Novel Boron–Nitrogen Containing Compounds from the Reaction of Organolithiums with Complexes between Dimesitylfluoroborane and Six- or Five-membered Aza Aromatic Compounds

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Treatment of an ether solution of dimesitylfluoroborane–pyridine with organolithium reagents at −30 °C gives 1-dimesitylboryl-2-substituted 1,2-dihydropyridines, whereas similar treatment of dimesitylfluoroborane–thiazole or 1-substituted imidazoles gives products possessing novel 1,4-diazonia-2,5-diboratacyclohexa-3,6-diene framework; the products from 1-substituted imidazoles are found to be in uniquely fixed conformation and partially optically resolvable.

Although trialkylborane–pyridine complexes are well known,[1] highly congested trimesitylborane does not form complexes with Lewis bases. Dimesitylfluoroborane (DMFB)[2] forms a complex with pyridine as shown by NMR spectrosopy: addition of an equivalent amount of pyridine to a C_6D_6 solution of DMFB in a NMR tube results in a change in chemical shifts of methyl and aromatic protons as well as an up-field shift (Δ = 11 ppm) of the ^{11}B chemical shift (δ 42.3). We report the syntheses and some properties of novel B–N containing compounds derived from the reaction of organolithium reagents with the complexes between DMFB and several six- or five-membered aza aromatic compounds such as pyridine, thiazole and *N*-substituted imidazole. The reactions are classified into two types depending on aza aromatic compounds (type A: pyridine; type B: thiazole and *N*-substituted imidazoles). Type A involves addition of organolithium reagents at 2-positions of aza aromatic compounds, whereas type B involves abstraction of the proton at 2-position of aza aromatic compounds.

When a mixture of DMFB and pyridine (1 : 1) in ether was treated with phenyllithium (1.2–3.0 equiv.) at −30 °C, followed by gradual warming up to room temperature, **1a** was produced in 31–46% yield along with hydrolysis products, bis(dimesitylboryl)ether and dimesitylhydroxyborane. The ^1H NMR spectrum of **1a** showed four nonequivalent *o*-methyl and aromatic protons from the mesityl groups and four alkene protons.[†,‡] The 1-dimesitylboryl-2-phenyl-1,2-dihydropyridine structure was confirmed by X-ray analysis (Fig. 1).[§] Although restricted rotation in anilinodimesitylboranes around B–N bond, which has partial double bond character, are precedented,[4] the observed nonequivalence of methyl (or aromatic) protons in the same mesityl groups indicates the hindered rotation of B–C(mesityl) bonds in addition to the restricted rotation of the B–N bond; the geared rotation of the mesityl group is restricted by the steric repulsion between the substituent at 2-position in dihydropyridine and the methyl of mesityl group. The rotational barriers are considerable, as these four singlets in deuteriated bromobenzene remain sharp up to 120 °C, above which decomposition begins. Similar products (**1b** and **1c**) were obtained in the reaction with butyllithium and 3-pyridyllithium in the yields of 40 and 27%, respectively.[‡] Interestingly, the corresponding 4-substituted dihydropyridine isomers[5] were not observed in all experiments.

In contrast to the reaction of DMFB–pyridine, similar treatment of an ether solution of DMFB and thiazole (1 : 1) with phenyllithium gave **2a** in 27% yield with a small amount of dimesitylphenylborane and bis(dimesitylboryl)ether. The ^1H NMR spectrum of **2a** is very simple and *o*-mesitylmethyl protons are equivalent even at −90 °C.[‡,¶] The compound **2a** has a new framework of 1,4-diazonia-2,5-diboratacyclohexa-3,6-diene. The formation of **2a** can be easily explained by the abstraction of proton at 2-position of the complexed thiazole and the successive bimolecular condensation of the produced anions with elimination of two fluoride ions.

However, a similar reaction of DMFB–*N*-methyl imidazole produced **2b** which shows four kinds of *o*-methyl and aromatic protons for the mesityl groups at room temperature.[‡,||] The structure was definitively established by X-ray analysis (Fig. 2).[§] The compound **2b** has a boat type six-membered ring containing two B–N bonds; the edges of the boat bend up *ca.* 29°. The folding angle (angle between two imidazole rings) is 128°. The dihedral angle between the two mesityl rings attached

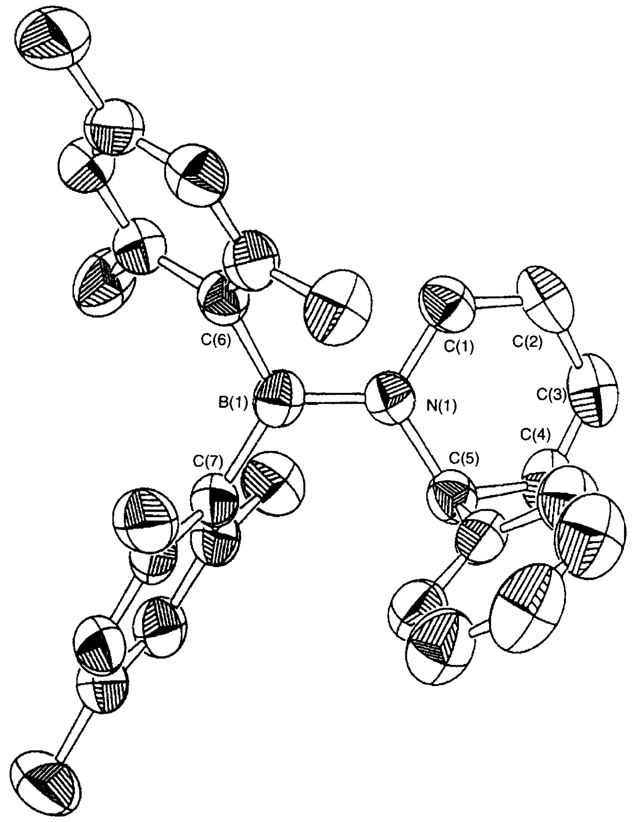
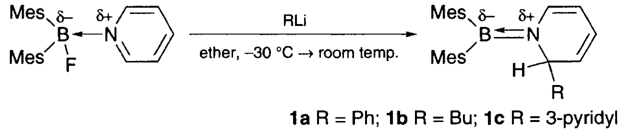
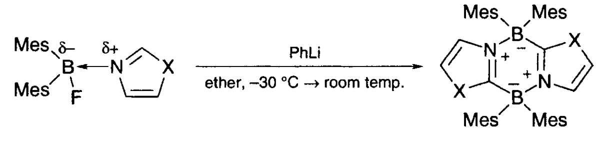


Fig. 1 ORTEP view of **1a** showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): B(1)–N(1) 1.428(4), N(1)–C(1) 1.401(5), N(1)–C(5) 1.494(5), C(1)–C(2) 1.343(5), C(2)–C(3) 1.436(6), C(3)–C(4) 1.304(6), C(4)–C(5) 1.503(5), B(1)–C(6) 1.586(6), B(1)–C(7) 1.590(6).



1a R = Ph; **1b** R = Bu; **1c** R = 3-pyridyl



2a X = S; **2b** X = NMe; **2c** X = NPh to the same boron atom is about 73°. Two mesityl rings (planes *B* and *C* in Fig. 2) stand almost in parallel to the pseudoaxial direction and the overall shape of **2b** is almost in C_2-symmetry. *N*-Phenylimidazole complex gave the similar product **2c** in 22% yield.[‡]

According to molecular models, the rotations of the mesityl groups can be allowed in the gear-type motions as indicated by the arrows in Fig. 2. Such rotation is locked by the steric interference between the *N*-substituents and mesityl groups. In these compounds, the transformation to the antipode is possible in principle by ring inversion of the central six-membered ring accompanied by the bond rotations of mesityl groups. The transformation to the antipode may be feasible in either a simultaneous or a stepwise manner. Simultaneous transformation would involve the flipping of two edges (borons) with the geared rotation of four mesityl groups. On the other hand, stepwise transformation would occur through one edge (boron) flipping and the geared rotation of two mesityl groups on the flipping boron *via* the strained *trans* form. Both processes would require high activation energies. Temperature dependent ^{1}H NMR showed that *o*-methyl or aromatic protons of mesityl groups broadens a little up to 150 °C and considerably broadens in the range of 180–200 °C where the decomposition begins.[**] As a result, compounds **2b** and **2c** were found to be partially resolvable by HPLC with use of column packed with chiral stationary phase at 0 °C.[††]

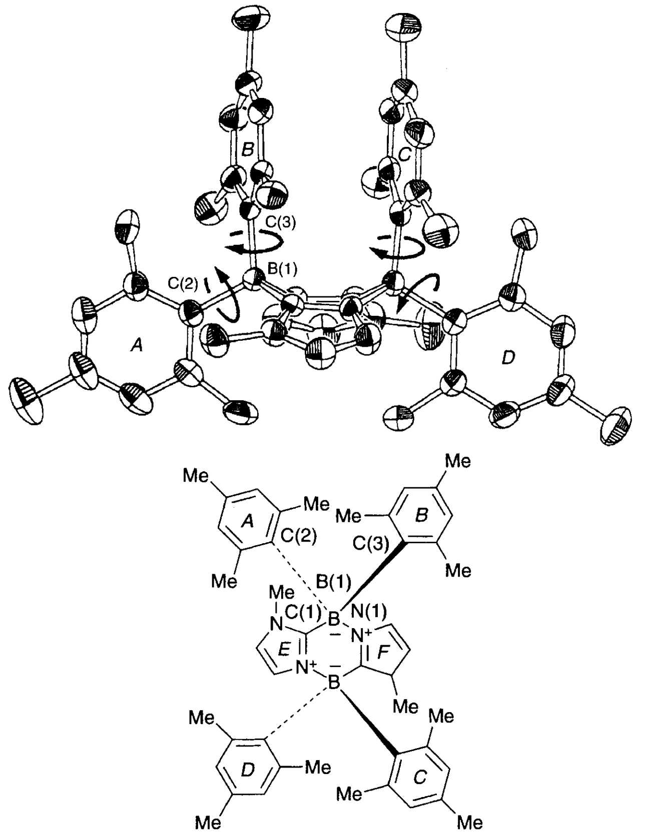


Fig. 2 ORTEP view of **2b** showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): B(1)–N(1) 1.638(4), B(1)–C(1) 1.627(4), B(1)–C(2) 1.657(4), B(1)–C(3) 1.652(4), Dihedral angles between the planes (*A*–*F*): *A*–*B* or *C*–*D* 71–74°; *B*–*C* 2°; *E*–*F* 128°.

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Footnotes

[†] *Selected data* for **1a**: colourless prisms, mp 145 °C; FABMS *m*/*z* 405 (M^+); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.74 (s, 3 H), 1.77 (s, 3 H), 1.99 (s, 3 H), 2.19 (s, 3 H), 2.29 (s, 3 H), 2.63 (s, 3 H), 5.19 (t-like, *J ca.* 6–7 Hz, 1 H), 5.50–5.58 (m, 2 H), 6.12 (dd-like, *J ca.* 8–9, 5–6 Hz, 1 H), 6.35 (d, *J* 7.6 Hz, ^{1}H), 6.65 (s, 1 H), 6.67 (s, 1 H), 6.73 (s, 1 H), 6.90 (s, 1 H) 7.09–7.24 (m, 5 H).

[‡] These compounds (**1a**, **1b**, **1c**, **2a**, **2b** and **2c**) are stable toward air and moisture, and can be purified using silica gel chromatography [eluent: hexane–benzene for **1a**, **1b**, **2a**, **2b** and **2c**; benzene–ethyl acetate (3 : 1) for **1c**.

[§] *Crystal data* for **1a**: $C_{29}H_{32}BN$, monoclinic, space group $P2_1$ (No. 4), a = 9.972(2), b = 8.859(2), c = 13.860(2) Å, β = 94.01(1)°, V = 1221.4(3) Å^3, $Z = 2$, D_c = 1.102 g cm^{-3}; Mo-Kα radiation [λ(Kα) = 0.71069 Å]; $3° < 2\theta < 50°$; 3786 unique reflections, of which 1705 were treated as observed [$F_o^2 > 3\sigma(F_o^2)$; R = 0.041, R_w = 0.044. For **2b** $C_{44}H_{54}B_2N_4$, triclinic, space group $P\bar{1}$ (No. 2), a = 10.846(4), b = 18.177(3), c = 10.278(3) Å, α = 102.05(2), β = 104.66(3), γ = 83.16(2)°, V = 1912.3(10) Å^3, $Z = 2$, D_c = 1.147 g cm^{-3}; Mo-Kα radiation [λ(Kα) = 0.71069 Å]; $3° < 2\theta < 50°$; 11157 unique reflections, of which 4849 were treated as observed [$F_o^2 > 3\sigma(F_o^2)$; R = 0.059, R_w = 0.068. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[¶] *Selected data* for **2a**: colourless plates, mp 193 °C; FABMS *m*/*z* 666 $[M]^+$; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.55 (s, 24 H), 2.19 (s, 12 H), 6.45 (s, 8 H), 7.19 (d, *J* 3.6 Hz, 2 H), 7.86 (d, *J* 3.6 Hz, 2 H).

[‖] *Selected data* for **2b**: colourless prisms, 293 °C (decomp); FABMS *m*/*z* 660 $[M]^+$; ^{1}H NMR (270 HMz, $CDCl_3$) δ 1.10 (s, 6 H), 1.35 (s, 6 H), 1.63 (s, 6 H), 2.09 (s, 6 H), 2.11 (s, 6 H), 2.22 (s, 6 H), 3.03 (s, 6 H), 5.78 (s, 2 H), 6.43 (s, 2 H), 6.52 (d, *J* 1.6 Hz, 2 H), 6.66 (s, 2 H), 6.70 (s, 2 H), 7.08 (d, *J* 1.6 Hz, 2 H).

[**] The barrier of ring inversion (racemization) is roughly estimated to be about $\Delta H^\ddagger$ = 21 kcal mol^{-1} and $\Delta S^\ddagger$ = −3.4 cal K^{-1} mol^{-1} by the line shape analysis of two *p*-methyl protons (δ 2.11 and 2.22 by NOE experiments), although the close chemical shift (δ 2.09) of one of the *o*-methyl protons disturbs the precise determination.

[††] By use of [CHIRAL OT(+)], Daicel Chemical Industries, Japan.

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