## Deprotonation from an *N*-Methyl Group in 2-[1-(Dimethylamino)-1-methylethyl]phenylborane Derivatives

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Summary: Reaction of 2-[1-(dimethylamino)-1-methylethyl]phenyllithium ( $Ar^*Li$ ) with a trialkyl borate,  $B(OR)_3$ , in the 3:1 ratio gave 1- $Ar^*$ -3,4,4-trimethyl-1,2,3,4-tetrahydro-3,1-benzazaborin as a major product together with the corresponding protonated compound and the boronic acid. The structure of the hetelocyclic compound was determined by X-ray analysis and NMR spectroscopy. This compound is formed via the deprotonation from one of the N-Me groups in  $Ar^*_2B(OR)$  by the remaining  $Ar^*Li$  followed by the facile intramolecular cyclization between the boron and carbon atoms.

## Introduction

Recently, we revealed that the amine ligand in 2-[1-(dimethylamino)-1-methylethyl]phenyl group 1 (Ar\*) coordinated to the attaching boron atom more tightly than that in 2-[1-(dimethylamino)methyl]phenyl group 2 (Ar) (Chart 1), on the basis of kinetic data.<sup>1-3</sup> By using the bulky C,N-bidentate ligand 1, we attempted to prepare sterically congested organoboron complexes, for instance BAr<sup>\*</sup><sub>2</sub>X and BAr<sup>\*</sup><sub>3</sub>, from the structural and stereodynamic interests.<sup>4</sup> However, the reaction of a trialkyl borate with an appropriate amount of Ar\*Li yielded no desired compounds but an unexpected compound (7), in which one of the N-Me carbons was bonded to the boron atom, as a major product: this type of product has never been reported in the series of studies of the intramolecular organoboron complexes to our knowledge.<sup>1–3,5</sup> This paper is to report the identification of the new heterocyclic product and a plausible mech-



anism of its formation, in which deprotonation from an N-Me group is the key step.

## **Results and Discussion**

The organolithium compound Ar\*Li (4), prepared from Ar\*Br (3) and BuLi by the literature method,<sup>1</sup> was treated with a 1:3 molar ratio of triisopropyl borate in ether. After the workup, three major products were found in the reaction mixture, Ar\*H (5), Ar\*B(OH)<sub>2</sub> (6), and another product, **7**, in 46, 9, and 40% yields, respectively (Scheme 1). The reactions with other trialkyl borates, B(OMe)<sub>3</sub>, B(OEt)<sub>3</sub>, and B(OPr)<sub>3</sub>, gave the same product, **7**, although the yields were low (ca. 5%).<sup>6</sup>

The structure of **7** was established by X-ray analysis (Figure 1). A molecule consists of one boron atom and two Ar\* groups, and an *N*-Me carbon in one of the Ar\*

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<sup>(6)</sup> It is difficult to explain the substituent effect of trialkyl borates on the yield of 7 from available data. We consider that the stability of the alkoxy boranes, 8 and 9 in Scheme 2, plays a role in determining the yield of 7. The reactions with  $BF_3$  or  $BCl_3$  gave a complicated mixture, in which no 7 was detected spectroscopically.



**Figure 1.** ORTEP drawing of **7** (50% probability ellipsoids). Selected structural parameters: N(1)-B 1.723-(5), C(1)-B 1.579(6), C(12)-B 1.608(6), C(22)-B 1.599(6) Å; C(1)-B-C(12) 115.8(4), C(1)-B-C(22) 115.8(4), C(12)-B-C(22) 105.2(4)°; tetrahedral character<sup>7</sup> 73%.



groups is attached to the boron atom. Further coordination of the amine ligand in the other Ar\* group allows the boron atom to take a tetrahedral structure. The B–N coordination bond in 7 (1.723 Å) is a little shorter than those in similar 9-BBN complexes (ca. 1.75 Å).<sup>7</sup>

The NMR data are consistent with the structure. The <sup>1</sup>H NMR spectrum of **7** showed seven methyl signals and an AB quartet in the aliphatic region, this signal pattern being expected from the structure with a chiral center at the boron atom. The <sup>11</sup>B NMR chemical shift of 3.3 ppm is typical for tetracoordinated boron atoms.<sup>8</sup>

A plausible mechanism of the formation of **7** is illustrated in Scheme 2. At first, the substitution of  $Ar^*$  groups at the boron atom affords  $Ar^*B(O^iPr)_2$  (**8**) and

then  $Ar_{2}B(O^{i}Pr)$  (9). The tight coordination and the steric hindrance prevent another molecule of  $Ar^{*}Li$  from attacking the boron atom in 9. Instead,  $Ar^{*}Li$  works as a base to abstract a proton from one of the *N*-Me groups. It is known that the acidity of  $\alpha$ -protons in *tert*-amines is considerably increased by the coordination of Lewis acids such as  $BF_{3.}^{9,10}$  Therefore, the deprotonation from an *N*-Me group at the coordinating amine ligand (9 $\rightarrow$ 10) is likely under the conditions. Thus formed 10 readily undergoes intramolecular substitution of the anionic carbon at the boron atom to give 7.

In the reaction mixture, we could not find any products derived from **9** such as  $Ar_{2}^{*}BOH$  by spectroscopic analyses, this indicating that the deprotonation takes place faster than the substitution of the second  $Ar^{*}$  group at the boron atom. The proposed mechanism explains the formation of a moderate amount of **5**, which is produced by the deprotonation of **9** by  $Ar^{*}Li$  and partly by hydrolysis of the unreacted  $Ar^{*}Li$  during the workup. Taking into account the reaction yields, ca. 60% of the original organolithium compound is consumed by the formation of **7** as a source of  $Ar^{*}$  groups (40%) and as a base (20%).

To see the influence of the benzylic methyl groups on the reactivity, 2-[1-(dimethylamino)methyl]phenyllithium (ArLi) was treated with triisopropyl borate under the same conditions. The reaction did not give a product like 7 but triarylborane, BAr<sub>3</sub> (12), together with the corresponding boronic acid. The presence of the *gem*dimethyl group strongly hinders the substitution of the third aryl group at the boron atoms.

## **Experimental Section**

<sup>1</sup>H NMR spectra were measured on a Varian Gemini-300 and a Bruker AMX-R400 spectrometer operating at 300 and 400 MHz, respectively. <sup>13</sup>C NMR were measured by the Varian machine at 75 MHz. <sup>11</sup>B NMR were measured on the Bruker machine at 128.4 MHz with external reference of BF<sub>3</sub>:OEt<sub>2</sub> at 0 ppm. Melting points are uncorrected. Mass spectra were measured on a JEOL MStation-700 spectrometer.

Reaction of 2-[1-(Dimethylamino)-1-methylethyl]phenyllithium (4) with Triisopropyl Borate. A solution of 500 mg (2.1 mmol) of 1-bromo-2-[1-(dimethylamino)-1methylethyl]benzene (3)<sup>1</sup> in 5 mL of dry ether was cooled to -78 °C, and to the solution was added 1.3 mL (2.1 mmol) of 15% butyllithium solution in hexanes under nitrogen atmosphere. The solution of 4 was allowed to warm to room temperature and then stirred for 2 h. To the solution was slowly added a solution of 132 mg (0.70 mmol) of triisopropyl borate in 2 mL of dry ether at -78 °C. After the removal of the cooling bath, the mixture was stirred for 15 h at room temperature. The volatile materials were removed by evaporation, and the residue was treated with 5 mL of wet dichloromethane. After the removal of insoluble materials by filtration, the solvent was evaporated to give a mixture of the products as an oil. The product distributions were determined by the integral intensities of <sup>1</sup>H NMR signals. [1-(Dimethylamino)-1-methylethyl]benzene (5) and 2-[1-(dimethylamino)-1-methylethyl]phenylboronic acid (6)<sup>1</sup> were identified by com-

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<sup>(10)</sup> Theoretical calculations of a model reaction ( $NH_3 + L:NMe_3 \rightarrow NH_4^+ + L:NMe_2CH_2^-$ ) also support this phenomenon. The energy required for the process is decreased by 31.7 kcal/mol by changing L from none to BF<sub>3</sub> at the HF/3-21G\* level.



**Figure 2.** ORTEP drawing of **12**·H<sub>2</sub>O (30% probability ellipsoids).

parison of their spectroscopic data with those of the authentic samples, the former being commercially available. The yields of the products **5**, **6**, and **7** were 150 mg (46%), 36 mg (9%), and 140 mg (40%), respectively, based on the organolithium reagent. The yield of **7** was decreased when the reaction mixture was stirred for longer time or at higher temperatures.

**1**-{**[1-(Dimethylamino)-1-methylethyl]phenyl**}-3,4,4**trimethyl-1,2,3,4-tetrahydro-3,1-benzazaborin (7).** The crude product was treated with an appropriate amount of hexane-dichloromethane to afford 56 mg (16% isolated yield) of **7** as colorless crystals. Mp: 157–158 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.27 (s, 3H), 1.52 (s, 3H), 1.58 (s, 3H), 1.59 (s, 3H), 1.94 and 2.28 (ABq, *J* = 13.7 Hz, 2H), 2.34 (s, 3H), 2.36 (s, 3H), 2.62 (s, 3H), 6.83–6.93 (m, 2H), 7.09–7.22 (m, 5H), 7.30 (d, 1H, *J* = 8.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 20.7, 25.4, 28.3, 29.8, 41.9, 43.9, 45.1, 59.6, 73.0, 120.7, 123.5, 125.9, 126.1, 126.2, 127.1, 130.1, 135.6, 148.9, 153.3. Signals due to carbons attaching to the boron atom could not be detected. <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$  = 3.3 (line width *h*<sub>1/2</sub> 193 Hz). HRMS (FAB, MH<sup>+</sup>): found 334.2695, calcd for C<sub>22</sub>H<sub>32</sub>BN<sub>2</sub> 334.2584.

**Reaction of 2-[1-(Dimethylamino)methyl]phenyllithium (ArLi) with Triisopropyl Borate.** A suspension of the organolithium compound in ether was prepared from 0.62 mL (4.1 mmol) of *N*,*N*-dimethylbenzylamine with butyllithium in an ordinary manner.<sup>11</sup> This compound was similarly treated with 263 mg (1.4 mmol) of triisopropyl borate as above. From the reaction mixture, 121 mg (20%) of BAr<sub>3</sub> (**12**) was isolated as an adduct with water. This compound slowly decomposed

Table 1. Crystal and Structure Analysis Data of7 and 12·H2O

	7	<b>12·</b> H <sub>2</sub> O
formula	C <sub>22</sub> H <sub>31</sub> BN <sub>2</sub>	C <sub>27</sub> H <sub>38</sub> BN <sub>3</sub> O
fw	334.31	431.43
crystal size (mm <sup>3</sup> )	$0.30 \times 0.13 \times 0.10$	$0.50\times0.25\times0.15$
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	8.160(2)	15.2299(9)
<i>b</i> (Å)	12.021(2)	8.5721(6)
<i>c</i> (Å)	20.478(2)	20.3491(6)
$\beta$ (deg)	93.50(1)	107.730(3)
$V(Å^3)$	2005.1(6)	2530.4(2)
Ζ	4	4
$D_{\rm c}$ (g/cm <sup>3</sup> )	1.107	1.132
$\mu$ (Cu K $\alpha$ ) (cm <sup>-1</sup> )	4.76	5.25
scan width (deg)	$1.31 \pm 0.30 \tan \theta$	$1.84 \pm 0.30  an  heta$
scan rate (deg/min)	8.0	12.0
no. of unique data	3161 ( $2^{\circ} < 2\theta < 120^{\circ}$ )	$3762 (2^{\circ} < 2\theta < 120^{\circ})$
no. of data used	<b>2506</b> ( $F_0 > 2.0\sigma(F)$ )	3762 ( $F_0 > 0.0\sigma(F)$ )
R(F)	0.066	0.053
$R_{\rm w}(F)$	0.072	0.061

in the air. Mp: 110.5–111.5 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.09 (br, 18H), 3.24 (br, 6H), 7.00–7.18 (m, 12H). HRMS (FAB, MH<sup>+</sup>): found 432.3212 and 413.3141, calcd for C<sub>27</sub>H<sub>37</sub>BN<sub>3</sub>·H<sub>2</sub>O and C<sub>27</sub>H<sub>37</sub>BN<sub>3</sub>, 432.3186 and 413.3117, respectively. *N*,*N*-Dimethylbenzylamine and 2-[(dimethylamino)methyl]phenylboronic acid<sup>11c</sup> were found in the reaction mixture.

**X-ray Crystallography.** Crystals of **7** and **12** (Figure 2) used for the X-ray measurements were grown from hexanedichloromethane and dichloromethane solutions, respectively. The diffraction data were collected on a Rigaku AFC7R fourcircle diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at room temperature. The scan mode was the  $\omega - 2\theta$  method. The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method by using a teXsan program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic ones for hydrogens. The reflection data were corrected for Lorentz and polarization effects and secondary extinction. The function minimized was  $\sum [w(|F_0| - |F_c|)^2]$ , where  $w = [\sigma_c^2 |F_0|]^{-1}$ . Additional crystal and analysis data are listed in Table 1.

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**Supporting Information Available:** Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles of **7** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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