Angewandte
Zuschriften

Structure Elucidation

DOI: 10.1002/ange.201210236

Borylated Dibenzoborepin: Synthesis by Skeletal Rearrangement and Photochromism Based on Bora-Nazarov Cyclization**

*Azusa Iida, Shohei Saito, Takahiro Sasamori, and Shigehiro Yamaguchi**

The incorporation of boron atoms into π-conjugated skeletons has emerged as a useful strategy to produce new optoelectronic materials with unusual electronic structures.[1] Indeed, many fascinating boron-containing π systems have been recently developed for various applications, such as organic light-emitting diodes,[2] two-photon absorption materials,[3] sensors,[4] and photochromic systems.[5] One key reason for the use of a tricoordinated boron atom from this point of view is its isosterism with a cationic tricoordinated carbon atom (Figure 1). Replacement of a cationic carbon atom in a π-conjugated skeleton by a boron atom enables transformation of the highly electron-accepting π skeleton into a noncharged, isolable form. It is noteworthy that, alternatively, the substitution of a carbon atom next to the cationic carbon atom by a boron atom also results in an overall noncharged isosteric form. We now report an example that these isosterisms lead to a new reaction and produce a unique π system.

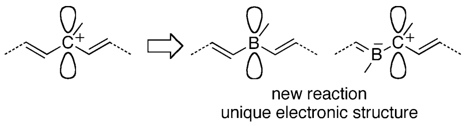
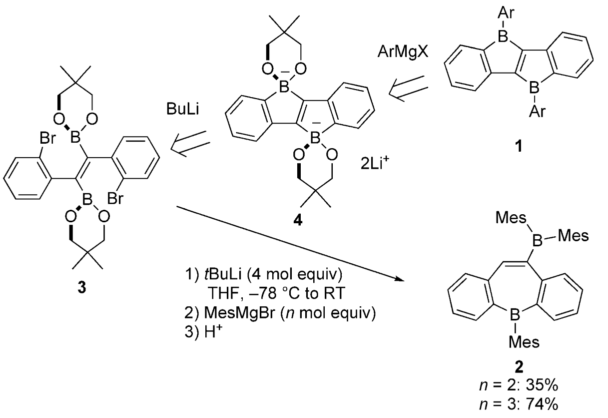


Figure 1. B/C$^+$ isosterism as a strategy for the development of new π-conjugated systems.

As a part of our study of the main group element containing ladder π systems,[6] we have attempted to synthesize the borole-fused borole **1** (hereafter, abbreviated as diborole) as a highly electron-accepting, antiaromatic scaffold (Scheme 1).[7] During the course of our research, the first synthesis of this skeleton was achieved by Piers and coworkers using an elegant photoisomerization of bi(benzoboratacyclobutylidene).[8] Meanwhile, in our efforts to synthesize this skeleton, we unexpectedly obtained the 10-borylated dibenzoborepin **2** by an anomalous skeletal rearrangement. To our surprise, this compound showed dramatic photochromic properties. The photoreactivity of **2** is unusual in light of the inherent high photostability of the dibenzoborepin skeleton.[9] We have now succeeded in unambiguously determining the structure of the photoproduct, and have disclosed its unusual electronic structure.



Scheme 1. Retrosynthesis of diborole **1** and transformation from **3** into the 10-boryl-substituted dibenzoborepin **2**.

Our original idea to synthesize the diborole **1** was to transform a bis(*o*-bromophenyl)ethene diboronic ester **3** into the diborate intermediate **4** through a halogen–lithium exchange reaction with BuLi, with subsequent introduction of an Ar group onto the boron atoms by treatment with ArMgX (Scheme 1). We conducted this reaction sequence using *t*BuLi in THF and 2 mol equivalents of MesMgBr. Purification by silica gel column chromatography afforded a colorless compound. However, X-ray crystal structure analysis revealed that the product was not the desired **1**, but the 10-dimesitylboryl-substituted dibenzoborepin **2** (Figure 2a). The yield of this compound was 35%, which was further improved to 74% by increasing the amount of MesMgBr to 3 mol equivalents and conducting protonation with water.

It is noteworthy that the anomalous skeletal rearrangement from **3** to **2** proceeds in high yield. To elucidate the mechanism of this transformation,[10] we isolated and identified the key intermediates in the reaction sequence. First, the halogen–lithium exchange reaction of **3** was performed using 4 mol equivalents of *t*BuLi at −78 °C in diethyl ether to obtain a product as an insoluble compound (Scheme 2). The

---

[*] Dr. A. Iida, Dr. S. Saito, Prof. Dr. S. Yamaguchi
Research Center for Materials Science and Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University and CREST (Japan) Science and Technology Agency (JST)
Furo, Chikusa, Nagoya 464-8602 (Japan)
E-mail: yamaguchi@chem.nagoya-u.ac.jp

Prof. Dr. T. Sasamori
Institute for Chemical Research, Kyoto University
Gakasho, Uji, Kyoto 611-0011 (Japan)

[**] This work was partly supported by CREST, JST, and a Grant-in-Aid for Scientific Research on Innovative Areas (Stimuli-responsive Chemical Species, No. 24109007) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. A. I. expresses her gratitude to the JSPS research fellowship for young scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201210236.

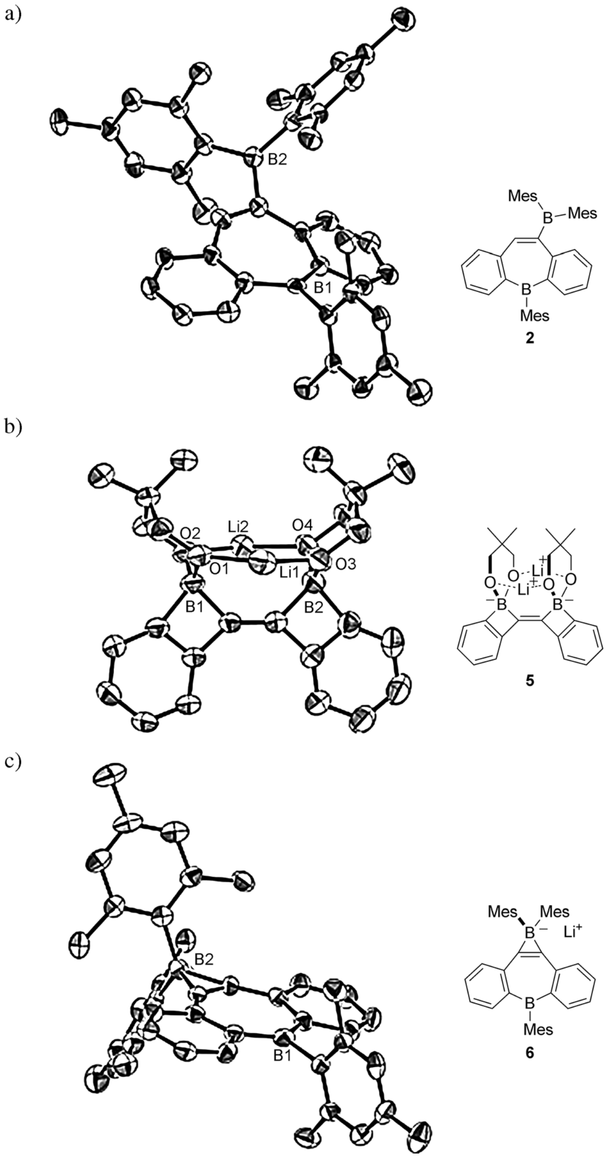
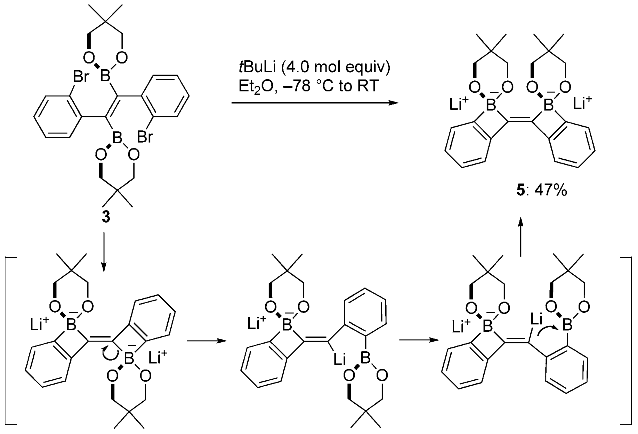


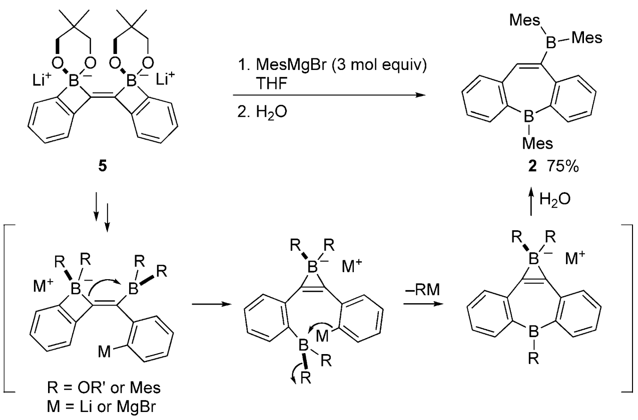
Figure 2. ORTEP drawings of a) **2**, b) **5**, and c) **6**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms, THF molecules coordinating to Li atoms in **5**, Li(thf)$_4^+$, and solvent molecules in **6** are omitted for clarity. For **6**, only one of two crystallographically independent structures is shown.



Scheme 2. Transformation from **3** into **5** and its plausible mechanism.

dilithiation cleanly proceeded and spontaneously produced precipitates. Recrystallization from THF gave a pure product as colorless needles. X-ray crystal structure analysis revealed that the compound was the bi(benzoboratacyclobutylidene) **5** (Figure 2b) instead of the expected diborole diborate **4**.[11] The yield of isolated **5** was 47%. This compound is likely produced through the formation of (*E*)-bis(benzoboratacyclobutylidene), instead of the five-membered borole rings, with subsequent *E*–*Z* isomerization (Scheme 2). The favorable formation of the four-membered ring over the five-membered ring seems rather general, since a similar reaction was also reported in the synthesis of **1** by Piers and coworkers.[8] The *E*–*Z* olefin isomerization may be based on the borate/borane equilibrium. An alkenyl group is dissociated from one of the borate moieties to produce a sp^2-hybridized carbanion, which undergoes inversion to eventually produce the *Z* isomer.[12] The driving force of this isomerization should be the formation of the energetically favorable chelate complex **5**, which binds two Li ions to the two vicinal borate oxygen atoms. The chelate structure was confirmed by X-ray structural analysis (Figure 2b).

The treatment of **5** with 3 mol equivalents of MesMgBr in THF indeed gave the borylated dibenzoborepin **2** in 75% yield (Scheme 3). When we tried to isolate an intermediate for this reaction without conducting the aqueous work-up, direct recrystallization of the mixture from THF gave red crystals of **6**. X-ray crystal structure analysis demonstrated that this compound has an unprecedented boratacyclopropene-fused borepin skeleton (Figure 2c).[11] The treatment of **6** with water quantitatively gave the product **2**, thus confirming that **6** is an intermediate in the formation of **2**. Although the details of the substitution reaction of the alkoxy groups on the boron atoms with MesMgBr are unclear, this skeletal rearrangement might be again based on the borate/borane equilibrium (Scheme 3). Thus, a phenyl anion is dissociated from one of the borate moieties and then the boratacyclopropene skeleton is produced. The eliminated phenyl anion



Scheme 3. Transformation from **5** into **2** and a plausible mechanism for skeletal rearrangement.

reacts with the other boron atom to form the borepin skeleton.

Upon irradiation with UV light ($\lambda = 320$ nm), a colorless solution of **2** in benzene turned to navy blue, as shown in Figure 3. In the absorption spectra of **2**, the intensity of two distinct and sharp bands at $\lambda = 346$ and 387 nm decreased and a new broad band appeared at $\lambda = 634$ nm with the isosbestic point at $\lambda = 398$ nm. This photochromic behavior was also observed in other common solvents including *n*-pentane, cyclohexane, CH_2Cl_2, $CHCl_3$, acetonitrile, and MeOH. Even a cast film of **2** prepared from a toluene solution showed the photochromic behavior (see the Supporting Information), whereas its crystals did not show the photochromic response, probably because of the immobility of the molecule in the crystal lattice.

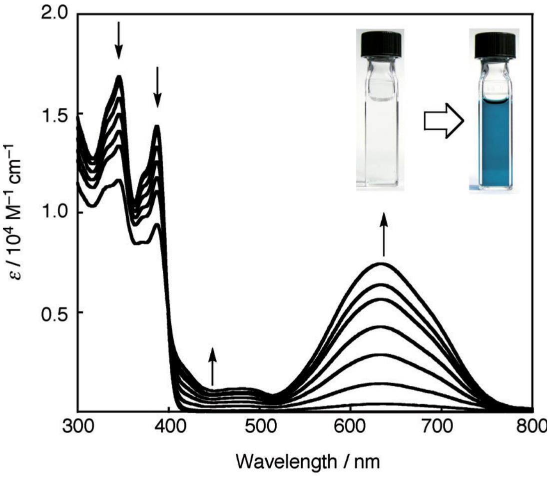


Figure 3. UV-Vis absorption spectra of **2** upon irradiation by UV light ($\lambda = 320$ nm) in benzene. Inset: Photographs of a benzene solution of **2** before (left) and after (right) irradiation of UV light.

Monitoring of the reaction by ^{1}H NMR spectroscopy in [D$_8$]THF (see the Supporting Information) showed that **2** was cleanly converted into the single product **7** by the photoirradiation. Notably, the photoproduct **7** cleanly reverted to the initial compound **2** upon storing the solution overnight in a dark at room temperature. Thus, this chromic reaction is reversible.

To characterize the structure of **7**, we successfully obtained single crystals from a cooled *n*-pentane solution. X-ray crystal structure analysis (Figure 4)[11] showed that the crystal structure contains two crystallographically independent molecules, **7A** and **7B**. As their structural parameters are similar to each other (see the Supporting Information), we only discuss the structure of **7A**. In this structure, a new C−C bond is formed between the *ortho*-carbon atom (C8) of one of the mesityl groups and the olefinic carbon atom (C4) of the borepin moiety to produce a five-membered ring. As a result, the mesityl group is transformed into a nonaromatic 1,3-cyclohexadiene-like structure (1.351–1.380 Å for C=C bonds and 1.423–1.487 Å for C−C bonds). It is important to note that the carbon atoms, C3 and C7, connected to the boron atom in the five-membered ring, still retain the sp^2 hybridization. The sums of the C-C-C and C-C-B angles are 360.0° for both the C3 and C7 atoms. The boron atom B2 also retains a trigonal-planar geometry with the sum of the C-B-C angles being 360.0°. The bond lengths for the C3−B2 and B2−C7 bonds are 1.527(5) Å and 1.522(5) Å, respectively. These values are between the bond lengths of typical C=B double bonds [e.g., $(Me_3Si)_2C{=}B(tBu)$ 1.361(5) Å][13] and ordinary C_{sp^2}−B single bonds (e.g., Ar_3B, 1.57–1.59 Å),[14] but still comparable or slightly longer than the shortest examples of the C_{sp^2}−B single bonds (1.48–1.52 Å).[15] Notably, the methyl group at C8 and the hydrogen atom at C4 have a *cis* configuration. No other stereoisomer was observed by ^{1}H NMR spectroscopy of the reaction mixture after the photoirradiation, thus implying that the formation of **7** proceeds in a stereospecific manner (see below).

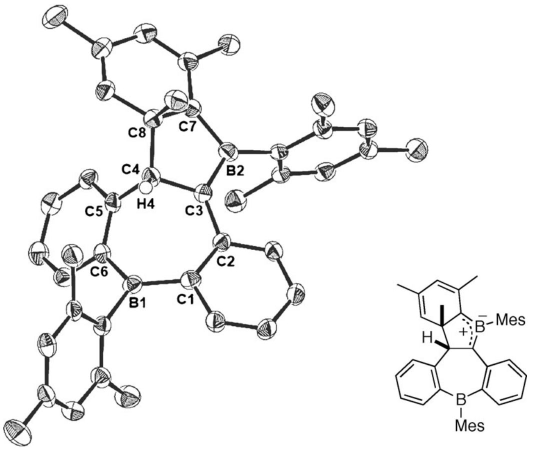


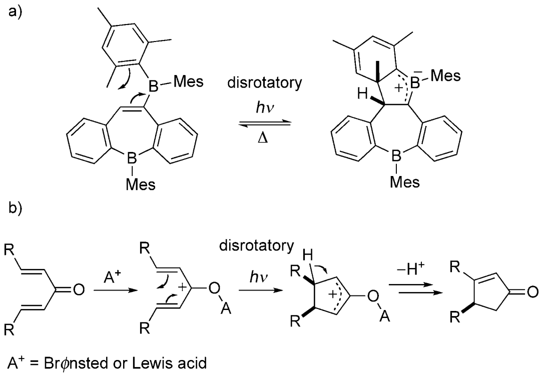
Figure 4. ORTEP drawing of **7A**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms, except H4, are omitted for clarity.

The most unique structural feature in **7** is the C-B-C substructure in the five-membered ring. Taking the number of π electrons assigned to this moiety into consideration, the C-B-C skeleton is isoelectronic to the allyl cation. To gain fundamental insights into this skeleton,[16] we first theoretically compared the electronic structures of $CH_2{=}BH^-{-}CH_2^+$ (**8**) and the allyl cation (**9**) as model systems. According to the geometry optimization at the B3LYP/6-31G* level of theory, the C−B bond length in **8** is 1.49 Å. The natural bond orbital (NBO) analysis (MP2/6-31G*//B3LYP/6-31G*)[17] showed that the Wiberg bond index of the C−B bond in **8** is 1.36, while that of the C−C bond in **9** is 1.51. This difference implies that **8** has a smaller double bond character compared to that of **9**.

The geometry optimization of **7** at the B3LYP/6-31G* level of theory nicely reproduced the crystal structure (see the Supporting Information).[18] In the optimized structure, the C3−B2 and B2−C7 bonds are 1.52 and 1.53 Å, respectively. According to the NBO analysis, the Wiberg bond index of the C−B bonds are 1.09 for B2-C7 and 1.22 for B2−C3, thus demonstrating that the single bond character of the C−B−C moiety becomes more pronounced in the extended π-conjugated skeleton of **7**, compared to the parent $CH_2{=}BH^-{-}CH_2^+$ skeleton. However, the C−B−C moiety in **7** still maintains the allyl cation-like charge distribution. Thus, the natural population analysis (NPA) of **7** showed that the atomic charges of C3, B2, and C7 are −0.19, +0.48, and −0.11, respectively. Compared to the charge distribution of ordinary C_{sp^2}−B bonds [e.g., C(−0.43)-B(+0.94) in Ph_3B], B2 is more negative, while C3 and C7 are more positive.

The blue color of **7** observed in the photochromism can be understood by considering its molecular orbitals. Both the HOMO and LUMO of **7** are spread over the polyene skeleton which consists of butadiene, an allyl cation-like C−B−C moiety, and a borylated phenyl group (see the Supporting Information). This skeleton is isoelectronic to the electron-deficient decatetraenyl dication, whose LUMO energy level should be highly stabilized. Indeed, the LUMO energy level of **7** calculated at the M06/6-31+G**//B3LYP/6-31G* level of theory is quite low at −3.01 eV, while the HOMO level is moderately high at −5.37 eV. The resulting narrow HOMO–LUMO gap should be responsible for the absorption band observed at the long wavelength in the visible region. Indeed, a time-dependent DFT calculation of **7** confirmed that the longest absorption band observed at $\lambda = 634$ nm is assignable to the HOMO–LUMO transition.

How can we rationalize the mechanism of the photoreaction from **2** to **7**? In this regard, noteworthy is the similarity of the present reaction to the Nazarov cyclization,[19] which is a 4π-electrocyclic reaction of a dialkenylketone to give a cyclopentenyl cation (Scheme 4b). The present photoreaction can be regarded as a bora-Nazarov cyclization (Scheme 4a) since **2** is isosteric to an intermediate of the Nazarov cyclization produced by the activation of the carbonyl group with a Brønsted or Lewis acid. The configuration of the newly formed C−C bond in **7** is consistent with the frontier orbital theory. Namely, the cyclization proceeds in a disrotatory fashion to produce the *cis* configuration between the methyl group at C8 and the hydrogen atom at C4. While the 6π-electrocyclic reactions of O-, N-, or S-containing substrates analogous to the Nazarov cyclization are well known,[20] the photoreactions based on the bora-Nazarov cyclizaion is unprecedented, to the best of our knowledge.[21] While the Nazarov cyclization generally proceeds under both thermal or photoirradiation conditions, the present bora-Nazarov cyclization requires photoirradiation. Even the heating of **2** at 80 °C for 12 h did not give the product at all. This is probably because of the thermodynamic instability of the thermally cyclized product compared with **2**. It is also noted that **7** is isoelectronic to a cyclopentenyl cation intermediate of the Nazarov cyclization. Thus, one can say that the B/C⁺ isosterism allows the isolation of the unstable cationic Nazarov intermediate as an overall noncharged form.



Scheme 4. Comparison between the transformation from **2** into **7** (a) and the Nazarov cyclization (b).

In summary, we have unexpectedly obtained a boryl-substituted dibenzoborepin in good yield in one pot from a diarylethene diboronic ester. The mechanistic study showed that this product is produced by a skeletal rearrangement through an unprecedented boratacyclopropene-fused borepin intermediate. The dimesitylboryl borepin showed dramatic photochromic behavior with a color change from colorless to deep blue, and the photoproduct was thermally reverted to the starting borepin. This photoreaction can be rationalized as a bora-Nazarov cyclization. Notably, the B/C⁺ isosterism is responsible for this new reactivity and renders a product having an unusual electronic structure. This photochromic behavior may have the potential to be a basis for the development of new photoresponsive materials. Further study to explore this possibility is in progress in our laboratory.

Received: December 22, 2012

Keywords: boron · cyclization · electrocyclic reactions · photochromism · structure elucidation

---

[1] For reviews: a) C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927; b) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574; c) S. Yamaguchi, A. Wakamiya, *Pure Appl. Chem.* **2006**, *78*, 1413; d) F. Jäkle, *Coord. Chem. Rev.* **2006**, *250*, 1107; e) N. Matsumi, Y. Chujo, *Polym. J.* **2008**, *40*, 77; f) Z. M. Hudson, S. Wang, *Acc. Chem. Res.* **2009**, *42*, 1584; g) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985.

[2] a) T. Noda, Y. Shirota, *J. Am. Chem. Soc.* **1998**, *120*, 9714; b) T. Noda, H. Ogawa, Y. Shirota, *Adv. Mater.* **1999**, *11*, 283; c) Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto, T. Ohara, *J. Am. Chem. Soc.* **2000**, *122*, 11021; d) W.-L. Jia, D.-R. Bai, T. McCormick, Q.-D. Liu, M. Motala, R.-Y. Wang, C. Seward, Y. Tao, S. Wang, *Chem. Eur. J.* **2004**, *10*, 994; e) W. L. Jia, X. D. Feng, D. R. Bai, Z. H. Lu, S. Wang, G. Vamvounis, *Chem. Mater.* **2005**, *17*, 164; f) D. Tanaka, T. Takeda, T. Chiba, S. Watanabe, J. Kido, *Chem. Lett.* **2007**, *36*, 262; g) C. Sun, Z. M. Hudson, M. G. Helander, Z.-H. Lu, S. Wang, *Organometallics* **2011**, *30*, 5552.

[3] a) Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz, L.-T. Cheng, *J. Chem. Soc. Chem. Commun.* **1990**, 1489; b) Z. Yuan, N. J. Taylor, Y. Sun, T. B. Marder, I. D. Williams, L.-T. Cheng, *J. Organomet. Chem.* **1993**, *449*, 27; c) K. C. Ching, M. Lequan, R.-M. Lequan, A. Grisard, D. Markovitsi, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 2225; d) M. Lequan, R. M. Lequan, K. Chane-Ching, *J. Mater. Chem.* **1991**, *1*, 997; e) C. Lambert, S. Stadler, G. Bourhill, C. Bräuchle, *Angew. Chem.* **1996**, *108*, 710; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 644; f) Z.-Q. Liu, Q. Fang, D. Wang, G. Xue, W.-T. Yu, Z.-S. Shao, M.-H. Jiang, *Chem. Commun.* **2002**, 2900; g) Z.-Q. Liu, Q. Fang, D. Wang, D.-X. Cao, G. Xue, W.-T. Yu, H. Lei, *Chem. Eur. J.* **2003**, *9*, 5074.

[4] a) S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2001**, *123*, 11372; b) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbaï, *Chem. Rev.* **2010**, *110*, 3958, and references therein.

[5] a) K. Ansorg, H. Braunschweig, C.-W. Chiu, B. Engels, D. Gamon, M. Hügel, T. Kupfer, K. Radacki, *Angew. Chem.* **2011**, *123*, 2885; *Angew. Chem. Int. Ed.* **2011**, *50*, 2833; b) Y.-L. Rao, H. Amarne, S. Wang, *Coord. Chem. Rev.* **2012**, *256*, 759, and references therein; c) Y.-L. Rao, L. D. Chen, N. J. Mosey, S. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 11026; d) K. Nagura, S. Saito, R. Frölich, F. Glorius, S. Yamaguchi, *Angew. Chem.* **2012**, *124*, 7882; *Angew. Chem. Int. Ed.* **2012**, *51*, 7762.

[6] A. Fukazawa, S. Yamaguchi, *Chem. Asian J.* **2009**, *4*, 1386.

[7] a) A. Iida, S. Yamaguchi, *J. Am. Chem. Soc.* **2011**, *133*, 6952; b) A. Iida, A. Sekioka, S. Yamaguchi, *Chem. Sci.* **2012**, *3*, 1461.

[8] J. F. Araneda, B. Neue, W. E. Piers, M. Parvez, *Angew. Chem.* **2012**, *124*, 8674; *Angew. Chem. Int. Ed.* **2012**, *51*, 8546.

[9] a) L. G. Mercier, W. E. Piers, M. Parvez, *Angew. Chem.* **2009**, *121*, 6224; *Angew. Chem. Int. Ed.* **2009**, *48*, 6108; b) A. Caruso, Jr., M. A. Siegler, J. D. Tovar, *Angew. Chem.* **2010**, *122*, 4309; *Angew. Chem. Int. Ed.* **2010**, *49*, 4213; c) D. R. Levine, A. Caruso, Jr., M. A. Siegler, J. D. Tovar, *Chem. Commun.* **2012**, *48*, 6256.

[10] Eisch and co-workers have reported the transformation from borole precursors to borepin rings: a) J. J. Eisch, J. E. Galle, *J. Am. Chem. Soc.* **1975**, *97*, 4436; b) J. J. Eisch, J. E. Galle, B. Shafii, A. L. Rheingold, *Organometallics* **1990**, *9*, 2342.

[11] CCDC 912372 (**2**), 912373 (**3**), 912374 (**5**), 915855 (**6**) and 916528 (**7**) 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.

[12] R. Knorr, E. Lattke, E. Räpple, *Chem. Ber.* **1981**, *114*, 1581.

[13] R. Boese, P. Paetzold, A. Tapper, R. Ziembinski, *Chem. Ber.* **1989**, *122*, 1057.

[14] a) F. Zettler, H. D. Hausen, H. J. Hess, *J. Organomet. Chem.* **1974**, *72*, 157; b) J. F. Blount, P. Finocchiaro, D. Gust, K. Mislow, *J. Am. Chem. Soc.* **1973**, *95*, 7019; c) M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1986**, *108*, 4235.

[15] a) A. Sundararaman, R. Varughese, H. Li, L. N. Zakharov, A. L. Rheingold, F. Jäkle, *Organometallics* **2007**, *26*, 6126; b) C. Fan, W. E. Piers, M. Parvez, R. McDonald, *Organometallics* **2010**, *29*, 5132; c) Z. Zhou, A. Wakamiya, T. Kushida, S. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 4529.

[16] A theoretical study on the singlet diradical character of CH_2-BH-CH_2 with the coordination of donor species has been reported: K. Kubota, H. Takahashi, H. Fukui, S. Bonness, K. Yoneda, R. Kishi, T. Kubo, K. Kamada, K. Ohta, B. Champagne, E. Botek, M. Nakano, *Chem. Phys. Lett.* **2009**, *477*, 309.

[17] NBO version 3.1, E. D. Glendening A. E. Reed, J. E. Carpenter, F. Weinghold.

[18] We also conducted the broken-symmetry UB3LYP/6-31G* calculation, which demonstrated no singlet biradical character of **7**. See references: a) L. Noodleman, *J. Chem. Phys.* **1981**, *74*, 5737; b) L. Noodleman, E. J. Baerends, *J. Am. Chem. Soc.* **1984**, *106*, 2316; c) L. Noodleman, C. Y. Peng, D. A. Case, J. M. Mouesca, *Chem. Rev.* **1995**, *95*, 199.

[19] L. Kürti, B. Czakó, *Strategic Applications of Named Reactions in Organic Synthesis*, Elsevier Academic Press, Amsterdam, **2005**, p. 304.

[20] A. G. Schultz, *Acc. Chem. Res.* **1983**, *16*, 210.

[21] Review for photoreactions of boron compounds: a) A. Pelter, R. T. Pardasani, P. Pardasani, *Tetrahedron* **2000**, *56*, 7339. For 6π-electrocyclic reaction of aminoboranes, see: b) P. J. Grisdale, J. L. R. Williams, *J. Org. Chem.* **1969**, *34*, 1675; c) P. Grisdale, M. Glogowski, J. L. R. Williams, *J. Org. Chem.* **1971**, *36*, 3821; d) M. E. Glogowski, P. J. Grisdale, J. L. R. Williams, T. H. Regan, *J. Organomet. Chem.* **1973**, *54*, 51; e) M. E. Glogowski, J. L. R. Williams, *J. Organomet. Chem.* **1980**, *195*, 123.