Synthesis and Structural Characterization of Pentaarylboroles and Their Dianions

Cheuk-Wai So, Daisuke Watanabe, Atsushi Wakamiya, and Shigehiro Yamaguchi*

Department of Chemistry, Graduate School of Science, Nagoya University, and SORST, Japan Science and Technology Agency, Furo, Chikusa, Nagoya 464-8602, Japan

Received March 31, 2008

A series of l-aryl-2,3,4,5-tetraphenylboroles [Ph_4C_4BAr] [Ar = *p*-MeC_6H_4 (**2**), *p*-$Me_3SiC_6H_4$ (**3**), *p*-FC_6H_4 (**4**)] were synthesized. The X-ray crystallography of **2**−**4** revealed that they have short distances between the borole boron atom and the phenyl rings of the neighboring molecules, suggesting the existence of certain intermolecular interaction. Despite this interaction, the borole rings in **2**−**4** remain planar and contain substantial bond alternation in the butadiene skeleton, which is consistent with the theoretically optimized structures of the singlet boroles. These results demonstrated that the boroles still have antiaromatic character in the crystalline state. Compound **3** and pentaphenylborole [Ph_4C_4BPh] (**5**) were further reacted with potassium or potassium graphite to form potassium borole dianion salts [$K_2\{Ph_4C_4B(p\text{-}Me_3SiC_6H_4)\}$] (**6**) and [$K_2(Ph_4C_4BPh)$] (**7**), respectively. In their X-ray crystal structures, compounds **6** and **7** are polymeric and have two K^+ ions lying on both sides of the borole plane with η^5-coordination.

Introduction

The cyclopentadienyl cation ($C_5H_5^+$), one of the fundamental 4π electron systems, is of great importance in the understanding of antiaromaticity.[1] Its triplet ground state predicted from simple Hückel theory has been confirmed by the electron spin resonance (ESR) spectra,[2] photoelectron spectroscopy,[3] and recent ab initio calculations.[4] The nucleus-independent chemical shift (NICS) calculations showed that the triplet $C_5H_5^+$ as well as other triplet $4n\pi$ electron systems are aromatic, while their singlet derivates are antiaromatic.[5] Until now, the solid-state structure of a simple cyclopentadienyl cation is still unknown.[6] On the other hand, in the case of the pentaphenylcyclopentadienyl cation ($Ph_5C_5^+$), the ESR spectroscopic detection of half-field transitions showed that it has a thermally populated and low-lying excited triplet state.[7] In this regard, pentaphenylborole [Ph_4C_4BPh],[8] isoelectronic with $Ph_5C_5^+$, would be a suitable molecule to elucidate the antiaromatic character of the singlet 4π electron system. Unlike $Ph_5C_5^+$, it does not consist of a low-lying excited triplet state, according to its ESR measurement, in which the half-field transitions cannot be detected.[8a] However, the borole is a strong Lewis acid and very prone to oxidation and Diels−Alder reactions.[8,9] The high reactivity has retarded the progress of its chemistry. While pentaphenylborole was first synthesized by Eisch and co-workers in 1969,[8a] its X-ray crystal structure has been determined by Braunschweig et al. recently.[10] Interestingly, they revealed that a certain intermolecular interaction between the borole boron atom and the substituents of the neighboring borole compounds in the crystalline state affects the bond alternation in the borole ring.

Herein, we report the synthesis and structural characterization of a series of pentaaryl-substituted boroles having various *p*-substituted phenyl groups on the boron atom. The X-ray structural data of the pentaarylboroles provide a new perspective to understand the nature of the borole antiaromatic system. Thus, in our compounds, while an intermolecular interaction is observed similar to that in the case of [Ph_4C_4BPh], the boroles still have substantial bond alternation in the borole ring. We will discuss the effect of the intermolecular interaction in the crystalline state toward the antiaromaticity.

Besides antiaromaticity, the borole is also of interest in view of reduction, since it has a vacant $2p_z$ orbital on the boron atom to accept electrons from the alkali metal. This would lead to the formation of a dianion with 6π aromatic character,[11a] which should be a useful building block for synthesizing novel organometallic complexes.[11−13] By reacting with potassium or potassium graphite, we have succeeded in transforming some of the pentaarylboroles into the corresponding dianions. The features of their crystal structures will be described.

---

* Corresponding author. E-mail: yamaguchi@chem.nagoya-u.ac.jp.

(1) Allen, A. D.; Tidwell, T. T. *Chem. Rev.* **2001**, *101*, 1333.

(2) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M., Jr.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. *J. Am. Chem. Soc.* **1973**, *95*, 3017.

(3) Wörner, H. J.; Merkt, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 293.

(4) (a) Jiao, H.; Schleyer, P.v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075. (b) Reindl, B.; Schleyer, P. v. R. *J. Comput. Chem.* **1998**, *19*, 1402. (c) Shiota, Y.; Kondo, M.; Yoshizawa, K. *J. Chem. Phys.* **2001**, *115*, 9243.

(5) (a) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1945. See also: (b) Baird, N. C. *J. Am. Chem. Soc.* **1972**, *94*, 4941. (c) Dougherty, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 7187. (d) Aihara, J. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1788. (e) Fratev, F.; Monev, V.; Janoschek, R. *Tetrahedron* **1982**, *38*, 2929. (f) Jug, K.; Malar, E. J. P. *J. Mol. Struct. (THEOCHEM)* **1987**, *153*, 221. (g) Wan, P.; Shukla, D. *Chem. Rev.* **1993**, *93*, 571.

(6) (a) Otto, M.; Scheschkewitz, D.; Kato, T.; Midland, M. M.; Lambert, J. B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2275. (b) Müller, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 2276. (c) Lambert, J. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2278. (d) Lambert, J. B.; Lin, L.; Rassolov, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 1429.

(7) (a) Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112. (b) Breslow, R.; Chang, H. W.; Yager, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 2033.

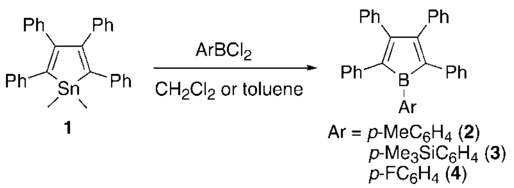
(8) (a) Eisch, J. J.; Hota, N. K.; Kozima, S. *J. Am. Chem. Soc.* **1969**, *91*, 4575. (b) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (c) Eisch, J. J.; Galle, J. E.; Shafii, B.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2342.

(9) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

(10) Braunschweig, H.; Fernández, I.; Frenking, G.; Kupfer, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 1951.

10.1021/om8002812 CCC: $40.75

Scheme 1. Synthesis of Pentaarylboroles 2−4



Results and Discussion

Synthesis of Pentaarylboroles. The displacement reaction of 1,1-dimethyl-2,3,4,5-tetraphenylstannole [$Ph_4C_4SnMe_2$] (**1**) with a stoichiometric amount of aryldichloroboranes $ArBCl_2$ in toluene or CH_2Cl_2 afforded unsolvated pentaarylboroles [Ph_4C_4BAr] [Ar = p-MeC$_6$H$_4$ (**2**), p- Me$_3$SiC$_6$H$_4$ (**3**), p-FC$_6$H$_4$ (**4**)] (Scheme 1). Pentaphenylborole [Ph_4C_4BPh] (**5**)[8,10] and ferrocenylborole [Ph_4C_4BFc] (Fc = ferrocenyl)[10] were previously synthesized in a similar manner. Compounds **2** and **3** are soluble only in CH_2Cl_2 at room temperature, and they were fully verified by NMR spectroscopy and elemental analysis. The ^{11}B NMR signals of **2** and **3** are δ 66.4 and 66.0 ppm, respectively. On the contrary, **4** shows extremely low solubility in noncoordinating solvents (e.g., benzene-d_6 and CD_2Cl_2); therefore the ^{13}C and ^{11}B NMR data for compound **4** could not be obtained due to its poor solubility.

Structural Characterization of Pentaarylboroles. Crystals of **2**−**4**, which were suitable for X-ray crystallography, were obtained by slow cooling of the corresponding hot saturated toluene or CH_2Cl_2 solution. Their crystallographic data and selected structural parameters are summarized in Tables 1 and 2, respectively, and their ORTEP drawings are shown in Figures 1 and 2. In all cases, the borole rings are planar and the aryl substituents are tilted toward this plane. The dihedral angles between the aryl substituent at the boron center and the borole ring [17.0° (**2**), 46.4° (**3**), 30.1° (**4**)] are smaller than those between the phenyl substituents and the borole ring [average: 57.5° (**2**), 47.5° (**3**), 52.4° (**4**)].

We compare the structures of compounds **2**−**4** with that of pentaphenylborole **5**, which was reported by Braunschweig et al.[10] They reported that **5** consists of dimeric subunits with the phenyl substituent at the boron center lying above or below the borole ring of the neighboring molecule. The shortest intermolecular B---C(phenyl) distance is 3.653 Å. Notably, the borole ring has less significant bond alternation in the butadiene moiety [C(1)−C(2) 1.428(2) Å, C(2)−C(3) 1.470(2) Å, B−C(1) 1.525(2) Å], which is totally different from the theoretically optimized structure for the singlet state. They explain this discrepancy is due to the intermolecular phenyl→boron interaction, which leads to some extent of delocalization of the 4π electrons in the borole ring. We found that compounds **2**−**4** also have comparable or even shorter B---C(phenyl) intermolecular distances, suggesting certain intermolecular interaction between the phenyl C−H bond and the boron atom. In contrast, the butadiene moiety in the borole ring has a large bond alternation, which is similar to that of the theoretically optimized structure for the singlet borole.[14]

Thus, in the packing of [Ph_4C_4B(p-CH$_3$C$_6$H$_4$)] (**2**), the boron center is sandwiched between two phenyl substituents of the adjacent molecules. The shortest intermolecular distance between the boron atom and the C(phenyl) atom of the adjacent borole in **2** is 3.610 Å. However, unlike [Ph_4C_4BPh] (**5**), the bonding within the four-carbon butadiene backbone is highly alternating. The short C(1)−C(2) bond (1.362(4) Å) and long C(2)−C(3) bond (1.529(6) Å) correspond to double and single bonds, respectively. Similarly, [Ph_4C_4B(p-Me$_3$SiC$_6$H$_4$)] (**3**) also consists of dimeric subunits with the phenyl substituent at the C(1) or C(4) position of the borole ring lying above or below the borole ring of the neighboring molecule. The shortest intermolecular B---C(phenyl) distance (3.553Å) is shorter than that of [Ph_4C_4BPh] (**5**) (3.653Å), but the bonding within the four-carbon butadiene backbone has pronounced bond alternation [C(1)−C(2) 1.358(3) Å, C(2)−C(3) 1.524(3) Å, B−C(1) 1.605(3) Å]. In the crystal packing of [Ph_4C_4B(p-FC$_6$H$_4$)] (**4**), similar to pentaphenylborole **5**, dimeric subunits are present with the aryl substituent at the boron center lying above or below the borole ring of the contiguous molecule. The shortest intermolecular B---C(p-FC$_6$H$_4$) distance (3.776 Å) in **4** is slightly longer than that of [Ph_4C_4BPh] (**5**) (3.653 Å). Although the p-FC$_6$H$_4$ group is introduced into the boron center, there is no dramatic change in the bond distance for **4** [C(1)−C(2) 1.362(2) Å, C(2)−C(3) 1.518(2) Å, B−C(1) 1.577(3) Å] compared with those of **2** and **3**.

These results demonstrate that the short interaction between the borole boron atom and the phenyl group of the neighboring molecule in the crystal packing is a common feature. The high Lewis acidity of the boron atom enhanced by the antiaromatic character may need stabilization by certain intermolecular B---phenyl(C−H bond) interactions. This interaction needs not to affect the planarity of the borole ring, as seen in compound **5**. However, compounds **2**−**4** maintain pronounced bond alternation in the borole butadiene moiety, which is different from **5**. Similar bond alternation is also found in the molecular structure of [Ph_4C_4BFc],[10] in which it has a short Fe---B distance (2.825 Å).

The observed crystal structures of **2**−**4** are very comparable to their calculated structures without consideration of the intermolecular interaction. These compounds were fully optimized with the DFT-variant UB3LYP as implemented in the Gaussian G03 program suite employing a basis set termed 6-31G*.[15] The calculated energy differences between the singlet ground state and the triplet state of **2**−**4** are 15.9, 15.4, and 15.7 kcal mol^{-1}, respectively. These results show that the triplet

---

(11) (a) Herberich, G. E.; Hostalek, M.; Laven, R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 317. (b) Herberich, G. E.; Buller, B.; Hessner, B.; Oschmann, W. *J. Organomet. Chem.* **1980**, *195*, 253. (c) Hong, F.-E.; Eigenbrot, C. W.; Fehlner, T. P. *J. Am. Chem. Soc.* **1989**, *111*, 949. (d) Herberich, G. E.; Hengesbach, J.; Kölle, U.; Huttner, G.; Frank, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 433.

(12) (a) Herberich, G. E.; Hessner, B.; Boveleth, W.; Lüthe, H.; Saive, R.; Zelenka, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 996. (b) Gleiter, R.; Hyla-Kryspin, I.; Herberich, G. E. *J. Organomet. Chem.* **1994**, *478*, 95. (c) Hyla-Kryspin, I.; Gleiter, R.; Herberich, G. E.; Bénard, M. *Organometallics* **1994**, *13*, 1795. (d) Braunstein, P.; Englert, U.; Herberich, G. E.; Neuschütz, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1010. (e) Braunstein, P.; Englert, U.; Herberich, G. E.; Neuschütz, M.; Schmidt, M. U. *J. Chem. Soc., Dalton Trans.* **1999**, *2807*.

(13) (a) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489. (b) Sperry, C. K.; Cotter, W. D.; Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 7791. (c) Pindado, G. J.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **1998**, *120*, 6816. (d) Woodman, T. J.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **2001**, *329*. (e) Woodman, T. J.; Thornton-Pett, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2001**, *20*, 4080. (f) Loginov, D. A.; Muratov, D. V.; Petrovskii, P. V.; Starikova, Z. A.; Corsini, M.; Laschi, F.; Fabrizi, F. de B.; Zanello, P.; Kudinov, A. R. *Eur. J. Inorg. Chem.* **2005**, 1737. (g) Muratov, D. V.; Petrovskii, P. V.; Starikova, Z. A.; Herberich, G. E.; Kudinov, A. R. *J. Organomet. Chem.* **2006**, *691*, 3251.

(14) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

(15) Frisch, M. J. ; et al. *Gaussian 03, revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004. For the complete reference, see the Supporting Information.

Table 1. Crystallographic Data for Compounds 2−4

	2	3	4
formula	$C_{35}H_{27}B$	$C_{37}H_{33}BSi$	$C_{34}H_{24}BF$
fw	458.38	516.53	462.34
color	purple	blue	greenish-blue
cryst syst	tetragonal	monoclinic	monoclinic
space group	$P4_12_12$ (#92)	$C2/c$ (#15)	$P2_1/n$ (#14)
a (Å)	10.099(8)	18.900(5)	10.975(5)
b (Å)	10.099(8)	15.875(4)	9.582(4)
c (Å)	25.157(2)	19.674(5)	24.482(11)
α (deg)	90.000	90.000	90.000
β (deg)	90.000	94.149(4)	97.028(7)
γ (deg)	90.000	90.000	90.000
V (Å^3)	2566.0(3)	5888(3)	2555(2)
Z	4	8	4
d_{calcd} (g cm^{-3})	1.187	1.159	1.202
F(000)	968	2168	968
μ (mm^{-1})	0.066	0.103	0.073
cryst size (mm)	0.10 × 0.10 × 0.10	0.20 × 0.05 × 0.02	0.20 × 0.20 × 0.20
2θ range (deg)	2.17−25.49	2.77−25.00	2.83−25.50
index range	$-12 \le h \le 12$, $-12 \le k \le 12$, $-30 \le l \le 27$	$-22 \le h \le 22$, $-13 \le k \le 18$, $-21 \le l \le 22$	$-12 \le h \le 13$, $-6 \le k \le 11$, $-28 \le l \le 29$
no. of rflns collected	16 891	19 415	8419
no. of indep rflns	2396	5134	4581
R_1, wR_2 ($I < 2\sigma(I)$)	0.0811, 0.2055	0.0633, 0.1568	0.0499, 0.1359
R_1, wR_2 (all data)	0.0863, 0.2112	0.0806, 0.1692	0.0659, 0.1498
goodness of fit, F^2	1.163	1.107	1.065
no. of data/restraints/params	2396/0/166	5134/56/475	4581/0/325
largest diff (e Å^{-3})	0.354 to −0.249	0.513 to −0.343	0.240 to −0.240

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds 2−4

	2	3	4
B(1)−C(1)	1.578(5)	1.605(3)	1.577(3)
C(1)−C(2)	1.362(4)	1.358(3)	1.362(2)
C(2)−C(3)	1.529(6)	1.524(3)	1.518(2)
C(3)−C(4)	1.362(4)	1.357(3)	1.365(2)
C(4)−B(1)	1.578(5)	1.606(3)	1.576(3)
B(1)−C(5)	1.537(7)	1.513(8)	1.536(3)
B(1)−C(1)−C(2)	107.4(3)	107.2(2)	107.16(14)
C(1)−C(2)−C(3)	110.54(17)	111.30(19)	110.46(15)
C(2)−C(3)−C(4)	110.54(17)	111.35(19)	111.36(15)
C(4)−B(1)−C(1)	104.0(4)	102.9(2)	104.39(14)
C(4)−B(1)−C(5)	128.02(19)	128.9(3)	127.85(16)
C(1)−B(1)−C(5)	128.02(19)	127.6(4)	127.71(16)

states of **2**−**4** are not significantly low-lying and the aryl substituents on the boron atom do not affect the energy differences between the singlet and triplet state. The calculated structural parameters of the singlet boroles **2**−**4** [**2**: B(1)C(1) 1.589 Å, C(1)−C(2) 1.363 Å, C(2)−C(3) 1.532 Å; **3**: B(1)−C(1) 1.588 Å, C(1)−C(2) 1.363 Å, C(2)−C(3) 1.533 Å; **4**: B(1)−C(1) 1.588 Å, C(1)−C(2) 1.363 Å, C(2)−C(3) 1.533 Å] are in good agreement with the crystallographic data. Therefore, we can conclude that compounds **2**−**4** still hold the antiaromatic character in the crystalline state even with the B---phenyl intermolecular interaction. Their antiaromaticity can be evaluated by the nucleus-independent chemical shift calculations at the HF/6-31+G**//B3LYP/6-31G* level [NICS(0) value: +12.65 ppm (**2**), +12.78 ppm (**3**), +12.94 ppm (**4**)],[16] while the NICS(0) value of the isoelectronic pentaphenylcyclopentadienyl cation ($C_5Ph_5^+$) is +21.51 ppm.

Synthesis and Structural Characterization of Pentaarylborole Dianions. Pentaaryl-substituted borole dianions [$K_2(Ph_4C_4BAr)$] [Ar = p-$Me_3SiC_6H_4$ (**6**), C_6H_5 (**7**)], isoelectronic to the cyclopentadienyl anion, were also prepared by the reaction of corresponding pentaarylboroles with excess potassium or potassium graphite in THF at room temperature (Scheme 2). The ^{11}B NMR signals of **6** (δ 29.6 ppm) and **7** (δ 28.7 ppm) show upfield shifts compared to those of neutral precursors **3** (δ 66.0 ppm) and **5** (δ 62.8 ppm). They are stable at room temperature under inert atmosphere. Compound **6** was isolated as red solids, which formed a crystalline derivative with tetramethylethylenediamine (tmeda) (Figure 3).

Herberich and his co-workers have already reported the synthesis of [$K_2(Ph_4C_4BPh)$] (**7**), but it has not been structurally characterized.[11b] We have determined the structures of **6** and **7** by X-ray crystallography. The crystallographic data of **6** and **7** are summarized in Table 3, and selected bond distances and angles are shown in Table 4. In these compounds, two potassium ions locate above and below the borole plane with η^5-coordination. The borole ring C_4B is planar and the aryl substituents are tilted toward this plane. The bond distances of C(1)−C(2) [1.441(4) Å (**6**), 1.469(2) Å (**7**)] and C(3)−C(4) [1.452(4) Å (**6**), 1.448(2) Å (**7**)] are longer, while the C(2)−C(3) [1.431(4) Å (**6**), 1.409(2) Å (**7**)], B(1)−C(1) [1.531(4) Å (**6**), 1.543(2) Å (**7**)], and B(1)−C(4) bonds [1.538(4) Å (**6**), 1.522(2) Å (**7**)] are shorter, compared with those of **3** and **5**, respectively. Thus, the bond alternation in the borole butadiene moiety is significantly smaller compared to the neutral precursors **3** and **5**. These bond patterns demonstrate the aromatic character (6π electron system) in the C_4B rings of **6** and **7**.

In the structure of **6**·tmeda, dimeric subunits, in which two borole dianions are bridged by coordinating the p-$Me_3SiC_6H_4$ benzene ring with K(2), form a polymeric structure by bonding tmeda to the potassium center K(1), as shown in Figure 3. Among the potassium atoms K(1) and K(2), the K(1) atom has a stronger coordination with the borole ring than K(2) (for example, B(1)−K(1) 2.982(3) Å, B(1)−K(2) 3.158(3) Å). Similarly, the dianion **7** has a polymeric structure through the coordination of the potassium atoms K(1) and K(2) with the phenyl substituents at C(1) and C(4) of the adjacent borole dianion molecules (Figure 4). These compounds would have

---

[16] Schleyer, P.v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

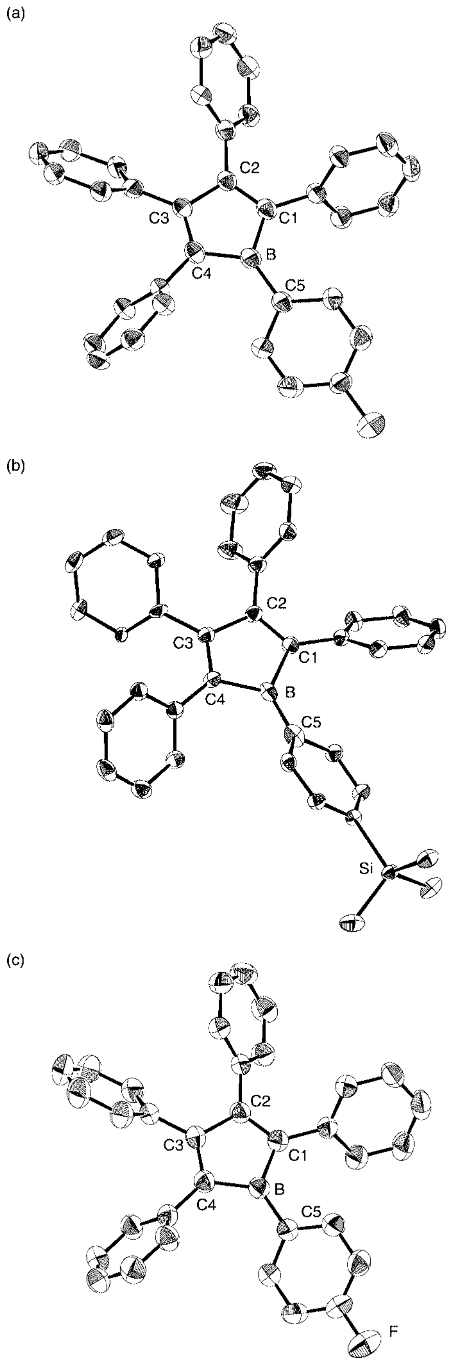


Figure 1. ORTEP drawings of (a) **2**, (b) **3**, and (c) **4** (50% probability for thermal ellipsoids). Hydrogen atoms are omitted for clarity.

great potential as precursors for novel multidecker-type organometallic polymers.[12,13]

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a JEOL AL-400 spectrometer. The NMR spectra were recorded in CD_2Cl_2 or THF-d_8, and the chemical shifts are relative to $SiMe_4$ for ^1H and ^{13}C and $BF_3 \cdot Et_2O$ for ^{11}B, respectively. Elemental analyses were measured on a Yanaco MT-6 instrument by the Chemical Instrumentation Facility, Nagoya University. Melting points were measured in a sealed glass tube on a Stanford Research Systems OptiMelt MPA100 instrument and are uncorrected. Dry solvents (hexane, CH_2Cl_2, ether, toluene, and THF) of dehydrated grade were purchased from Kanto Chemical Co. Ltd. [$Ph_4C_4SnMe_2$] (**1**),[8] [Ph_4C_4BPh] (**5**),[8] [p-$CH_3C_6H_4BCl_2$],[17] [p- $Me_3SiC_6H_4BCl_2$],[18] and [p-$FC_6H_4BCl_2$][19] were prepared as described in the literature.

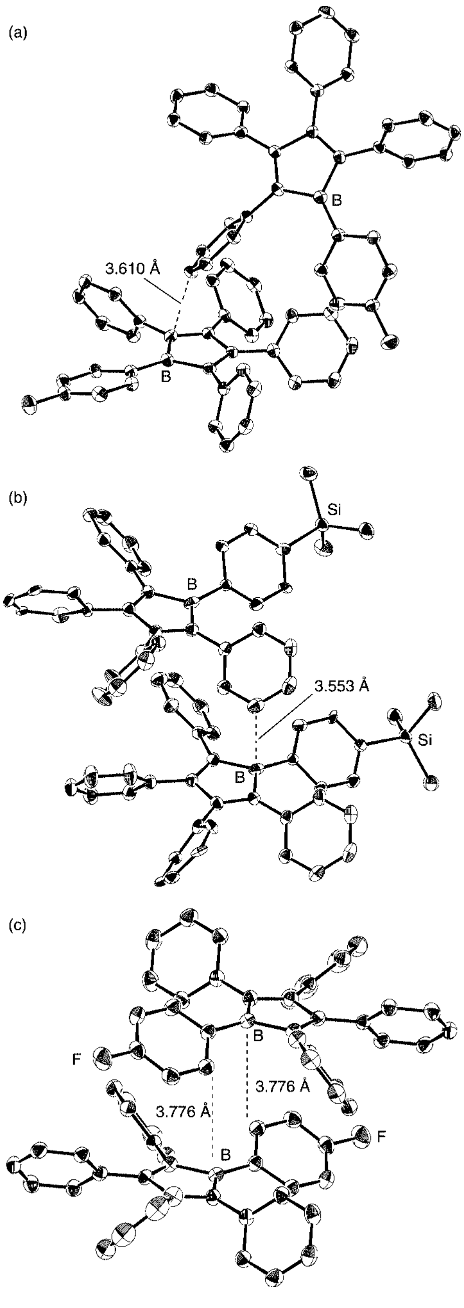
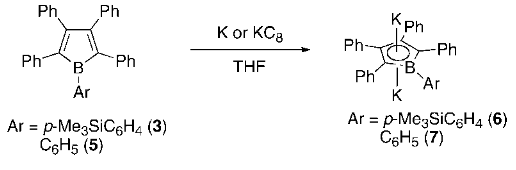


Figure 2. Dimeric subunits in the crystal lattices of (a) [$Ph_4C_4B(p$-$CH_3C_6H_4)$] (**2**), (b) [$Ph_4C_4B(p$-$Me_3SiC_6H_4)$] (**3**), and (c) [$Ph_4C_4B(p$-$FC_6H_4)$] (**4**) (50% probability for thermal ellipsoids).

Scheme 2. Synthesis of Borole Dianions 6 and 7



[$Ph_4C_4B(p$-$CH_3C_6H_4)$] (2). A solution of p-$CH_3C_6H_4BCl_2$ (0.18 g, 1.01 mmol) in toluene (15 mL) was added dropwise to [$Ph_4C_4SnMe_2$] (**1**) (0.51 g, 1.01 mmol) in toluene (15 mL) at room temperature. The reaction mixture was stirred for 18 h, and a dark

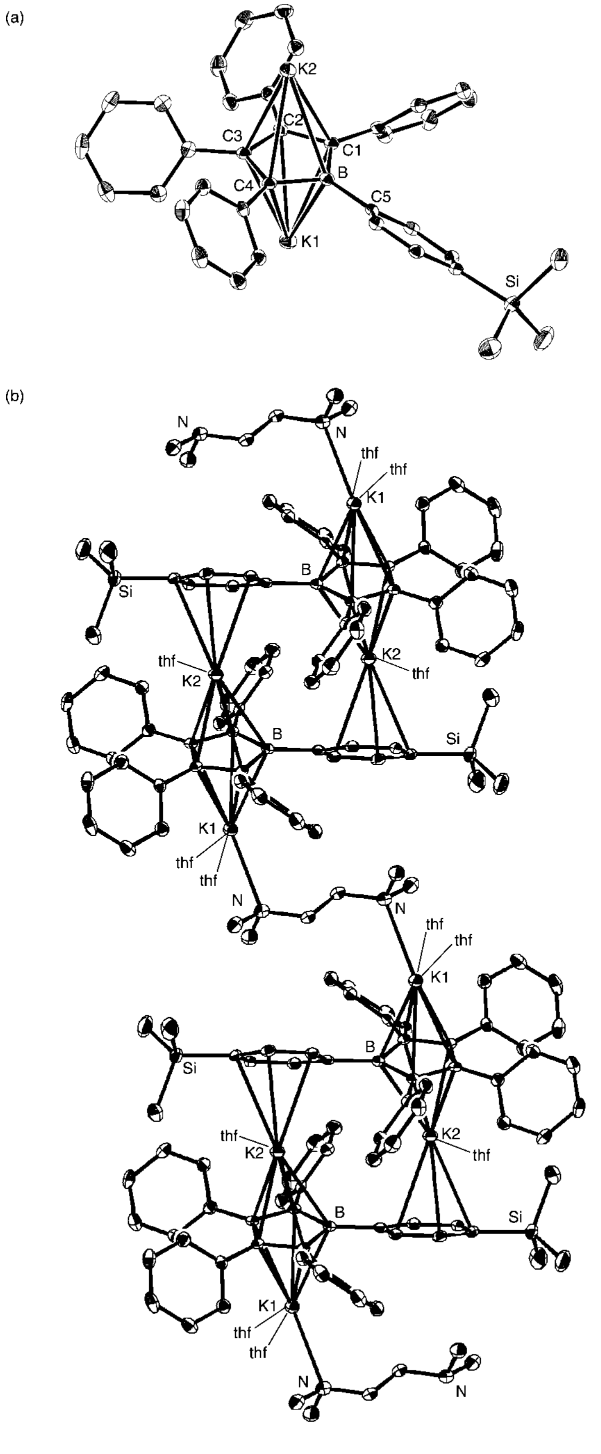


Figure 3. ORTEP drawings of $[K_2\{C_4Ph_4B(p\text{-}Me_3SiC_6H_4)\}]\cdot(tmeda)_{0.5}\cdot(THF)_3$ (50% probability thermal ellipsoids): (a) perspective view of the molecule and (b) its polymeric structure. Hydrogen atoms and solvent molecules (TMEDA and THF) are omitted for clarity.

Table 3. Crystallographic Data for Compounds 6 and 7

	6	7
formula	$C_{61}H_{81}BK_2N_2O_{4.5}Si$	$C_{42}H_{41}BK_2O_2$
fw	1031.38	666.76
color	red	red
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a (Å)	14.755 (1)	12.980(3)
b (Å)	14.739(2)	13.155(3)
c (Å)	16.506(2)	13.210(3)
α (deg)	80.90(7)	106.0948(16)
β (deg)	65.208(6)	112.6165(17)
γ (deg)	63.435(5)	108.9784(16)
V (Å^3)	2912.7	1747.5(7)
Z	2	2
d_{calcd} (g cm^{-3})	1.176	1.267
F(000)	1108	704
μ (mm^{-1})	0.230	0.307
cryst size (mm)	0.10 × 0.10 × 0.10	0.20 × 0.20 × 0.20
2θ range (deg)	2.54−25.00	2.68−25.50
index range	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-18 \leq l \leq 19$	$-14 \leq h \leq 15$, $-15 \leq k \leq 15$, $-15 \leq l \leq 14$
no. of rflns collected	19 749	12 218
no. of indep rflns	10 97	6363
R_1, wR_2 ($I > 2\sigma(I)$)	0.0571, 0.1401	0.0309, 0.0789
R_1, wR_2 (all data)	0.0760, 0.1531	0.0376, 0.0822
goodness of fit, F^2	1.063	1.068
no. of data/restraints/params	10 097/ 0/685	6363/0/424
largest diff peaks (e Å^{-3})	1.087 to −0.406	0.436 to −0.294

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compounds 6 and 7

	6	7
B(1)−C(1)	1.531(4)	1.543(2)
C(1)−C(2)	1.441(4)	1.469(2)
C(2)−C(3)	1.431(4)	1.409(2)
C(3)−C(4)	1.452(4)	1.448(2)
B(1)−C(4)	1.538(4)	1.522(2)
B(1)−C(5)	1.583(4)	1.572(2)
B(1)−K(1)	2.982(3)	3.1773(17)
B(1)−K(2)	3.158(3)	3.0361(17)
B(1)−C(1)−C(2)	107.8(2)	106.44(12)
C(1)−C(2)−C(3)	110.3(2)	110.09(12)
C(2)−C(3)−C(4)	110.1(2)	111.02(12)
C(3)−C(4)−B(1)	107.2(2)	107.41(12)
C(1)−B(1)−C(4)	104.6(2)	105.04(12)
C(1)−B(1)−C(5)	125.5(2)	129.19(13)
C(4)−B(1)−C(5)	129.1(2)	125.48(13)

blue solution was formed. Volatiles of the mixture were removed under reduced pressure, and Me_2SnCl_2 was then evacuated from the residue by sublimation *in vacuo* at 40 °C. The residue was extracted with hot toluene (8 mL) and filtered. The solution was cooled slowly to room temperature to yield 0.39 g (0.85 mmol) of **2** as purple crystals in 85% yield. Mp: 162 °C. ^1H NMR (CD_2Cl_2): δ 2.32 (s, 3H, CH_3), 6.76−7.16 (m, 24H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.9 (CH_3), 125.5, 127.1, 127.2, 127.4, 127.6, 128.0, 129.4, 129.7, 136.6, 137.8, 140.0, 144.1, 162.5 (Ar) (two signals for the carbon atoms bonding to the boron atom are not observed due to the quadrupolar relaxation). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 66.4. Anal. Calcd for $C_{35}H_{27}B$: C, 91.71; H, 5.94. Found: C, 91.61; H, 5.94.

$[Ph_4C_4B(p\text{-}Me_3SiC_6H_4)]$ (3). An analogous experimental procedure to that for **2** was used. The reaction of $p\text{-}Me_3SiC_6H_4BCl_2$ (0.24 g, 1.03 mmol) and **1** (0.52 g, 1.03 mmol) in toluene (30 mL) afforded 0.49 g (0.95 mmol) of **3** as blue crystals in 92% yield. Mp: 148 °C. ^1H NMR (CD_2Cl_2): δ 0.22 (s, 9H $SiMe_3$), 6.77−6.80 (m, 2H, Ar), 6.91−7.20 (m, 20H, Ar), 7.33−7.35 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −1.49 ($SiMe_3$), 125.6, 127.2, 127.37, 127.4, 127.6, 129.4, 129.7, 131.9, 136.5, 139.8, 146.9, 162.8 (Ar) (two signals for the carbon atoms bonding to the boron atoms are not observed due to the quadrupolar relaxation). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 66.0. Anal. Calcd for $C_{37}H_{33}BSi$: C, 86.03; H, 6.44. Found: C, 86.02; H, 6.43.

$[Ph_4C_4B(p\text{-}FC_6H_4)]$ (4). An analogous experimental procedure to that for **2** was used. The reaction of $p\text{-}FC_6H_4BCl_2$ (0.18 g, 1.01

---

(17) Muetterties, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 2597.

(18) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901.

(19) Fraenk, W.; Klapötke, T. M.; Krumm, B.; Mayer, P.; Nöth, H.; Piotrowski, H.; Suter, M. *J. Fluorine Chem.* **2001**, *112*, 73.

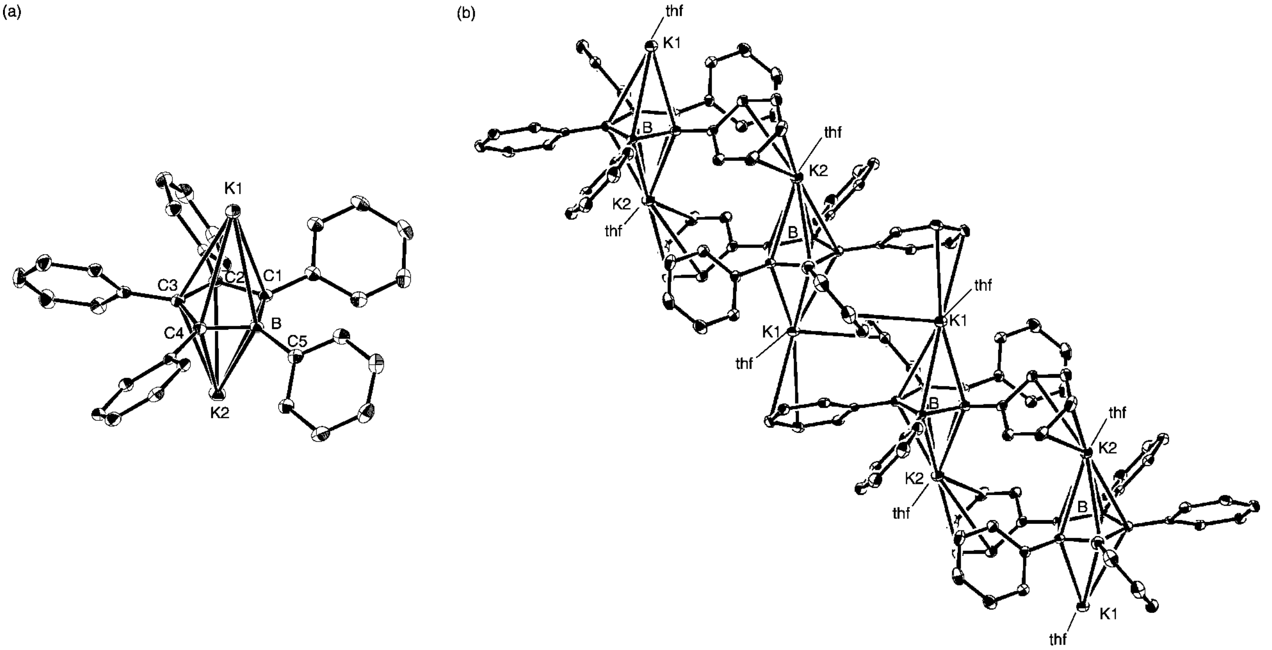


Figure 4. ORTEP drawings of [$K_2(Ph_4C_4BPh)$]·$(THF)_2$ (50% probability for thermal ellipsoids): (a) perspective view of the monomeric unit and (b) its polymeric structure. Hydrogen atoms are omitted for clarity.

mmol) and **1** (0.51 g, 1.01 mmol) in CH_2Cl_2 (30 mL) afforded 3.9 mg (0.0084 mmol) of **4** as greenish-blue crystals in 0.8% yield. Mp: 153 °C. ^{1}H NMR (CD_2Cl_2): δ 6.54−6.58 (m, 2H, Ar), 6.83−7.05 (m, 20H, Ar), 7.37−7.39 (m, 2H, Ar). Anal. Calcd for $C_{34}H_{24}BF$: C, 88.32; H, 5.23. Found: C, 88.05; H, 5.17.

[$K_2\{Ph_4C_4B(p\text{-}Me_3SiC_6H_4)\}$] (6). THF (30 mL) was added to a mixture of **3** (0.52 g, 1.01 mmol) and excess potassium chunks (0.39 g, 0.01 mol) at ambient temperature. The resulting red solution was stirred for 17 h. The insoluble solid was filtered. Volatiles of the mixture were removed under reduced pressure. The residue was washed with 10 mL of toluene three times to give 0.52 g of **6** as a red powder. Mp: 72 °C (dec). ^{1}H NMR (THF-d_8): δ 0.16 (s, 9H $SiMe_3$), 1.77−1.78 (m, 2H, THF), 3.59−3.62 (m, 2H, THF), 6.33−6.36 (m, 2H, Ar), 6.54−6.78 (m, 18H, Ar), 6.92 (m, 2H, Ar).7.29 (m, 2H, Ar). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 0.61 ($SiMe_3$), 118.3, 120.9, 124.9 127.6, 127.7, 129.9, 130.0, 130.7, 132.0, 132.3, 133.4, 136.5, 147.2, 152.3 (Ar). $^{11}B\{^1H\}$ NMR (THF-d_8): δ 28.7. Attempts to obtain acceptable elemental analysis data for compound **6** failed due to its extreme air sensitivity. Red crystals of **6**, which were suitable for X-ray crystallography, were obtained from its concentrated TMEDA/THF solution.

[$K_2(Ph_4C_4BPh)$] (7). THF (3.5 mL) was added to a mixture of **5** (0.23 g, 0.53 mmol) and an excess amount of potassium graphite (0.18 g, 4.6 mmol) at ambient temperature. The resulting dark red solution was stirred for 34 h. The insoluble solid was filtered off, and hexane was diffused into the red filtrate to afford 0.34 g (0.52 mmol) of **7**·$(THF)_2$ as a red powder in 98% yield. The spectroscopic data are the same as those reported in the literature.[11b] Red crystals of **7**·$(THF)_2$, which were suitable for X-ray crystallography, were obtained from its concentrated THF solution.

X-ray Structure Analysis. Intensity data for compounds **2**−**4**, **6**, and **7** were collected using a Rigaku single crystal CCD, by means of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals of **2**−**4**, **6**, and **7** were measured at 100(2) K. The structures were solved by direct phase determination (SHELXTL-97)[20] and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were subjected to anisotropic refinement. Hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms. A summary of crystal data for **2**−**4**, **6**, and **7** is given in Tables 1 and 3, respectively.

For compound **3**, the trimethylsilylphenyl moiety (C5−C10, Si1, and C11−C13) and one phenyl ring (C26−C31) are disordered and solved using appropriate disordered models. Thus, two sets of trimethylsilylphenyl moieties, (C5A-C10A, Si1A, C11A, C12, C13) and (C5B−C10B, Si1B, C11B, C12, C13), were placed and their occupancies were refined to be 0.50. Similarly, two sets of phenyl rings, (C26A−C31A) and (C26B−C31B), were placed and their occupancies were refined to be 0.46 and 0.54, respectively. All non-hydrogen atoms, except for C5B, were refined anisotropically, and all hydrogen atoms, except for those on C11A and C11B, were placed using AFIX instructions.

For compound **6**, besides THF and tmeda coordinating to the potassium, THF and tmeda molecules are included as solvent molecules in a lattice. One disordered THF solvent molecule, (O5, C62−C65), sits on the symmetry axis, which is placed with its occupancy as 0.5.

Computational Method. All calculations were conducted using the Gaussian 03 series of electronic structure programs.[15] The geometries were optimized with the unrestricted Becke hybrid (UB3LYP) method at the 6-31G* level for singlet and triplet borole derivatives. Their minimum energies were confirmed by the frequency calculations. The energy differences between the singlet state and the triplet state were corrected using zero-point energy. The NICS calculations were carried out at the HF/6-31+G** level for the optimized geometries at the B3LYP/6-31G* level.

Acknowledgment. C.-W.S. thanks Japan Society for the Promotion of Science for a Research Fellowship. This work was partially supported by Grants-in-Aid (Nos. 19685004 and 19675001) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, and SORST, Japan Science and Technology Agency.

Supporting Information Available: Complete ref 15, calculated molecular coordinates for **2**−**5**, and X-ray data (CIF) of **2**−**4**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8002812

---

(20) Sheldrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*; University of Gottingen: Gottingen, Germany, 1997.