Structure Elucidation

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Boracyclophanes: Modulation of the σ/π Character in Boron–Benzene Interactions**

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Friedel–Crafts alkylation is a powerful methodology in organic synthesis for the modification of aromatic compounds. The reaction is categorized as an electrophilic aromatic substitution, in which a carbocation–arene σ complex, namely the arenium ion, has been assumed to be an intermediate. Characterizations of the arenium ions have long been investigated both theoretically and experimentally.[1,2] It is also known that silylium ions (silyl cations) interact with an arene to form a silylarenium species. However, this intermediate exhibits a greater π-complex character rather than the σ-complex character.[3] The character of the arenium intermediates generated with p-block-element electrophiles vary from a η^1 π complex to a σ complex, as shown in Figure 1.

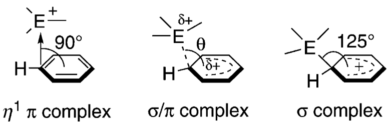
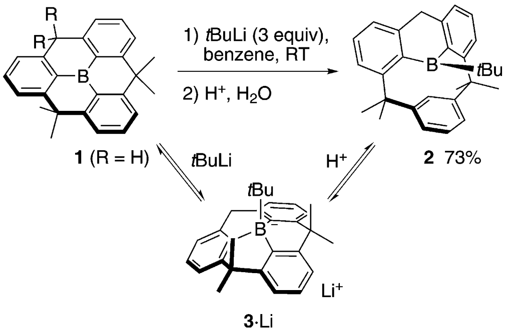


Figure 1. Structural variation of the interaction between the p-block electrophiles (e.g. $E^+ = C^+$, Si^+) and benzene.



Scheme 1. Synthesis of the boracyclophane **2** through an intermediate **3**·Li.

The tricoordinate group 13 element species ER_3 (E = B, Al, Ga, or In), which are isoelectronic to the carbocation, are also potent Lewis acids and would interact with arenes to form zwitterionic arenium complexes.[4] The interaction of BX_3 (X = H, F, or Cl) with benzene has been investigated by an ab initio study, in which the binding energy for the η^1 π complexes are estimated to be 3–6 kcal mol^{-1}.[5] In contrast, experimental characterizations of the boron–arene complexes are still limited to only a few examples, including those with triarylboranes[6] or borenium cations.[7] In these examples, constrained arrangements between the boron and arene moieties in close proximity assist in forming the boron–benzene interactions, which are relatively weak and tend to have a η^1 π-complex character rather than a σ-complex character.

Recently, we synthesized the planarized triphenylboranes **1** (Scheme 1, R = H or Me) with three methylene bridges and demonstrated their high stability toward air and moisture. Based on this result, we claimed that the structural constraint is an effective strategy for the stabilization of the reactive triarylboranes.[8] However, we also demonstrated that the planarized triphenylboranes still possess a sufficient Lewis acidity to react with anionic Lewis bases, such as a fluoride ion, thus resulting in the formation of a bowl-shaped tetracoordinate borate species. These results prompted us to study the reactivity of the planarized triphenylboranes with Lewis bases in more detail. We now employed a stronger carbon nucleophile, *t*BuLi, as the Lewis base. We found that the reaction produced a boracyclophane, in which a tricoordinate boron moiety was fixed above an eliminated benzene ring in close proximity. Notably, this molecular structure provides an ideal scaffold to study the intrinsic character of the interaction between a tricoordinate boron and a benzene ring. We succeeded in modulating the character of the boron–benzene interaction from a π- to σ-complex character by changing the electron-donating character of the benzene ring.

In our previous study, when we treated the planarized triphenylborane **1** (R = H) with bases, such as potassium hydride and lithium tetramethylpiperidide, we cleanly obtained a highly fluorescent borataanthracene anion.[9] In contrast, we now found that the reaction of **1** with 3 equivalents of *t*BuLi followed by quenching with water gave a one benzene ring-eliminated product, namely the boracyclophane **2**, as a single product (Scheme 1). This compound was isolated by preparative-scale gel permeation chromatography (GPC) in 73 % yield as colorless solids. The structure of **2** was unambiguously characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography.

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The reaction of **1** with *t*BuLi cleanly proceeded, and any product produced by the elimination of the other benzene moieties was not observed in the crude reaction mixture, thus indicating that the boron–benzene bond was selectively cleaved. The yield of **2** was highly dependent on the amount of *t*BuLi. When 1 equivalent of *t*BuLi was employed, **2** was obtained only in 18% yield. In contrast, the use of 5 equivalents of *t*BuLi gave **2** in 71%, which is comparable to that obtained with 3 equivalents of *t*BuLi (Scheme 1). These results can be rationalized by considering the equilibrium between the tricoordinate borane **1** and tetracoordinate *tert*-butylborate **3**·Li. The use of excess *t*BuLi shifts the equilibrium to the borate side, from which the protonation of the most electron-rich benzene ring selectively produces the boracyclophane **2**.

The clean formation of the intermediate **3**·Li was confirmed by monitoring the reaction mixture by NMR spectroscopy (see the Supporting Information). In the ^{11}B NMR spectrum of a 1:1 mixture of **1** and *t*BuLi in C_6D_6, only two signals were observed. One is a broad signal of **1** at $\delta = 45.9$ ppm. The other one is a sharp signal at $\delta = -20.1$ ppm, which is assignable to the borate intermediate **3**·Li (see Figure S4 in the Supporting Information). The ^{1}H NMR spectrum also showed the signals of **1** and a new set of signals corresponding to **3**·Li (see Figure S5 in the Supporting Information). Upon the addition of water to the solution, the signals of the boracyclophane **2** appeared in the ^{1}H NMR spectrum, in addition to those of the unreacted **1**. Based on the integration ratio of the ^{1}H NMR signals, the binding constant of **1** with *t*BuLi was estimated to be $4.0 \times 10\,\text{M}^{-1}$, which is rather low compared to that with a fluoride ion ($7.0 \times 10^5\,\text{M}^{-1}$).[8] Therefore, an excess amount of *t*BuLi was necessary to completely shift the equilibrium to the product side.

The X-ray crystallographic analysis of the boracyclophane **2** revealed the characteristic structural features (Figure 2).[10] The tricoordinate boron atom is slightly pyramidalized. The sum of the three C-B-C angles is 349.1°. The most notable feature is that the boron atom is fixed above the eliminated benzene moiety in close proximity. The B1⋯C1 distance of 2.23 Å is shorter than the sum of the van der Waals radii of the boron and carbon atoms (3.62 Å).[11] This structure indicates that an interaction occurs between the boron atom and the benzene ring to some extent. In addition, the ^{11}B NMR spectrum of **2** in $CDCl_3$ showed a signal at $\delta = 51.1$ ppm, which is upfield-shifted compared to that of the alkyldiphenylboranes, such as Ph_2BMe ($\delta = 70.6$ ppm),[12] and indicative of the electronic perturbation from the eliminated benzene ring to the boron atom. To gain detailed insights into the electronic structure of the boracyclophane **2**, we conducted theoretical calculations.

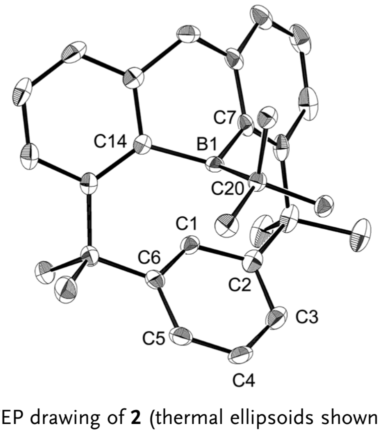


Figure 2. ORTEP drawing of **2** (thermal ellipsoids shown at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C7 1.595(2), B1–C14 1.596(2), B1–C20 1.627(2), C1–C2 1.411(2), C1–C6 1.402(2), C2–C3 1.393(2), C3–C4 1.380(3), C4–C5 1.388(3), C5–C6 1.395(2); C7-B1-C14 110.42(13), C7-B1-C20 118.95(13), C14-B1-C20 119.87(14).

The optimized structure of **2**, calculated at the B3LYP/6-31G(d) level of theory,[13] showed good agreement with the X-ray structure, except that the B1⋯C1 distance was slightly overestimated to be 2.35 Å. While the HOMO is mainly localized on the two benzene rings connected to the boron atom, the LUMO essentially consists of a vertical orbital interaction between the vacant p orbital of the boron atom and the π* orbital of the eliminated benzene ring (Figure 3a).

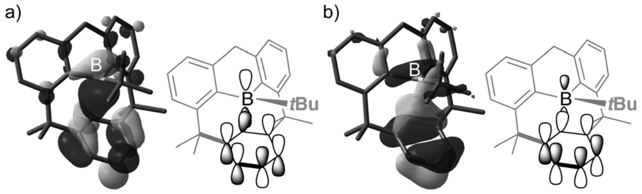
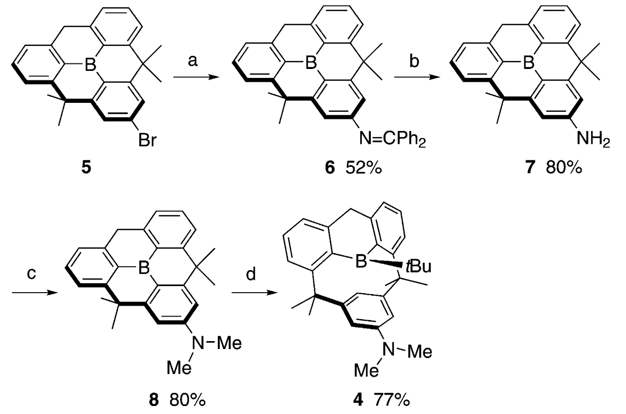


Figure 3. The Kohn–Sham plots of the a) LUMO and b) HOMO−5 of the boracyclophane **2** (B3LYP/6-31G(d) level, isovalue 0.04).

This interaction is in stark contrast to an ordinary p–π* orbital interaction in conventional arylboranes.[14] In contrast, the HOMO−5 indicated a bonding interaction between the boron moiety and the π orbital of the benzene ring (Figure 3b). Therefore, we conducted the atoms in molecules (AIM) analysis[15] of **2** using its crystal structure to evaluate the bonding interaction between the B1 atom and the closest C1 atom in the benzene ring. We found a bond path between the B1 and C1 atoms with a bond critical point, in which the electron density $\rho(\mathbf{r})$ was 0.037. The small positive value of the $\nabla^2\rho(\mathbf{r})$ value (0.046) suggested that the bonding interaction is slightly ionic.

These results demonstrated that the vertical p-π orbital overlapping between the boron atom and the benzene ring results in the attractive interaction. However, this interaction should be inherently weak because of the low Lewis acidity of the boron moiety and low nucleophilicity of the benzene ring. We envisioned that the introduction of an electron-donating group onto the eliminated benzene ring would enhance the orbital interaction. Based on this idea, we synthesized the boracyclophane **4** with a dimethylamino group at the *para*-position of the benzene ring.

The compound **4** was synthesized in four steps from the monobrominated precursor **5** (Scheme 2). The planarized triphenylborane **6** with a diphenylimino moiety was prepared by the palladium-catalyzed coupling of **5** with benzophenone imine.[16] Hydrolysis of **6** under acidic conditions gave the amino derivative **7**. The subsequent reductive methylation



Scheme 2. Synthesis of **4**. Reagents and conditions: a) HN=CPh$_2$ (1.2 equiv), [Pd(dba)$_2$] (5 mol %), dppf (10 mol %), *t*BuONa (1.3 equiv), toluene, reflux, 12 h; b) 4 N aq. HCl, THF, RT, 18 h; c) 37 % aq. HCHO, NaBH$_4$, 3 M aq. H$_2$SO$_4$, THF, 0 °C then RT, 15 h; d) *t*BuLi (3 equiv), benzene, RT, 1 h, then 1 N aq. HCl, RT. dba = dibenzylideneacetone, dppf = 1,1′-bis(diphenylphosphino)ferrocene, THF = tetrahydrofuran.

with aqueous formaldehyde and NaBH$_4$ in the presence of H$_2$SO$_4$ successfully produced the dimethylamino-substituted planarized triphenylborane **8** in good yield. Finally, the treatment of **8** with *t*BuLi and subsequent quenching with aqueous HCl produced the boracyclophane **4** in 77 % yield.

The structure of the dimethylamino-substituted **4** was successfully determined by X-ray crystallography.[10] The crystal structure consists of two crystallographically independent molecules, whose structural parameters are almost comparable to each other. Therefore, the structural data for one of these molecules are considered in this discussion, in which the H1 atom was located on the difference Fourier maps and isotropically refined (Figure 4). There are several notable features. First, the structure of **4** has a short contact between the boron atom and the benzene ring. The B1-C1 distance is 1.842(3) Å, which is shorter than that in **2** (2.23 Å). The boron atom is more pyramidalized compared to that in **2**, where the sum of the three angles, C5-B1-C5*, C5-B1-C12, and C5*-B1-C12, is 338.7°. In addition, the C1 atom adopts a tetrahedral-like geometry. The H1-C1-C4 angle is 141.7°. These structural features indicated the strong coordination of the benzene ring to the boron. The AIM analysis using the crystal structure of **4** showed a bond path between the B1 and C1 atoms. At the bond critical point, the $\rho(\mathbf{r})$ value was 0.085, which is larger than that of **2**, and indicative of the bonding interaction enhancement.

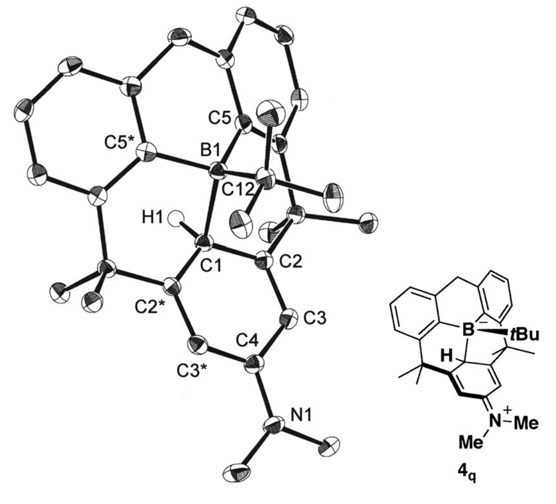


Figure 4. ORTEP drawing of **4** (thermal ellipsoids shown at 50 % probability) and a postulated canonical structure **4**$_\mathrm{q}$. Hydrogen atoms except H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C1 1.842(3), B1–C5 1.610(2), B1–C12 1.663(3), C1–C2 1.4338(18), C2–C3 1.371(2), C3–C4 1.4202(19), C4–N1 1.353(3); C5-B1-C5* 108.96(17), C5-B1-C12 114.88(10), C2-C1-H1 114.1(5), C2-C1-C2* 119.56(18).

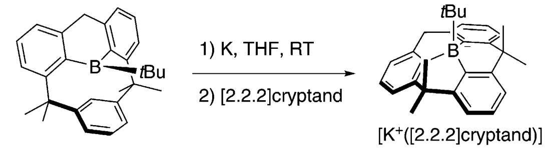
The second notable feature is that **4** has a significant bond alternation in the eliminated benzene ring. The compound **2** only has the small bond alternation in the eliminated benzene ring (1.380(3)–1.411(2) Å). In contrast, the C1-C2 and C3-C4 bond lengths in **4** are elongated to 1.4338(18) and 1.4202(19) Å, respectively, while the C2-C3 bond is shortened to 1.371(2) Å. The C4-N1 bond length is also shortened to 1.353(3) Å, which is indicative of a double bond character. These data suggest that the benzene ring is significantly deformed to a quinoidal structure like **4**$_\mathrm{q}$ in Figure 4.

To confirm the zwitterionic and quinoidal characters in **4**, we investigated the solvent effect on the structure of **4** by NMR analysis. In CDCl$_3$, the ^{11}B NMR spectrum of **4** showed a signal at $\delta = 23.0$ ppm with the full width at half maximum (FWHM) of 280 Hz. The chemical shift is highly upfield-shifted and the signal is sharpened compared to those of **2** ($\delta = 51.1$ ppm; FWHM, 660 Hz). This observation was consistent with the shortened B1-C1 distance in the crystal structure of **4**. Furthermore, the ^{11}B NMR chemical shift of **4** was downfield-shifted to $\delta = 24.5$ ppm in C$_6$D$_6$, and upfield-shifted to $\delta = 17.7$ ppm in [D$_6$]acetone, thus indicating that the interaction between the boron atom and the benzene ring is strengthened as the solvent becomes more polar. In conjunction with these changes, the chemical shift of the H1 atom was also shifted upfield as the solvent polarity increased from C$_6$D$_6$ ($\delta = 6.38$ ppm) to CDCl$_3$ ($\delta = 6.19$ ppm) to [D$_6$]acetonce ($\delta = 5.85$ ppm). Importantly, these results imply that the degree of the boron–benzene interaction can be modulated by the environment around the molecule. The structural optimization calculations (B3LYP/6-31G(d)) taking the solvent polarity into consideration using the polarizable continuum model (PCM) also supported this consideration. While the optimized structure in benzene showed the B1-C1 distance of 2.07 Å, it was shortened to 1.94 Å in acetone.[13]

The natural bond orbital (NBO) analysis at the B3LYP/6-31G(d) level of theory[13] provided insights into the bonding interaction between the boron atom and the eliminated benzene ring. In the boracyclophane **2**, we found six σ-bonding NBOs and three π-bonding NBOs in the benzene ring, thus indicating that the benzene ring remains as a "benzene". No bonding NBO was found between the B1 and C1 atoms. However, the electronic perturbation from the C1-C2 π-bonding orbital to the p orbital on the boron atom was suggested. The charge-transfer stabilization energy was estimated to be 33.86 kcal mol^{-1}. The occupancy (1.58) of the C1-C2 π-bonding NBO was less than 2.0, while that of the boron p orbital was 0.25 (Supporting Information). The Wiberg bond index[17] was calculated to be 0.18 for the B1···C1 of **2**. These results demonstrated that the boracyclophane **2** can be regarded as a π complex between the Lewis acidic boron atom and the benzene ring with electron donation from the π orbital of the benzene to the boron atom.

In contrast, in the dimethylamino-substituted **4**, while the eliminated benzene ring has six σ-bonding NBOs, only two π-bonding NBOs (C2-C3 and C2*-C3*) were found. These NBOs also support the quinoidal structure of the benzene ring as previously mentioned. Most importantly, the analysis showed a σ-bonding NBO between the B1 and C1 atoms, and consists of the hybrid orbitals of the boron and carbon atoms with a high p character (B: $sp^{4.77}$, C: $sp^{5.08}$). This σ-bonding NBO clearly demonstrated that the boracyclophane **4** has a high σ-complex character, in which the boron atom and the benzene ring are strongly bound to each other. The natural localized molecular orbital (NLMO) also suggested the σ-bonding character (see the Supporting Information). The Wiberg bond index for the B1-C1 bond of **4** was 0.49, which was much higher than that for **2**. In addition, the deformation of the benzene ring in **4** was supported by the nucleus independent chemical shift (NICS).[18] While the NICS(0) value of the benzene ring in **2** was calculated to be −6.66 ppm at the B3LYP/6-31+G(d) level of theory, that of **4** was −3.12 ppm, which is indicative of the reduced aromaticity in **4**.

Finally, we investigated the reduction of the boracyclophane **2** to generate a radical anion species. As previously mentioned, its LUMO consists of the vertical orbital interaction between the vacant p orbital of the boron atom and the π* orbital of the benzene ring. We envisioned that the one-electron reduction would produce a radical anion with a one-electron B–C bond.[19–21] The treatment of **2** with potassium metal in THF and subsequent recrystallization in the presence of [2.2.2]cryptand produced colorless crystals (Scheme 3).



2　　**3**·K 66%

Scheme 3. Reduction of boracyclophane **2**.

The NMR spectroscopy and X-ray crystallographic analysis revealed that the product was not the expected radical anion, but a potassium salt of the *tert*-butylborate **3**·K. Although the mechanism of the generation of **3**·K is unclear at this stage, one possibility is the formation of the radical anion and subsequent elimination of a hydrogen radical. This result was consistent with the cyclic voltammogram of **2**, which showed an irreversible reduction wave with the cathodic peak potential E_{pc} of −2.38 V vs. Fc/Fc^+.

In the X-ray crystal structure of **3**·K (Figure 5),[10] similar to the previously reported corresponding fluoroborate,[8] the borate 3^- has a bowl-shaped structure. The bowl depth, defined by the distance between the B1 atom and the plane that consists of three carbon atoms (C4, C10, and C17) on the *para*-position of the benzene rings, is 1.36 Å. Thus, the bowl structure of the *tert*-butylborate **3**·K is shallower than the corresponding fluoroborate, whose bowl depth is 1.65 Å in the crystal structure.[8] Interestingly, the B1-C20 bond adopts an eclipsed conformation, which likely results from avoiding the steric repulsion with the peripheral methyl groups. Consequently, the B1-C20 bond of 1.737(5) Å is rather long. In addition, although the boracyclohexadiene ring with the CH_2 moiety adopts a boat conformation, the two CMe_2 moieties are not significantly deviated from the planes of the remaining four carbon atoms in the boracyclohexadiene. This is also likely due to steric repulsion with the *tert*-butyl group and the methyl groups on the benzyl position.

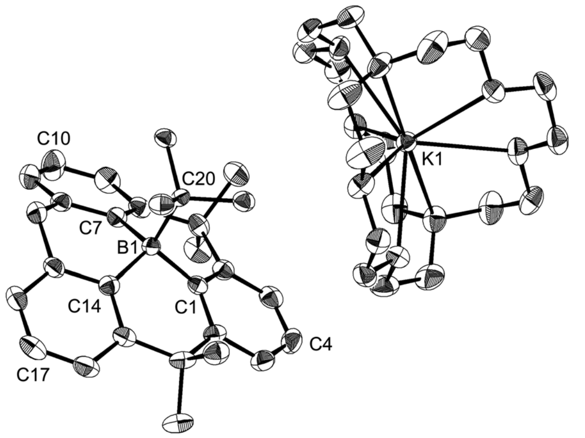


Figure 5. ORTEP drawing of **3·K** (thermal ellipsoids shown at 50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–C1 1.608(5), B1–C7 1.608(5), B1–C14 1.610(5), B1–C20 1.737(5); C1-B1-C7 108.4(3), C1-B1-C14 108.1(3), C7-B1-C14 107.5(3).

In summary, we have investigated the reaction of the planarized triphenylboranes **1** and **8** with *t*BuLi and obtained **2** and **4**, respectively. Despite the structural constraint in the planarized triphenylboranes, they underwent the formal nucleophilic substitution reaction on the boron center through a tetracoordinate borate intermediate. The structural elucidation of the boracyclophanes **2** and **4** provided insights into the interaction between the boron atom and the eliminated benzene ring. Notably, the interaction mode, that is, the degree of the σ- and π-complex character, is dependent on the electron-donating character of the benzene ring. Thus, the introduction of the dimethylamino group to the benzene ring strongly alters the interaction from a π-complex character to a σ-complex character. These structures can be regarded as the snapshots for the activation of an aromatic benzene ring with a Lewis acid. These findings should be important for the coordination chemistry of the main group compounds.

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[1] a) N. C. Baenziger, A. D. Nelson, *J. Am. Chem. Soc.* **1968**, *90*, 6602; b) P. C. Miklis, R. Ditchfield, T. A. Spencer, *J. Am. Chem. Soc.* **1998**, *120*, 10482; c) D. Heidrich, *Angew. Chem.* **2002**, *114*, 3343; *Angew. Chem. Int. Ed.* **2002**, *41*, 3208.

[2] a) S. M. Hubig, J. K. Kochi, *J. Org. Chem.* **2000**, *65*, 6807; b) C. A. Reed, K.-C. Kim, E. S. Stoyanov, D. Stasko, F. S. Tham, L. J. Mueller, P. D. W. Boyd, *J. Am. Chem. Soc.* **2003**, *125*, 1796; c) D. Lenoir, *Angew. Chem.* **2003**, *115*, 880; *Angew. Chem. Int. Ed.* **2003**, *42*, 854.

[3] a) J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917; b) L. Pauling, *Science* **1994**, *263*, 983; c) G. A. Olah, G. Rasul, X.-y. Li, H. A. Buchholz, G. Sandford, G. K. S. Prakash, *Science* **1994**, *263*, 983; d) J. B. Lambert, S. Zhang, *Science* **1994**, *263*, 984; e) C. A. Reed, Z. Xie, *Science* **1994**, *263*, 985; f) P. v. R. Schleyer, P. Buzek, T. Müller, Y. Apeloig, H.-U. Siehl, *Angew. Chem.* **1993**, *105*, 1558; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1471; g) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325; h) M. F. Ibad, P. Langer, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2011**, *133*, 21016.

[4] a) G. S. Hair, A. H. Cowley, R. A. Jones, B. G. McBurnett, A. Voigt, *J. Am. Chem. Soc.* **1999**, *121*, 4922; b) J. F. Malone, W. S. MacDonald, *J. Chem. Soc. A* **1970**, 3362; c) M. Schulte, F. P. Gabbaï, *Chem. Eur. J.* **2002**, *8*, 3802; d) M. Gorlov, L. Kloo, *Coord. Chem. Rev.* **2008**, *252*, 1564.

[5] a) P. Tarakeshwar, J. Y. Lee, K. S. Kim, *J. Phys. Chem. A* **1998**, *102*, 2253; b) P. Tarakeshwar, S. J. Lee, J. Y. Lee, K. S. Kim, *J. Phys. Chem. B* **1999**, *103*, 184.

[6] J. D. Hoefelmeyer, S. Solé, F. P. Gabbaï, *Dalton Trans.* **2004**, 1254.

[7] H. B. Mansaray, A. D. L. Rowe, N. Phillips, J. Niemeyer, M. Kelly, D. A. Addy, J. I. Bates, S. Aldridge, *Chem. Commun.* **2011**, *47*, 12295.

[8] Z. Zhou, A. Wakamiya, T. Kushida, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 4529.

[9] T. Kushida, Z. Zhou, A. Wakamiya, S. Yamaguchi, *Chem. Commun.* **2012**, *48*, 10715.

[10] CCDC 936367 (**2**), 936368 (**4**), and 936369 (**3**K) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806.

[12] B. Wrackmeyer, H. Nöth, *Chem. Ber.* **1976**, *109*, 1075.

[13] The theoretical calculations were performed with the Gaussian09 program.

[14] a) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574; b) S. Yamaguchi, A. Wakamiya, *Pure Appl. Chem.* **2006**, *78*, 1413.

[15] a) "Atoms in Molecules: A Quantum Theory": R. F. W. Bader in *the International Series of Monographs of Chemistry* (Eds.: J. Halpen, M. L. H. Green), Clarendon, Oxford, **1990**; b) R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893; c) R. F. W. Bader, *J. Phys. Chem. A* **1998**, *102*, 7314.

[16] a) J. P. Wolfe, J. Åhman, J. P. Sadighi, R. A. Singer, S. L. Buchwald, *Tetrahedron Lett.* **1997**, *38*, 6367; b) G. Mann, J. F. Hartwig, M. S. Driver, C. Fernández-Rivas, *J. Am. Chem. Soc.* **1998**, *120*, 827; c) T. Agou, M. Sekine, J. Kobayashi, T. Kawashima, *Chem. Eur. J.* **2009**, *15*, 5056; d) B. Qu, Y, Ma, Q. Ma, X. Liu, F. He, C. Song, *J. Org. Chem.* **2009**, *74*, 6867.

[17] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083.

[18] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) P. v. R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta, N. J. R. van Eikema Hommes, *Org. Lett.* **2001**, *3*, 2465; c) P. v. R. Schleyer, M. Manoharan, H. Jiao, F. Stahl, *Org. Lett.* **2001**, *3*, 3643; d) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

[19] The radical anions with a one-electron σ bond between the two boron atoms: a) R. L. Hudson, F. Wlliams, *J. Am. Chem. Soc.* **1977**, *99*, 7714; b) J. D. Hoefelmeyer, F. P. Gabbaï, *J. Am. Chem. Soc.* **2000**, *122*, 9054.

[20] The neutral radical species with a one-electron π bond between the boron and carbon atoms: a) C.-W. Chiu, F. P. Gabbaï, *Angew. Chem.* **2007**, *119*, 1753; *Angew. Chem. Int. Ed.* **2007**, *46*, 1723; b) C.-W. Chiu, F. P. Gabbaï, *Angew. Chem.* **2007**, *119*, 7002; *Angew. Chem. Int. Ed.* **2007**, *46*, 6878; c) T. Matsumoto, F. P. Gabbaï, *Organometallics* **2009**, *28*, 4252.

[21] A boron–copper one-electron σ bond: M.-E. Moret, L. Zhang, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 3792.