

Switching of Two Amine Ligands via an S_N2 -type Mechanism in a Coordinated Form of 2,6-Bis(*N,N*-dimethylaminomethyl)phenylboronates

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Facile exchange between the intramolecularly coordinated and uncoordinated amine ligands in the title compounds is evidenced by NMR spectroscopy in solution, whereas the dynamic process is frozen in the solid phase as shown by X-ray crystallography.

Dynamic NMR studies of 2-(*N,N*-dimethylaminomethyl)-phenylboronates **1** revealed that the dissociation of the intramolecular N–B coordination bond was significantly accelerated in nucleophilic solvents such as diethyl ether and acetone, and this rate enhancement was attributed to the assistance of solvent molecules by approaching from the back-side of the leaving amine ligand (S_N2 -type mechanism).¹ Although this mechanistic explanation was indirectly supported by introducing a bulky moiety around the boron atom,² further studies to gain direct evidence for this explanation were limited because of the structural constraints of the system. Introduction of another amine ligand at the remaining *o*-position is another approach to the verification of the mechanism, where the second amine ligand instead of solvent molecules can strongly interact with the boron atom from the back-side of the coordinated ligand. Therefore, we synthesized the title organoboron complexes **2** with a 2,6-bis(*N,N*-dimethylaminomethyl)phenyl group.³ This communication reports the interesting dynamic behaviour of these organoboron compounds, involving facile exchange of the two amine ligands as well as the X-ray crystallographic structure.

Compounds **2a** and **2b**† were synthesized from 2,6-bis(*N,N*-dimethylaminomethyl)phenylboronic acid⁴ with an appropriate 1,2-diol in 79 and 97% yield, respectively.¹ The ¹H NMR spectrum of **2a** gave three singlets in the aliphatic region at δ 2.41 (NCH₃), 3.69 (NCH₂) and 4.10 (OCH₂) at room temperature in CD₂Cl₂, these signals showing no line shape changes even though the sample was cooled to -100°C . Compound **2b** also gave three singlets for the aliphatic groups at room temperature. Among them, only the benzylic methylene protons exhibited line shape changes from a singlet to an AB quartet as the temperature was lowered, whereas the signals due to the *N*-methyl and *O*-methylene protons were singlets throughout the temperature range examined.

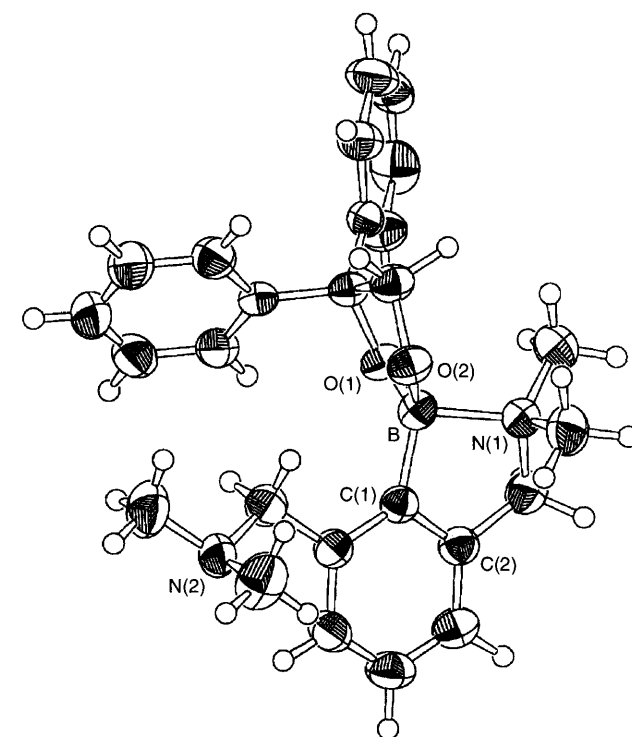
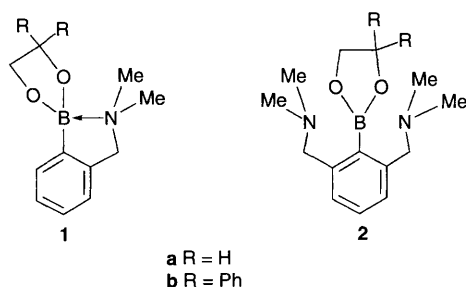
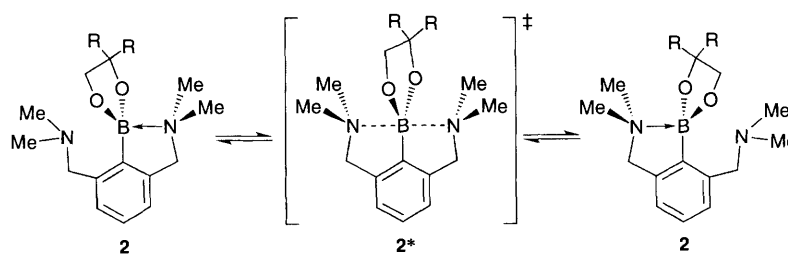
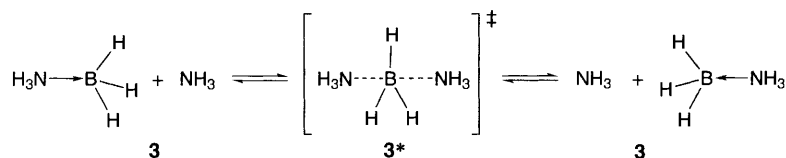


Fig. 1 Crystal structure of **2b** with thermal ellipsoids with 50% probabilities. Selected bond distances (pm) and angles ($^\circ$): B–N(1) 176.2(3), B–C(1) 159.9(3), B–O(1) 144.3(3), B–O(2) 143.2(2), N(1)–B–C(1) 96.2(1), O(1)–B–C(1) 116.1(2), O(2)–B–C(1) 121.0(2), B–C(1)–C(2) 111.6(2).



Scheme 1



Scheme 2

atom is favourable from the entropy viewpoint. Therefore, the energy gap between the transition state and the initial state for the N–B bond dissociation is considerably decreased by the introduction of the second ligand. This process can be regarded as an isoelectronic model for the $\text{S}_{\text{N}}2$ reaction at a carbon atom.

MO (*ab initio*) calculations \ddagger for a simplified model also support this idea. In the $\text{S}_{\text{N}}2$ -type process shown in Scheme 2, the trigonal-bipyramidal structure at the boron atom 3^* (D_{3h}) was the transition state, whose energy level is higher by 56.5 kJ mol^{-1} than the original state **3**, a system of 1:1 complex and ammonia. This energy gap is much smaller than the dissociation energy of a borane–ammonia complex (144.7 kJ mol^{-1}) 5 calculated at the same level as an $\text{S}_{\text{N}}1$ -type process. This result implies the importance of the $\text{S}_{\text{N}}2$ -type dissociation in boron chemistry although the solvation is ignored in the calculations.

The kinetic parameters for the site exchange of the benzylic methylene protons in **2b** were obtained as $\Delta H^\ddagger = 67.3 \pm 1.2$ kJ mol^{-1} , $\Delta S^\ddagger = 41 \pm 5$ $\text{J mol}^{-1} \text{K}^{-1}$ and $\Delta G_{273}^\ddagger = 56.0$ kJ mol^{-1} from the total line shape analysis. \S The rate-limiting step of this dynamic behaviour must be the restricted rotation around the $\text{C}_{\text{Ph}}\text{--B}$ bond. If the bond rotation were much faster than the nitrogen inversion at the free amine ligand 6 and the ligand exchange, the observed line shape changes, where all signals except the benzylic protons remain unchanged in the temperature range, would not rationally be explained.

The single crystal X-ray structure of **2b** \parallel indicates that the molecule takes a singly-coordinated structure, where the boron atom has tetrahedral geometry with one coordinated amine ligand while the other amine ligand remains uncoordinated (Fig. 1). The N–B bond distance of 176.2 pm is comparable to that in compound **1b**. 7 This structure is consistent with the ^{13}C NMR data at the solid state, \parallel in which two sets of the dimethylamino-methyl groups were observed.

In conclusion, these experimental and theoretical data suggest that the organoboron complexes **2** exist as singly coordinated structures both in crystal and in solution, whereas the switching between the two amine ligands takes place very fast only in solution *via* a pentacoordinated boron species. The unstable nature of the pentacoordinated structure 2^* is attributed to the lack of sufficient electronegativity of the amine ligand, 8 because boron-centred hypervalent compounds with strongly electronegative apical ligands are reported. 9

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Footnotes

\ddagger Selected data for **2a**: mp 88–89 °C; ^1H NMR (400 MHz, CDCl_3 , 20 °C) δ 2.41 (12 H, s), 3.69 (4 H, s), 4.10 (4 H, s), 7.11 (2 H, d, J 7.4 Hz) and 7.20

(1 H, t, J 7.4 Hz); ^{13}C NMR (100 MHz, CDCl_3 , 27 °C) δ 45.4, 63.1, 64.7, 124.6, 127.9 and 141.6. For **2b**: mp 139.5–141.5 °C; ^1H NMR (400 MHz, CDCl_3 , 20 °C) δ 2.16 (12 H, s), 3.49 (4 H, s), 4.81 (2 H, s), 7.12 (2 H, d, J 7.1 Hz), 7.14 (2 H, t, J 7.3 Hz), 7.22 (1 H, t, J 7.1 Hz), 7.26 (4 H, t, J 7.4 Hz) and 7.56 (4 H, d, J 7.1 Hz); ^{13}C NMR (100 MHz, CDCl_3 , 27 °C) 45.5, 63.1, 74.5, 84.5, 124.2, 125.5, 126.2, 127.9, 128.1, 141.8 and 148.9; ^{11}B NMR (128.3 MHz, CDCl_3 , 20 °C, $\text{BF}_3 \cdot \text{OEt}_2$) δ 14.4.

\ddagger *Ab initio* calculations were performed by GAUSSIAN 92 program 10 on a Convex computer. Total energies for the transition state (3^*) and the initial state (**3**) were -139.20578 and -139.22736 Hartree, respectively, at the MP2/6-31G* basis set level.

\S Total line shape analysis of the signals due to the benzylic methylene protons in **2b**, where the prochirality arises from the tetrahedral boron atom, was performed by DNMR3K program, a modified version of DNMR3 program 11 by Prof. H. Kihara of Hyogo University of Teacher Education, Japan.

\parallel Crystal data for **2b**: $\text{C}_{26}\text{H}_{31}\text{N}_2\text{BO}_2$, $M_w = 414.35$, orthorhombic, space group $Pbca$, $a = 2059.1(3)$, $b = 2432.2(3)$, $c = 919.5(2)$ pm, $V = 4.604(1)$ nm^3 , $Z = 8$, $D_c = 1.195$ g cm^{-3} , $\mu = 5.83$ cm^{-1} . Rigaku AFC7R diffractometer using Cu-K α radiation ($\lambda = 154.178$ pm), 3900 reflections with $2\theta < 120^\circ$, of which 2775 with $[I > 1.0\sigma(I)]$ was used for the refinement. The structure was solved by the direct method (SHELXS86). $R = 0.039$, $R_w = 0.028$. Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

\parallel Solid state ^{13}C NMR data for **2b**: (75.5 MHz, CP-seltics, spin rate 4000 Hz) δ 44.5 and 48.0 (NCH_3), 60.9 and 66.0 (NCH_2), 73.0 (OCH_2), 84.0 (OCPh_2) (only aliphatic signals are shown).

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