Notes

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

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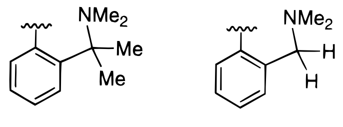
*Summary: Reaction of 2-[1-(dimethylamino)-1-methylethyl]phenyllithium (Ar*Li) with a trialkyl borate, B(OR)$_3$, in the 3:1 ratio gave 1-Ar*-3,4,4-trimethyl-1,2,3,4-tetrahydro-3,1-benzazaborin as a major product together with the corresponding protonated compound and the boronic acid. The structure 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*$_2$B(OR) by the remaining Ar*Li followed by the facile intramolecular cyclization between the boron and carbon atoms.*

Introduction

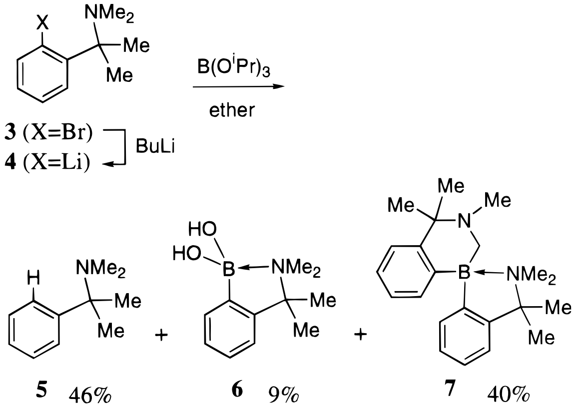
Recently, we revealed that the amine ligand in 2-[1-(dimethylamino)-1-methylethyl]phenyl group **1** (Ar*) coordinated to the attaching boron atom more tightly than that in 2-[1-(dimethylamino)methyl]phenyl group **2** (Ar) (Chart 1), on the basis of kinetic data.[1−3] By using the bulky *C*,*N*-bidentate ligand **1**, we attempted to prepare sterically congested organoboron complexes, for instance BAr*$_2$X and BAr*$_3$, from the structural and stereodynamic interests.[4] 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.[1−3,5] This paper is to report the identification of the new heterocyclic product and a plausible mechanism of its formation, in which deprotonation from an *N*-Me group is the key step.

Chart 1



1 (Ar*) **2** (Ar)

Scheme 1



3 (X=Br)
4 (X=Li)
5 **6** **7**

Results and Discussion

The organolithium compound Ar*Li (**4**), prepared from Ar*Br (**3**) and BuLi by the literature method,[1] 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)$_2$ (**6**), and another product, **7**, in 46, 9, and 40% yields, respectively (Scheme 1). The reactions with other trialkyl borates, B(OMe)$_3$, B(OEt)$_3$, and B(OPr)$_3$, gave the same product, **7**, although the yields were low (ca. 5%).[6]

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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[1] Toyota, S.; Asakura, M.; Futawaka, T.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1879.

[2] Toyota, S.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1168.

[3] For recent other papers in the series: (a) Toyota, S.; Futawaka, T.; Ikeda, H.; Ōki, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2499. (b) Toyota, S.; Futawaka, T.; Asakura, M.; Ikeda, M.; Ōki, M. *Organometallics* **1998**, *17*, 4155. (c) Toyota, S.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1554.

[4] (a) Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019. (b) Brown, H. C.; Dodson, V. H. *J. Am. Chem. Soc.* **1957**, *79*, 2302.

[5] (a) Lauer, M.; Wulff, G. *J. Organomet. Chem.* **1983**, *256*, 1. (b) Kalbarczyk, E.; Pasynkiewicz, S. *J. Organomet. Chem.* **1984**, *262*, 11. (c) Horner, L.; Kaps, U.; Simons, G. *J. Organomet. Chem.* **1985**, *287*, 1. (d) Lauer, M.; Böhnke, H.; Grotstollen, R.; Salehnia, M.; Wulff, G. *Chem. Ber.* **1985**, *118*, 246. (e) Schlengermann, R.; Sieler, J.; Hey-Hawkins, E. *Main Group Chem.* **1997**, *2*, 141.

[6] 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.

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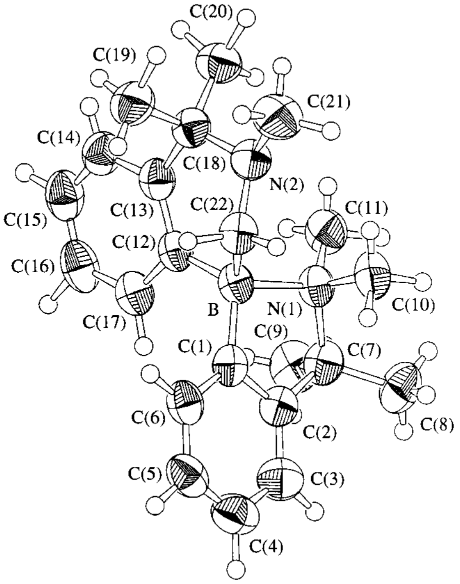
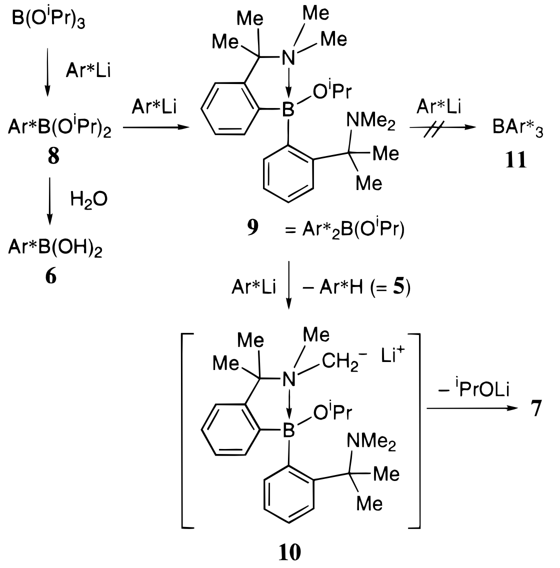


Figure 1. ORTEP drawing of **7** (50% probability ellipsoids). Selected structural parameters: N(1)−B 1.723(5), C(1)−B 1.579(6), C(12)−B 1.608(6), C(22)−B 1.599(6) Å; C(1)−B−C(12) 115.8(4), C(1)−B−C(22) 115.8(4), C(12)−B−C(22) 105.2(4)°; tetrahedral character[7] 73%.

Scheme 2



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).[7]

The NMR data are consistent with the structure. The ^{1}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 ^{11}B NMR chemical shift of 3.3 ppm is typical for tetracoordinated boron atoms.[8]

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^{i}Pr)$_2$ (**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 α-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**→**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$_3$ (**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

^{1}H NMR spectra were measured on a Varian Gemini-300 and a Bruker AMX-R400 spectrometer operating at 300 and 400 MHz, respectively. ^{13}C NMR were measured by the Varian machine at 75 MHz. ^{11}B NMR were measured on the Bruker machine at 128.4 MHz with external reference of BF$_3$:OEt$_2$ 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)-1-methylethyl]benzene (**3**)[1] 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 ^{1}H NMR signals. [1-(Dimethylamino)-1-methylethyl]benzene (**5**) and 2-[1-(dimethylamino)-1-methylethyl]phenylboronic acid (**6**)[1] were identified by com-

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[7] Toyota, S.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1832.

[8] Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Eds.; Academic Press: London, 1983; Vol. 2, Chapter 3.

[9] (a) Kessar, V. S.; Singh, P. *Chem. Rev.* **1997**, *97*, 721, and references therein. (b) Kesser, V. S.; Singh, P.; Vohra, R.; Kaur, N. P.; Singh, K. N. *J. Chem. Soc., Chem. Commun.* **1991**, 568.

[10] Theoretical calculations of a model reaction (NH$_3$ + L:NMe$_3$ → NH$_4^+$ + L:NMe$_2$CH$_2^-$) also support this phenomenon. The energy required for the process is decreased by 31.7 kcal/mol by changing L from none to BF$_3$ at the HF/3-21G* level.

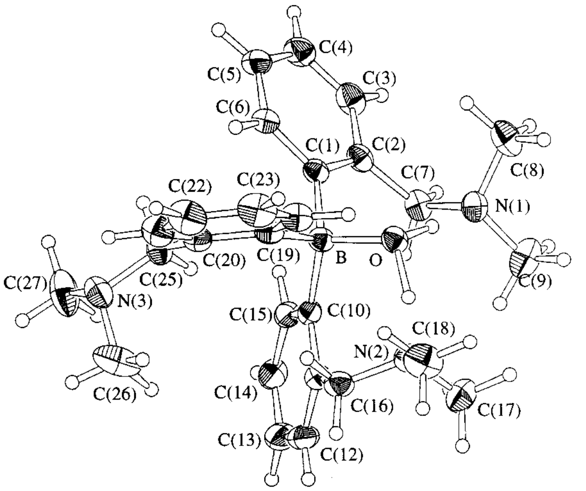

Figure 2. ORTEP drawing of **12**·H$_2$O (30% probability ellipsoids).

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. ^{1}H NMR (CDCl$_3$): $\delta = 1.27$ (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). ^{13}C NMR (CDCl$_3$): $\delta = 20.7$, 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. ^{11}B NMR (CDCl$_3$): $\delta = 3.3$ (line width $h_{1/2}$ 193 Hz). HRMS (FAB, MH$^+$): found 334.2695, calcd for $C_{22}H_{32}BN_2$ 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.[11] 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$_3$ (**12**) was isolated as an adduct with water. This compound slowly decomposed in the air. Mp: 110.5–111.5 °C. ^{1}H NMR (CDCl$_3$): δ 2.09 (br, 18H), 3.24 (br, 6H), 7.00–7.18 (m, 12H). HRMS (FAB, MH$^+$): found 432.3212 and 413.3141, calcd for $C_{27}H_{37}BN_3 \cdot H_2O$ and $C_{27}H_{37}BN_3$, 432.3186 and 413.3117, respectively. *N*,*N*-Dimethylbenzylamine and 2-[(dimethylamino)methyl]phenylboronic acid[11c] were found in the reaction mixture.

Table 1. Crystal and Structure Analysis Data of 7 and 12·H$_2$O

	7	**12**·H$_2$O
formula	$C_{22}H_{31}BN_2$	$C_{27}H_{38}BN_3O$
fw	334.31	431.43
crystal size (mm^3)	0.30 × 0.13 × 0.10	0.50 × 0.25 × 0.15
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	8.160(2)	15.2299(9)
b (Å)	12.021(2)	8.5721(6)
c (Å)	20.478(2)	20.3491(6)
β (deg)	93.50(1)	107.730(3)
V (Å^3)	2005.1(6)	2530.4(2)
Z	4	4
D_c (g/cm^3)	1.107	1.132
μ(Cu Kα) (cm^{-1})	4.76	5.25
scan width (deg)	$1.31 + 0.30 \tan \theta$	$1.84 + 0.30 \tan \theta$
scan rate (deg/min)	8.0	12.0
no. of unique data	3161 ($2° < 2\theta < 120°$)	3762 ($2° < 2\theta < 120°$)
no. of data used	2506 ($F_o > 2.0\sigma(F)$)	3762 ($F_o > 0.0\sigma(F)$)
$R(F)$	0.066	0.053
$R_w(F)$	0.072	0.061

X-ray Crystallography. Crystals of **7** and **12** (Figure 2) used for the X-ray measurements were grown from hexane-dichloromethane and dichloromethane solutions, respectively. The diffraction data were collected on a Rigaku AFC7R four-circle diffractometer with Cu Kα 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 $\sum[w(|F_o| - |F_c|)^2]$, where $w = [\sigma_c^2|F_o|]^{-1}$. 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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[11] (a) Jones, F. N.; Vaulx, R. L.; Hauser, C. R. *J. Org. Chem.* **1963**, *28*, 3461. (b) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068. (c) Lauer, M.; Wulff, G. *J. Organomet. Chem.* **1983**, *256*, 1.