Synthesis and Structure of Pentacoordinate Hypervalent Boron Compounds Bearing a 1,8-Dimethoxy-10-methylacridinium Skeleton

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Pentacoordinate hypervalent boron compounds **4a** and **4b** with a newly prepared 1,8-dimethoxy-10-methylacridinyl ligand were synthesized. X-ray crystallography revealed that the distances between the central boron and both oxygen atoms of the tridentate ligand were in the range of 2.37–2.53 Å, showing the pentacoordinate structure. Cyclic voltammetry of **4b** showed that the potential of the reduction ($E_{1/2} = -0.57$ V in CH_2Cl_2, vs. SCE) is much lower than that of the corresponding Gabbaï's system **5** (−0.28 V), probably due to the difference in coplanarity between the boryl group and the acridinyl skeleton in **4b** and **5** (twist angle = 44.8° in **5** and 88.2° in **4b**).

Hypervalent compounds,[1] which have more than eight electrons in their valence shell, are widely known in the chemistry of heavier main group elements but are very rare in second-row elements such as carbon[2a–2d] and boron.[2b,3] Recently, we reported two series of hypervalent boron compounds **1**[2b,3a] and **2**[3b] using a sterically rigid anthracene ligand or a relatively flexible van Koten-type ligand (Chart 1). However, we found that the interaction between the central boron atom and the coordinating oxygen atoms varies with the rigidity of the skeleton and with the substituents on the central boron. For example, with the same substituent (catecholate), B–O distances in **1a** [2.379(2), 2.441(2) Å: av. 2.41 Å] are significantly shorter than those in **2a** [2.527(9), 2.660(10) Å (1st crystal), 2.496(10), 2.702(10) Å (2nd crystal): av. 2.60 Å], indicating that steric rigidity plays an important role in the strength of the interaction between B and O, although the substituent on the oxygen is different. In addition, the structure itself is different between **2a** and **2b** [B–O distance: 3.024(3), 3.155(3) Å; no coordination between B and O], indicating that the electronic and/or steric effects of the substituents of the central boron is large for the weakly coordinating system. Because we were not successful in preparing **1b** bearing a pinacolate substituent, we have been interested in creating another sterically rigid tridentate ligand system. Here we report a new acridinium tridentate ligand skeleton **3** and the boron compounds **4** bearing the skeleton because of our additional interests in the redox behavior in comparison with the corresponding Gabbaï's system **5**[4] (Chart 2). It is expected that 1,8-dimethoxy-9-lithio-10-methylacridan, which is the precursor of **4**, would react with boron reagents easier than that of **1**, 1,8-dimethoxy-9-lithioanthracene, due to a steric reason.

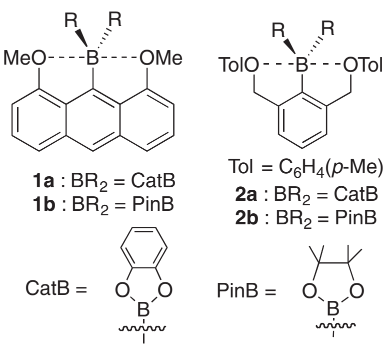
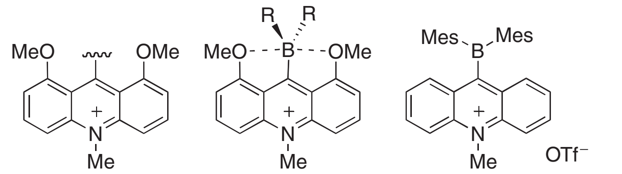
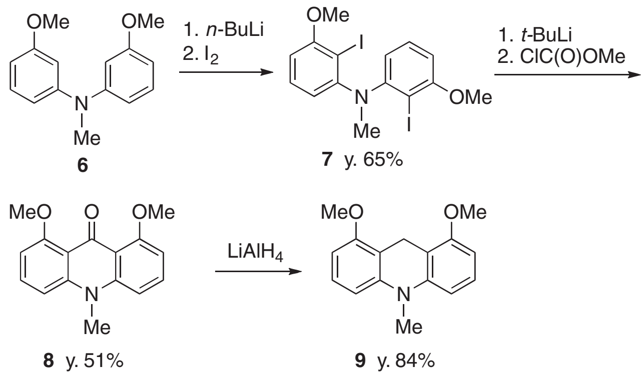


Chart 1.



3 4 5

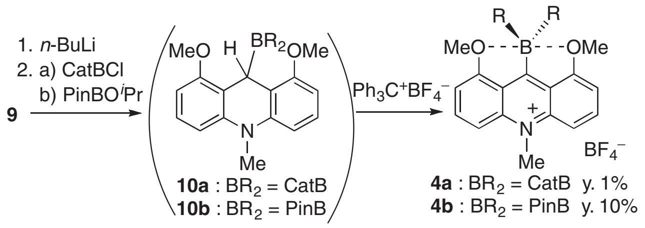
Chart 2.



Scheme 1.

As shown in Scheme 1, 1,8-dimethoxy-10-methylacridan (**9**), which is the precursor of the new tridentate ligand, was synthesized. Bis(3-methoxyphenyl)methylamine (**6**) was synthesized by the Pd-catalyzed cross coupling reaction of 3-iodoanisole with *m*-anisidine followed by methylation with NaH and MeI. The amine **6** was selectively dilithiated by refluxing in *n*-hexane, and bis(2-iodo-3-methoxyphenyl)methylamine (**7**) was obtained after treatment with I_2. The treatment of **7** with *t*-BuLi and ClC(O)OMe afforded 1,8-dimethoxy-10-methylacridone (**8**). The reduction of **8** with $LiAlH_4$ afforded the acridan **9**.

The introduction of boryl groups is illustrated in Scheme 2. The reaction of the acridan **9** with *n*-BuLi followed by treatment with the corresponding boron reagent afforded the desired **10a** and **10b**. Without isolation of unstable **10a** and **10b**, the reaction with $Ph_3C^+BF_4^-$ gave the boron compounds **4a** and **4b** in very low yields, but **4a** and **4b** could be isolated by recrystallization from THF/CH_3CN.[5] The ^1H NMR spectra of **4a** and **4b** show a symmetrical pattern of the tridentate ligand (one OMe group



Scheme 2.

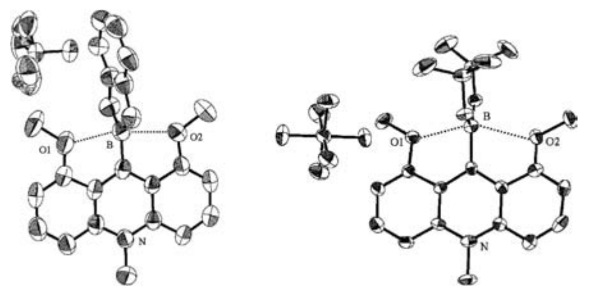


Figure 1. ORTEP drawings (50% elliposoid) of **4a**$\cdot BF_4^-$ and **4b**$\cdot PF_6^-$ (solvent is omitted).

(6H), one NMe group (3H), three aryl-H (2H × 3)). The results are similar to the cases of the anthracene system **1** and the flexible van Koten-type system **2**.

Although the conversion from **9** to **4** is not efficient, especially in **4a** which is not quite stable, we managed to obtain single crystals of **4a**$\cdot BF_4^-$ and **4b**$\cdot PF_6^-$, which was obtained by a counter anion exchange using $K^+PF_6^-$, suitable for X-ray analysis. The ORTEP drawings of **4a**$\cdot BF_4^-$ and **4b**$\cdot PF_6^-$ are illustrated in Figure 1.[6] The boron atoms of **4a** and **4b** are almost planar as indicated by the sum of the bond angles around the boron atom being almost 360°. The B–O1 and B–O2 distances between the central boron atom and the oxygen atoms of the two methoxy groups in **4a** were 2.375(8) and 2.437(8) Å, respectively. Because the distances and the O1–B–O2 angle of **4a** [165.2(4)°] are almost the same as those of **1a** [B–O1(O2) = 2.379(2), 2.441(2) Å, O1–B–O2 = 167.10(7)°][2b] where the B–O attractive interaction was confirmed by experimental electron density distribution analysis, the structure of **4a** should be regarded as pentacoordinate.

The corresponding B–O distances in **4b** were 2.525(9) and 2.501(9) Å, respectively, which are slightly longer than those in **4a** but are still much shorter than the sum of the van der Waals radius of B and O (3.48 Å).[7] In the case of the flexible van Koten-type ligand system **2**, **2b** is concluded to be a tricoordinate based on the long B–O distances [3.024(3) and 3.155(3) Å]. The B–O1 and B–O2 distances in **4b** are much shorter than those in **2b** because of the steric rigidity of the tridentate ligand **4** (Table 1). Therefore, it is concluded that in a sterically rigid acridinium ligand the electronic and/or steric effects of the substituents of the central boron are not as large as those in a van Koten-type ligand.

Although pure **4a** could not be obtained for the study of redox behavior, the cyclic voltammetry of **4b** in CH_2Cl_2 could be measured. A single reversible redox wave ($E_{1/2} = -0.57$ V in CH_2Cl_2, vs. SCE) and a subsequent irreversible wave ($E_p = -1.48$ V vs. SCE) were observed, and the potentials of reductions are much lower than that of corresponding Gabbaï's system **5**,[4] which shows two reversible redox waves ($E_{1/2} = -0.28$, -0.98 V vs. SCE). Furthermore, the potential of the first reduction of **5** is distinctly more positive than that of Mes_3B and 10-methylacridinium, but the peak potential of the first reduction of **4b** ($E_p = -0.60$ V vs. SCE) is same to that of 1,8-dimethoxy-10-methylacridinium ($E_p = -0.60$ V vs. SCE), which is the side-product of the synthesis of **4** and shows an irreversible redox wave. Although the difference can be due to the presence of electron-donating methoxy groups in **4** and the difference in the substituent on the central boron, we think that the difference in coplanarity between the boryl group and the acridinyl skeleton (twist angle = 44.8° in **5** and 88.2° in **4b**) should be one of the reasons, because the conjugation between the central boron and the π system in the acridinium skeleton should reduce the reductive potential. The distortion in **4b** is caused by the steric repulsion between the boryl group and the two methoxy groups of the ligand. The introduction of other substituents on the boron atom and examination of the structure and the reduction potential are in progress.

Table 1. Selected structural parameters for **1a**, **2a**, **2b**, **4a**, and **4b**

	1a[2b]	**2a**[3b]	**2b**[3b]	**4a**	**4b**
Average B–O/Å	2.41	2.60	3.09	2.41	2.51
O–B–O/°	167.1	160.5[a]	145.0	165.2	147.9

[a]Average of two independent molecules.

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5 Data for **4a**$\cdot BF_4^-$: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 6H), 4.90 (s, 3H), 7.12 (d, 2H, $^3J = 8$ Hz), 7.20–7.22 (m, 2H), 7.34–7.36 (m, 2H), 8.19 (d, 2H, $^3J = 8$ Hz), 8.33 (t, 2H, $^3J = 8$ Hz); HRMS m/z: calcd for $C_{22}H_{19}BNO_4$ ([M]$^+$), 372.1407; found: 372.1411. Data for **4b**$\cdot BF_4^-$: ^{1}H NMR (400 MHz, CD_3CN): δ 1.53 (s, 12H), 4.22 (s, 6H), 4.58 (s, 3H), 7.33 (d, 2H, $^3J = 8$ Hz), 7.96 (d, 2H, $^3J = 9$ Hz), 8.25 (dd, 2H, $^3J = 8$ and 9 Hz); HRMS m/z: calcd for $C_{22}H_{28}BNO_4$ ([M + H]$^+$), 381.2111; found: 381.2115.

6 Crystal Data for **4a**$\cdot BF_4^-\cdot CH_3CN$: $C_{24}H_{22}B_2F_4N_2O_4$, *M*r: 500.06, monoclinic, $P2_1/n$ (No. 14), $a = 11.2300(7)$, $b = 11.4590(7)$, $c = 18.1700(12)$ Å, $V = 2337.5(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.421$ g cm^{-3}, $R = 0.1021$ ($I > 2\sigma(I)$), $Rw = 0.3754$ (all data), GOF = 1.113 for 4460 reflections and 357 parameters (CCDC-733927). Crystal Data for **4b**$\cdot PF_6^-$: $C_{22}H_{27}BF_6NO_4P$, *M*r: 525.23, monoclinic, $P2_1/c$ (No. 14), $a = 7.1230(6)$, $b = 27.711(2)$, $c = 11.8230(12)$ Å, $V = 2320.8(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.503$ g cm^{-3}, $R = 0.0917$ ($I > 2\sigma(I)$), $Rw = 0.3431$ (all data), GOF = 1.130 for 4311 reflections and 323 parameters (CCDC-733928). The data were collected at 200 K (for **4a**$\cdot BF_4^-$) or 173 K (for **4b**$\cdot PF_6^-$) using a Mac Science DIP 2030 imaging plate equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

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