followed by introduction of the *ortho*-aminophenolate ligand. Following approach a, $BF_3 \cdot Et_2O$ was reacted with the trimethylsilyl ether $Me_3SiOC_6H_4(CH_2NMe_2)$-2 (**3**), to give the difluoroboron *ortho*-aminophenolate [$BF_2(OC_6H_4(CH_2NMe_2)$-2)] (**4**) (Scheme 1, i). It ap



Scheme 1. (i) One equivalent $Me_3SiOC_6H_4(CH_2NMe_2)$-2 (**3**), Et_2O, r.t.; (ii) Two equivalents PhMgBr, THF, reflux; (iii) One equivalent $HOC_6H_4(CH_2NMe_2)$-2, Et_2O, reflux; (iv) Two equivalents PhMgBr, Et_2O, −75°C; (v) Two equivalents PhMgBr, Et_2O, −75°C; 1 M HCl; (vi) One equivalent $HOC_6H_4(CH_2NMe_2)$-2, Et_2O, r.t.

peared that the reaction of **4** with two equivalents of phenylmagnesium bromide did not lead to the formation of the desired compound **2** (Scheme 1, ii) even after refluxing in THF for 5 days. The reason is probably that fluoride is too poor a leaving group to allow substitution of fluoride by phenyl anions.

For this reason the same reaction sequence was attempted starting from trimethylborate, $B(OMe)_3$. This was reacted with the *ortho*-aminophenol $HOC_6H_4(CH_2NMe_2)$-2 in refluxing Et_2O (Scheme 1, iii). Unfortunately, this reaction resulted in an equilibrium mixture of $[B(OMe)_2(OC_6H_4(CH_2NMe_2)\text{-}2)]$ (**5**) and the starting phenol $HOC_6H_4(CH_2NMe_2)$-2 in a 2:1 molar ratio. The desired boron compound could not be separated from the *ortho*-aminophenol due to similar solubilities.

The second approach b requires that first a diphenylboron compound is prepared. This is problematic because it is known that substitution at boron halides is difficult to stop at the stage of diorganoboron products [8]. Indeed, treatment of $BF_3{\cdot}Et_2O$ with two equivalents of phenylmagnesium bromide (Scheme 1, iv) did not result in the formation of Ph_2BF, as was shown by ^{11}B-NMR. However, starting from alkyl borates it is possible to introduce the phenyl groups and subsequently the *ortho*-aminophenolate anion, according to the synthesis of $BPh_2(OC_2H_4NH_2)$ [9]. Consequently, in a one-pot procedure $B(OMe)_3$ was reacted with two equivalents of phenylmagnesium bromide, followed by hydrolysis with HCl (Scheme 1, v). The resulting borinic acid, $BPh_2(OH)$, was not isolated, but was directly reacted with $HOC_6H_4(CH_2NMe_2)$-2 (Scheme 1, vi). Compound **2** was obtained as an analytically pure solid after crystallization from THF albeit in a relatively low yield. We have not optimized the reaction conditions as we were primarily interested in the properties and spectroscopic data of **2**.

Similarly, also the preparation of the analogous boron compound containing a bis(*ortho*-amino)phenolate ligand, $[BPh_2(OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4)]$ (**6**), was attempted. Compound **6** could not be obtained in pure form, because a second compound, i.e. the phenylboron (bis)phenolate $[BPh(OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4)_2]$ (**7**), was always present as an impurity. At first we believed that the presence of **7** was caused by the disproportionation of **6** into BPh_3 and **7**. A similar reaction has been reported earlier for the dimethylaluminium analogue, $[AlMe_2(OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4)]$, which disproportionates into $[AlMe(OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4)_2]$ and $(AlMe_3)_2$ [10]. However, ^{1}H-NMR analysis never showed any evidence for this disproportionation reaction. Even after prolonged heating in either $CDCl_3$ or THF-d_8 no formation of **7** was observed. Hence, it appears that the origin of **7** has to be found in the formation of boronic acid, $BPh(OH)_2$, during the hydrolysis step.

The stability of **6** towards disproportionation is sharply contrasted by the stability of the aluminium analogue. In the latter case the compound itself was never observed except as a 1:1 $AlMe_3$ adduct, $[AlMe_2(OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4)(N\text{–}AlMe_3)]$. A difference in size of the metal center ($B < Al$) and the organic group ($Ph > Me$) may be the reason for this difference. A μ^2-*O*-bridging dimer has been postulated as the first intermediate for the disproportionation of $[AlMe_2(OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4)]$ [10]. Both the size of the metal center and the organic group make the formation of this dimeric intermediate in the case of **6** more difficult and accordingly the disproportionation reaction slower, viz. not occurring. A similar difference in steric requirements is also the basis of the fact that all organo–boron compounds (except hydrides and some fluorides and alkoxides) are monomeric, whereas most organo–aluminium compounds are dimeric [11,12].

4. X-ray of $BPh_2(OC_6H_4(CH_2NMe_2)\text{-}2)$ (2)

The crystals of **2** originally obtained from THF–dioxane turned out to produce a poor data set during the X-ray measurement. However, crystallization of **2** from THF gave single crystals suitable for X-ray structure analysis. Its molecular structure is depicted in Fig. 1 and selected bond lengths and angles are given in Table 2.

The molecular structure shows the boron atom to be surrounded tetrahedrally by the η^2-*O*,*N*-bonded aminophenolate anion and the two phenyl groups. A search in the Cambridge Crystallographic Database revealed that although six structures with a similar general formula '$Ar_2(ArO)B{\cdot}N$' (N; nitrogen donor ligand) have been structurally characterized, none of these involve a sp^3-hybridized nitrogen atom coordinating to the boron [13].

In this structure the B–C, B–O and O–C distances fall in the range reported for four-coordinate boron–phenyl and –phenolate complexes, (1.597–1.630 Å) [13a,13e], (1.450–1.513 Å) [13b,14] and (1.326–1.364 Å) [13e,14], respectively. The C–O–B angle is about 5° larger than in these Schiff base complexes, but is comparable to the C–O–B angle of the non-chelating phenolate in the tetrahedral boron phenolate compound $[BPh(OPh)(OCH_2CH_2NMe_2)]$ [15]. The difference in bond angle is probably caused by the shorter sp^2-nitrogen–carbon distance in the Schiff base complexes. The six-membered chelate ring in **2** is puckered with the NMe_2 group above the B–O–C1–C2–C7 plane.

This crystal structure is a polymorph of the crystal structure originally obtained from THF–dioxane. Both crystal systems are orthorhombic, but the crystals from THF have a $P2_12_12_1$ space group with unit cell dimensions $a = 10.2595(6)$; $b = 12.6171(6)$ and $c = 12.7453(8)$

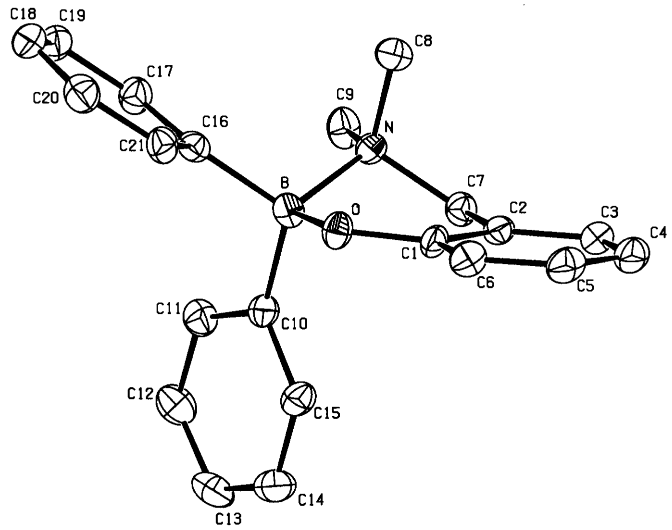


Fig. 1. Displacement ellipsoid plot of **2**, drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
B–O	1.486(4)	B–C10	1.625(4)
B–N	1.674(5)	B–C16	1.616(5)
O–C1	1.357(3)		
Bond angles			
B–O–C1	125.6(2)	N–B–C10	109.4(2)
O–B–N	104.5(2)	N–B–C16	112.7(2)
O–B–C10	110.2(3)	C10–B–C16	113.7(2)
O–B–C16	105.8(2)		

Å, whereas the crystals from THF–dioxane have a *Pbca* space group with unit cell dimensions $a = 13.1885(10)$; $b = 12.8710(10)$ and $c = 19.8890(20)$ Å.

5. Properties and NMR analysis of 2, 4 and 6

Both compounds **2** and **4** are white solids which melt at 182 and 143°C, respectively. The ^{11}B-NMR chemical shifts of 5.41, 0.71 and 4.97 ppm found for **2**, **4** and **6**, respectively, are indicative for four-coordinate boron compounds [16]. Compound **4** shows a coupling to the two fluorine atoms with a splitting of 17 Hz. The same splitting is visible in the ^{19}F-NMR, in which the fluorine resonance appears as a 1:1:1:1 quartet due to coupling with the ^{11}B nuclear spin of 3/2.

The fluxional behavior of **6** having two *ortho*-CH_2NMe_2 substituents was studied with variable temperature ^{1}H-NMR both in toluene-d_8 from −85 to 60°C and in $CDCl_3$ from −65 to 60°C. In toluene-d_8 at low temperatures (below −75°C) two sets of signals, A and B, respectively, are observed for both the benzylic protons and the Me protons of the NMe_2 groups. The benzylic protons are visible as a poorly resolved doublet (CH_2-A) and an AB-pattern (CH_2-B), whereas the NMe_2 groups are seen as one singlet (NMe_2-A) and one pair of singlets (NMe_2-B). The *ortho*-protons of the phenyl rings (*o*-Ar–H) are visible as a pair of singlets. The coupling to the *meta*-protons of the phenyl ring ($^3J_{H,H}$) was not observed because of the broadness of the signals. Upon increasing the temperature the signals for CH_2-A, CH_2-B, NMe_2-B and *o*-Ar–H coalesce and they appear as four singlets. For both NMe_2-B and CH_2-B the coalescence temperature in toluene-d_8 is −68°C ($\Delta G^{\ddagger} = 41$ kJ mol^{-1}), while the coalescence temperature for *o*-Ar–H is −63°C ($\Delta G^{\ddagger} = 41$ kJ mol^{-1}). All three energies of activation have equal values, which indicates that one process is responsible for the coalescence of the signals of NMe_2-B, CH_2-B and *o*-Ar–H. The coalescence temperature for CH_2-A has not been determined.

Above −60°C the signals for the two NMe_2 groups, the two pairs of benzylic protons and the two *meta*-protons of the phenolate ring are visible as three pairs of singlets. Above 50°C these three pairs appear as three singlets in both $CDCl_3$ and toluene-d_8. In $CDCl_3$ $\Delta\delta$ is smaller than in toluene-d_8. Consequently, the signals in $CDCl_3$ suffer less broadening near the coalescence temperature, which makes the determination of the coalescence temperature more accurate. The coalescence temperature in $CDCl_3$ for the NMe_2 groups is 45°C ($\Delta G^{\ddagger} = 65$ kJ mol^{-1}) and is concentration independent within experimental error, whereas the coalescence temperature for the benzylic protons is concentration dependent (17°C at 7 mM; 32°C at 133 mM; $\Delta G^{\ddagger} = 65$ kJ mol^{-1}). Also the chemical shift difference ($\Delta\delta$) between the two singlets of both the benzylic protons as well as the NMe_2 protons is concentration dependent (see Fig. 2). The $\Delta\delta$ for the benzylic protons increases upon increasing the concentration, whereas the $\Delta\delta$ for the NMe_2 protons becomes smaller. Similar behavior is observed upon the addition of Lewis bases like benzyldimethylamine or 2-methoxytoluene. Apart from this, also a change is observed in the linewidths of the signals associated with the coordinated amine function; i.e. they decrease with an increase of the concentration. The linewidths of the signals for the non-coordinated amine function are constant within experimental error. Unfortunately, the coalesence temperature for the aryl protons could not be determined as the signals coincided with those of the other aromatic protons.

To account for these observations two dynamic processes have to be considered. At low temperatures (below 10°C) the B–N bond is rigid on the NMR time scale and a stable six-membered chelate ring exists. Consequently, there is no molecular plane of symmetry perpendicular to the arene ring, which contains both C1 and C4. As a result, two signals are observed for the benzylic protons, the NMe_2 protons as well as the *meta*-protons of the arene ring. The first dynamic process occurring in toluene-d_8 at temperatures below −60°C involves the six-membered chelate ring. This ring is puckered as was shown by the X-ray structure of **2**. Since the puckering of the ring represents an element of dissymmetry, the molecule exists in two enantiomeric conformations (λ and δ) [17]. These conformations can interconvert by means of flipping of the chelate ring (see Fig. 3). In the slow exchange limit (below −68°C) the benzylic protons (H1 and H2), the methyl groups on nitrogen (Me1 and Me2) and the phenyl groups on boron (Ph1 and Ph2) are diastereotopic and they appear as an AB-pattern and two sets of singlets. The prochiral benzylic protons of the non-coordinated amine functionality (CH_2-A) are diastereotopic as well. However, the difference in chemical shift between the two protons is of approximately the same order of magnitude as the coupling constant, and a pseudo-doublet is observed. The two methyl groups of the non-coordinated NMe_2 group (NMe_2-A) appear as one singlet, because both pyramidal inversion and rotation around the benzylic carbon–nitrogen axis, which can take place in a non-coordinated CH_2NMe_2 group, are processes with very small activation barriers. Increasing the temperature makes the ring-flip fast on the NMR time scale and this introduces an apparent molecular plane of symmetry. This renders the substituents on the chelate ring as well as the benzylic protons of the non-coordinated amine functionality enantiotopic and they appear as singlets.

The second dynamic process involves exchange between the coordinated and the non-coordinated amine functionalities. This process requires initial B–N bond dissociation and becomes detectable above 10°C. Above this temperature the CH_2, NMe_2 and *meta*-arene protons start to coalesce indicating that a second dynamic process introduces an apparent molecular plane of symmetry in the molecule. As the coalesence temperature for the benzylic protons is concentration dependent, it seems likely that the exchange is intermolecularly assisted, i.e. by reversible coordination of an external base. The effect of addition of either benzyldimethylamine or 2-methoxytoluene on the $\Delta\delta$ of both CH_2 and NMe_2 is similar to that of increasing the concentration, thus indicating that in a solution of **6** coordination can occur either via an amine nitrogen or via a phenolate oxygen atom. We propose that coordination of a free amine nitrogen N′ to a second molecule of **6** (see Scheme 2) results in a de-coordination of N*. Subsequent rotation around the B–O axis, coordination of N and de-coordination of N′ results in an exchange of the amino-functionalities and re-formation of two monomeric species. The second coordination mode would be via a μ^2-bridging phenolate oxygen. Such a coordination mode would result in formation of a dimeric species that is similar to the first intermediate in the disproportionation reaction of the aluminium analogue of **6**. However, it was found that this disproportionation reaction is not observed for **6** (vide supra). This was tentatively assigned to a difference in steric requirements of the metal center (B < Al) and the organic group (Ph > Me) and these two parameters make the formation of the μ^2-*O*-bridging dimeric intermedi-

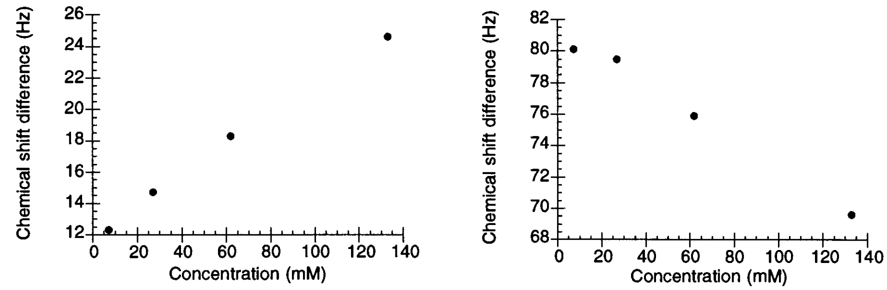


Fig. 2. $\Delta\delta$ (at 0°C) against the concentration for CH_2 (left) and NMe_2 (right) of **6**.

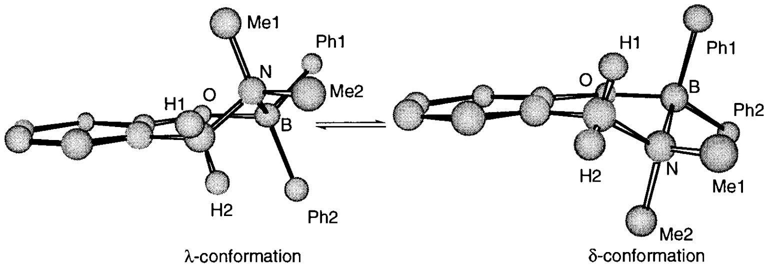
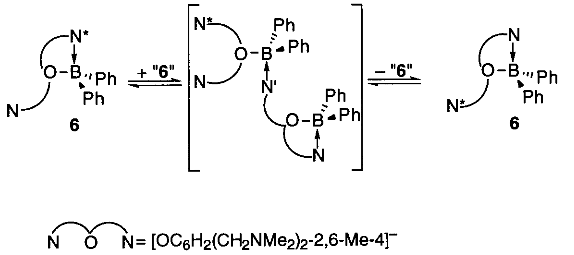


Fig. 3. Ring-flip of the six-membered chelate ring of **6**. The second *ortho*-CH_2NMe_2 substituent is omitted for clarity.



Scheme 2. Possible intermolecularly-assisted exchange mechanism in **6** with *N*-donor ligands.

ate less favorable. Based on the data obtained for the present exchange reaction it is not possible to prove which mechanism is operative, but the kinetics of the disproportionation reaction seem to suggest that amine-assisted exchange is most likely. It must be noted that it is not possible to exclude the role of intramolecular exchange.

6. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 137 899 for compound **2** and CCDC no. 137 888 for the polymorph obtained from THF–dioxane. Copies can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: + 44-1123-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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