Organic LETTERS
Letter
pubs.acs.org/OrgLett

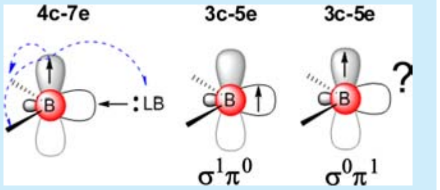
3-Center-5-Electron Boryl Radicals with $\sigma^0\pi^1$ Ground State Electronic Structure

Dongmei Lu,*[,†] Chao Wu,[‡] and Pengfei Li*[,‡]

[†]Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, China
[‡]Frontier Institute of Science and Technology and Frontier Institute of Chemistry, Xi'an Jiaotong University, Xi'an 710054, China

Supporting Information

ABSTRACT: Five- and six-membered boron heterocycle-based three-center-five-electron (**3c−5e**) type boryl radicals with unusual $\sigma^0\pi^1$ ground state electronic structures are predicted theoretically. Compared to $\sigma^1\pi^0$ analogs, their unique electronic structure leads to both lower reactivity toward H-atoms and stronger coordination with Lewis bases. The corresponding Lewis base-stabilized four-center-seven-electron (**4c−7e**) type boryl radicals are even more unreactive toward H-atoms than the conventional **4c−7e** ones.



Although boryl radicals have great potential in organic and polymer chemistry, their applications are far less developed than other main group element-based radicals, such as stannyl, silyl, etc.[1−3] This is largely attributed to limited available methods for generating boryl radicals with tunable stability. Generally, the B−H bonds in boranes are very strong (bond dissociation energy >312 kJ/mol);[4] therefore forming boryl radicals through homolytic cleavage has been very challenging. To overcome this limitation, over the past three decades, researchers have developed generations of boryl radicals (LB→•BH_2) derived from borane−Lewis base complexes containing relatively weakened B−H bonds. The effective Lewis bases (LBs) include amines,[5] phosphines,[6] nitrogen heterocycles,[7] and more recently N-heterocyclic carbenes (NHCs).[8] Very recently, the effects of substituents on boron have also been examined as a means for tuning the properties of boryl radicals.[9] In 2012, Yamashita and Nozaki et al. isolated a stable, persistent 1,3,2-diazaborinine neutral radical that exhibited reactivity as a boryl radical.[10]

In a recent paper,[11] to fully understand the effects of substituents on boron and the coordinating Lewis bases, we studied a series of boryl radicals using DFT methods and found that these two types of moieties on the central boron may function synergistically to efficiently stabilize a boryl radical. In combination with the previous developments,[4−11] we concluded the following: (1) in a three-center-five-electron (**3c−5e**, Figure 1) type boryl radical, the unpaired electron usually occupies the energetically low lying sp^2 orbital and is unable to be effectively stabilized by any substituents; (2) in a four-center-seven-electron (**4c−7e**, Figure 1) type boryl radical, the coordinating Lewis base takes the sp^2 orbital while the unpaired electron, now occupying the p_z orbital, can be effectively stabilized by appropriate substituents and the π-accepting Lewis base.

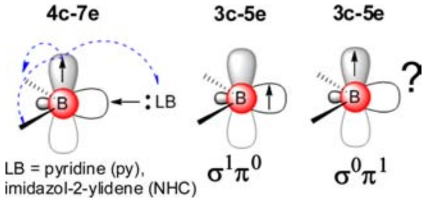


Figure 1. Electronic configuration of **4c−7e** and **3c−5e** boryl radicals.

At that point, a question immediately arose: Is it possible that the unpaired electron occupies the p_z orbital in the absence of a Lewis base? If so, such a **3c−5e** boryl radical would have a $\sigma^0\pi^1$ ground state, which might be effectively stabilized by proper substituents.[11] This type of boryl radical should form weaker bonds with H-atoms than the radicals with the $\sigma^1\pi^0$ configuration, since the unpaired electron has to adopt the higher energy sp^2 orbital to bond with the H-atom to reach the common trigonal planar product BHR_2. Moreover, the coordination of Lewis bases might be stronger toward the now empty in-plane sp^2 orbital. Thus, a shorter dative bond may in turn enhance the delocalization of spin density, a descriptor that strongly correlates with the hydrogen radical reaction enthalpy.[4,11,12] In this way, a new approach to making more stable boryl radicals may be possible.

For a **3c−5e** boryl radical to have the $\sigma^0\pi^1$ ground state electronic configuration, the energy level of the p_z orbital must be lower than that of the sp^2 orbital. This might be achieved by stabilizing the p_z-π orbital and/or destabilizing the sp^2-σ orbital. For this reason, we believe that conjugated ring systems such as 1,3,2-diazaborinine[10] might serve as good templates for our study. They have the following advantages: (1) the sp^2-σ and p_z-π orbitals can be unambiguously defined,[13] (2) the N−B−N segment within the ring system may allow σ-destabilization through lone pairs or bulky substituents on the two N-atoms, and (3) introducing π-electron-withdrawing groups (EWGs) on other atoms in the conjugated ring systems may promote π-

Received: January 27, 2014
Published: February 19, 2014

stabilization. Remarkably, during our study, a very recent publication by Hoffmann and Borden et al. on the electronic configuration of carbenes came to our attention. In their work, the authors predicted the existence of $\sigma^0\pi^2$ (singlet) ground state carbenes by applying a strategy similar to ours.[14] Encouraged and inspired by their results, we conducted the current work focusing on boryl radicals in particular.

We designed five- and six-membered boron-heterocyclic ring structures with or without ring conjugation for comparison. When π-stabilization is desired, a truncated 1,3,2-diazaborinine backbone, C=N–B–N=C (Figure 2), is introduced in several cases as a channel for efficiently transferring the electronic effects of substituents.[15] Furthermore, the C=N–B–N=C moiety should show π-attracting effects due to the strain of the antiaromatic 4π system[16] that can be relaxed by additional π-electrons. Accordingly, 20 heterocyclic boryl radicals (Table 1) were investigated. Structures **1–8**, **9–17** are five- and six-membered rings respectively, and **18–20** are annulated polycyclic structures. We performed computations with the objective of locating **3c–5e** type boryl radicals with the $\sigma^0\pi^1$ ground state electronic configuration. Afterward, the reactivity of all boryl radicals toward H-atoms and Lewis bases were examined. The relationships between their electronic configuration, spin density distribution, and reactivity were discussed.

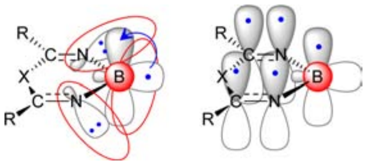
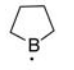
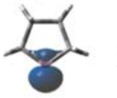
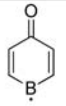
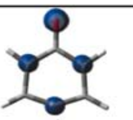
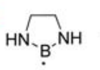
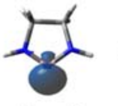
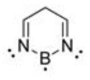
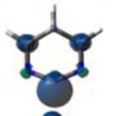
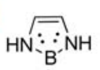
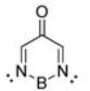
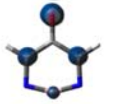
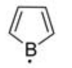
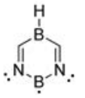
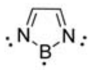
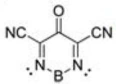
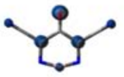
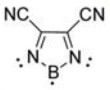
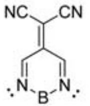
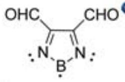
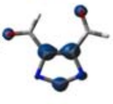
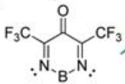
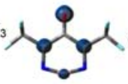
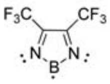
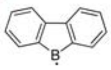
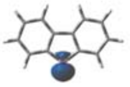
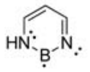
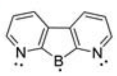
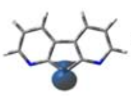
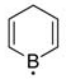
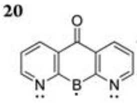
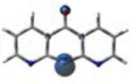


Figure 2. σ-Destabilizing (left) and π-stabilizing (right) effects of **3c–5e** boryl radicals. Red circles highlight the repulsion between nitrogen lone pairs and the σ direction sp^2 orbital.

As expected,[11] five-membered ring structures **1–3** do not show characteristics of the $\sigma^0\pi^1$ configuration.[17] No apparent π-stabilizing effect was observed, irrespective of whether it is a saturated ring (**1** and **2**) or an unsaturated ring (**3**), *or* with (**2** and **3**) or without (**1**) lone pairs on the (nitrogen) substituents. Borole is an antiaromatic 4π system. Hence, the calculation results showed that the spin density of the borole-based radical **4** is clearly located in the π direction with only a 0.57 spin population on boron. Its preference for the $\sigma^0\pi^1$ configuration can be understood as a strain release of the antiaromaticity. Interestingly, **4** presents a nonplanar structure with the boron buckling out of the plane (the dihedral angle of H–C–C–B is 162.4°). In comparison, 1,3,2-diazaborole radical **5**, which has both the σ-destabilization effect due to double electron repulsion of the two nitrogen lone pairs and π-stabilization effect due to an antiaromatic 4π system, shows a higher degree of spin density delocalization, leaving only a 0.25 spin population on boron. By introducing π-EWGs on the 4,5-positions of 1,3,2-diazaborole, radicals **6–7** show more extensive spin density delocalization, both with spin populations on boron of 0.22. Notably, the trifluoromethyl group, a σ-EWG, exhibits little effect on π-stabilization, as can be seen from **8**.

Table 1. Spin Density Plot of Boryl Radicals

no.		plot[a]	Bd[b]	no.			Bd
1[c]			0.92	11			0.24
2			0.97	12			0.68
3			1.10	13			0.14
4			0.57	14			0.15
5			0.25	15			0.14
6			0.22	16			0.07
7			0.22	17			0.16
8			0.26	18			0.96
9			0.95	19			0.89
10			0.96	20			0.56

[a] Top view of the molecules with the spin density isosurface (0.01 a.u). [b] Bd is the NBO spin population on boron. All calculations were done with DFT at the level of (U)MPW1K/6-31+G(d). Comparison with the (U)MP2/6-31+G(d) method is in the Supporting Information. [c] Red color denotes the $\sigma^1\pi^0$ configuration, and black color indicates the $\sigma^0\pi^1$ configuration.

For six-membered rings, we start with the 1,2-dihydro-1,3,2-diazaborinine radical **9**, which has a similar π electronic structure to the boryl radical reported by Yamashita and Nozaki et al.[10] The result showed that, alone, the single lone pair repulsion in **9** is not strong enough to force the unpaired electron to the 6e π system; hence, the spin population almost entirely remains on boron. Unlike **4** where a closed ring electron flow is present, 1,4-dihydroborinine radical **10** has an open C=C–B–C=C 4e π system. Thus, it does not show a significant π-attracting effect. As a result, the spin density remains in the sp^2-σ direction and the spin population on boron is close to unity (0.96). When the methylene group in **10** is replaced by a strongly π-EWG carbonyl group, the resulting borinin-4-one radical **11** can be viewed as a closed 6c-4e ring π system substituted by an oxyanion, where the carbonyl carbon holds an empty p_z orbital. Indeed, the calculated electronic structure of **11** exhibits extensive delocalization of the spin density over the π system, with the largest population (0.38) residing on the carbonyl oxygen and with a small spin population (0.24) on boron. This result indicates that, without in-plane destabilizing lone pair repulsion, the strongly electron-deficient conjugated π-ring system alone not only may induce a

$\sigma^0\pi^1$ ground state dramatically but also may lead to extensive delocalization of the spin density.

In a different approach, a 2,5-dihydro-1,3,2-diazaborinine-based radical **12** invokes an open conjugation unit C═N−B−N═C which introduces double in-plane destabilizing lone pair repulsions together with electron-deficient imine carbons which may exert a π-attractive conjugation effect. As a result, significant characteristics of the $\sigma^0\pi^1$ configuration are observed from the electronic structure of **12**, with a spin population on boron of 0.68. In searching for more stabilized $\sigma^0\pi^1$ type boryl radicals, we designed a 1,3,2-diazaborinin-5-one radical **13** and four structural variants (**14**−**17**) as examples that combine the structural features of **11** and **12**. The calculation results show that all of these structures display obvious characteristics of $\sigma^0\pi^1$ **3c−5e** type boryl radicals, with generally low spin density on boron (0.07−0.16). The lowest spin is observed in **16**, which incorporates a malononitril-2-ylidene unit in place of the oxygen in **13**, thus exhibiting extensive long distance delocalization of the spin density, apparently via allylic conjugation effects. Again, trifluoromethyl groups in **17** delocalize spin density less effectively compared to the cyano groups in **15**. Remarkably, a second boron atom can be incorporated into the six-membered ring to provide an empty p_z orbital and to greatly promote the spin density delocalization, analogous to the role of the carbonyl group in **13**. The resulting 2,5-dihydro-1,3,2,5-diazadiborinin-2-yl radical **14** has both di- and trisubstituted boron atoms, and the spin populations on B1 atom and B5 atom are 0.15 and 0.36, respectively.

In order to probe the effects of fusion with (hetero)aromatic rings and of other types of lone pair repulsions, we additionally designed structures **18**−**20**. Unlike **4**, the dibenzoborole-based radical **18** hardly shows any $\sigma^0\pi^1$ type characteristics. According to Clar's rule,[18] **18** can be represented by a dominant resonance structure consisting of two disjointed π-sextets and a π-electron "empty" central borole ring. Like before, the two 6π phenyl rings do not display a π-attractive effect. The same argument applies to **19**, whose weak but noticeable $\sigma^0\pi^1$ feature (spin population on boron 0.89) presumably originates from the σ-destabilizing nitrogen lone pairs. By combining spin delocalizing effects, such as a π-EWG, σ-destabilizing nitrogen lone pairs, and a less constrained six-membered central ring, **20** features a $\sigma^0\pi^1$ configuration, whose boron spin population (0.56) is significantly higher than that of **11** (0.24). Hence, limited by Clar's rule, multiple-ring structures may not be ideal candidates for spin delocalization.

In brief, **3c−5e** type boryl radicals with $\sigma^0\pi^1$ ground state electronic structures are formed when σ-destabilizing effects of lone pair electron repulsion and/or π-stabilizing effects of allylic conjugation systems are appropriately introduced into five- or six-membered boron heterocyclic structures. Generally, conjugated ring structures deficient of π-electrons can lead to effective spin density delocalization and the spin population on the central boron atom can be lowered down to 0.07 in our proposed structures.

With the $\sigma^0\pi^1$ ground state **3c−5e** type boryl radicals identified, we next examined the reactivity of **1**−**20** toward H-atoms. The results are plotted in Figure 3a. Consistent with previous studies,[4,11,12] the B−H binding energy strongly correlates with the spin population on boron. It is evident that the data points populate into four groups. Group I features the near unity boron spin population and the highest reactivity. These are the normal $\sigma^1\pi^0$ boryl radicals. Group II includes **4**, **12**, and **20** and has a medium boron spin population near 0.6. Group III consists of five-membered rings (**5**−**8**) that are shaped by both σ-destabilization and π-stabilization, and a six-membered ring **11** with only π-stabilization effects. Group IV features very low boron spin population (0.07−0.16) and also low reactivity. Particularly, **14** and **16** show reactivity toward H-atoms similar to some **4c−7e** boryl radicals,[11] suggesting the unusual stability of some $\sigma^0\pi^1$ type **3c−5e** boryl radicals in radical−radical reactions.

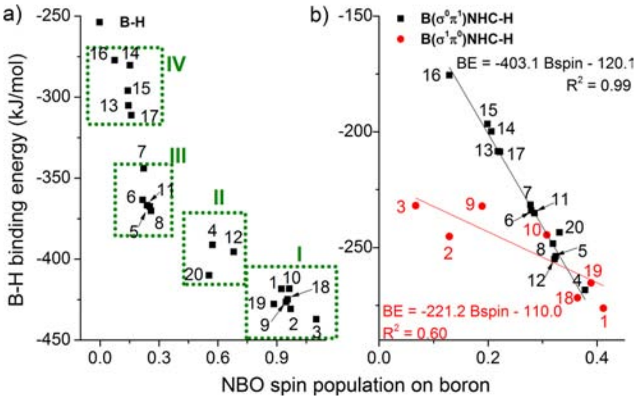


Figure 3. Binding energy of boryl radicals with H-atoms vs NBO spin population on boron. (a) **1** to **20**. (b) NHC-coordinated **1** to **20**. BE(X, kJ/mol) = E($B_{radical}$−X) − E($B_{radical}$) − E(X); X can be NHC or H-atom. Energy includes electronic energy and zero-point energy.

Further, we examined the reaction of these Lewis acidic boryl radicals with Lewis bases, such as pyridine and NHC. As expected, for the five- and six-membered boron heterocyclic radicals, the B-LB bindings for the $\sigma^0\pi^1$ radicals are generally moderately stronger than the $\sigma^1\pi^0$ ones. For example, the B-NHC binding energy for $\sigma^0\pi^1$ radicals is usually lower (more exothermic) than −350 kJ/mol, while the $\sigma^1\pi^0$ ones are higher (more endothermic) (see Supporting Information (SI), Figure S1). The coordination is exceptionally strong for fused N-heterocyclic radicals **19** and **20**, which is at least partly due to the formation of hydrogen bonds (~2.1 Å) between the N-atoms on the radical and protons on the NHC.

Next, the resulting LB-stabilized **4c−7e** radicals were also reacted with H-atoms (NHC-coordinated radicals in Figure 3b and pyridine-coordinated ones in SI, Figure S2). In general, the NHC-coordinated **4c−7e** radicals show about 100 kJ/mol weaker binding to H-atoms compared with their **3c−5e** counterparts, following the similar trend of the **3c−5e** ones in Figure 3a. However, two distinctive correlation patterns between binding energy and the boron spin population can be observed for the **4c−7e** radicals in Figure 3b. The correlation pattern of the red dots (**1**−**3**, **9**−**10**, and **18**−**19**) originates from **3c−5e** $\sigma^1\pi^0$ type boryl radicals and is consistent with our previous results.[11] In contrast, the black squares originating from **3c−5e** $\sigma^0\pi^1$ radicals reveal a much steeper linear correlation. These results suggest that the "putative formation process" of **4c−7e** type boryl radicals may be invoked to understand their reactivity, highlighting the significance of properly designing **3c−5e** type boryl radicals. Boryl radicals consisting of six-membered rings (**13**−**17**) show the highest stability toward (hydrogen) radicals with unprecedented weak binding energies (> −200 kJ/mol).

In conclusion, we have designed an array of five- and six-membered boron heterocycle-based **3c−5e** boryl radicals and found that some of them adopt the unusual $\sigma^0\pi^1$ type ground states. Compared to their $\sigma^1\pi^0$ counterparts, two electronic effects are responsible for switching the energetics: (1) destabilizing lone-pair repulsion in the σ direction and (2) stabilizing electron-withdrawing conjugation in the π direction, with the latter as the leading effect. Furthermore, these $\sigma^0\pi^1$ radicals show lower reactivity toward H-atoms but stronger coordination with Lewis bases. The corresponding LB-coordinated **4c−7e** radicals exhibit even lower reactivity toward H-atoms than other conventional **4c−7e** ones.[4,11,12] These results provide new insights and novel structural types for designing boryl radicals with a broader range of stability.

ASSOCIATED CONTENT

Supporting Information

Calculation methods and optimization archive files. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: lvdongmei@mail.xjtu.edu.cn (D. Lu).
*E-mail: lipengfei@mail.xjtu.edu.cn (P. Li).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Mr. Thomas P. Senftle at the Department of Chemical Engineering at The Pennsylvania State University for helpful discussions. We are grateful for financial support of this work by China Postdoctoral Science Foundation (Project No. 2013M542354), Shaanxi Province Postdoctoral Research Foundation, and National Science Foundation of China (Grant No. 21202129). We acknowledge use of computational resources at the Materials Physics Center and the Center of Microstructure Science of FIST.

REFERENCES

(1) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2013**, *4*, 3020.

(2) Walton, J. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 1726.

(3) Wille, U. *Chem. Rev.* **2013**, *113*, 813.

(4) The estimated B−H bond dissociation energy in boranes varies from 312 to 447 kJ/mol depending on different experimental and theoretical methods. For a detailed discussion, see: Hioe, J.; Karton, A.; Martin, J. M. L.; Zipse, H. *Chem.—Eur. J.* **2010**, *16*, 4.

(5) (a) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1224. (b) Baban, J. A.; Marti, V. P. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1723. (c) Robert, B. P. *Chem. Soc. Rev.* **1999**, *28*, 25.

(6) (a) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1195. (b) Barton, D. H. R.; Jacob, M. *Tetrahedron Lett.* **1998**, *39*, 1331.

(7) (a) Lalevée, J.; Blanchard, N.; Chany, A.-C.; Tehfe, M.-A.; Allonas, X.; Fouassier, J.-P. *J. Phys. Org. Chem.* **2009**, *22*, 986. (b) Lalevée, J.; Blanchard, N.; Tehfe, M.-A.; Chany, A.-C.; Fouassier, J.-P. *Chem.—Eur. J.* **2010**, *16*, 12920.

(8) (a) Ueng, S.-H.; Brahmi, M. M.; Derat, E.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. *J. Am. Chem. Soc.* **2008**, *130*, 10082. (b) Ueng, S.-H.; Solovyev, A.; Yuan, X.; Geib, S. J.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Newcomb, M.; Walton, J. C.; Curran, D. P. *J. Am. Chem. Soc.* **2009**, *131*, 11256. (c) Matsumoto, T.; Gabbaï, F. o. P. *Organometallics* **2009**, *28*, 4252. (d) Curran, D. P.; Solovyev, A.; Brahmi, M. M.; Fensterbank, L.; Malacria, M.; Lacôte, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 10294.

(9) Walton, J. C.; Brahmi, M. M.; Monot, J.; Fensterbank, L.; Malacria, M.; Curran, D. P.; Lacôte, E. *J. Am. Chem. Soc.* **2011**, *133*, 10312.

(10) (a) Aramaki, Y.; Omiya, H.; Yamashita, M.; Nakabayashi, K.; Ohkoshi, S.-i.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 19989. Note that charged boryl radicals have also been studied, for example, borole radical anions and boryl radical cations; see: (b) Braunschweig, H.; Breher, F.; Chiu, C. W.; Gamon, D.; Nied, D.; Radacki, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 8975. (c) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610.

(11) Lu, D.; Wu, C.; Li, P. *Chem.—Eur. J.* **2014**, *20*, 1630.

(12) (a) Rablen, P. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 4648. (b) Rablen, P. R. *J. Am. Chem. Soc.* **1997**, *119*, 8350.

(13) A linear $\cdot BR_2$ radical has two degenerate orbitals, but the geometry makes the designation of the p_z orbital difficult. This argument has been *inversely* applied by Hoffmann et al. in the 1960s when proposing carbenes with a singlet ground state. For examples, see: (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (b) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457.

(14) Chen, B.; Rogachev, A. Y.; Hrovat, D. A.; Hoffmann, R.; Borden, W. T. *J. Am. Chem. Soc.* **2013**, *135*, 13954.

(15) Utilizing the conjugation backbone in transferring the electronic effects of substitutions has been successfully applied for designing functional molecules, for example, in designing ionic liquids for CO_2 capture. (a) Gurkan, B.; Goodrich, B. F.; Mindrup, E. M.; Ficke, L. E.; Massel, M.; Seo, S.; Senftle, T. P.; Wu, H.; Glaser, M. F.; Shah, J. K.; Maginn, E. J.; Brennecke, J. F.; Schneider, W. F. *J. Phys. Chem. Lett.* **2010**, *1*, 3494. (b) Wu, C.; Senftle, T. P.; Schneider, W. F. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13163. (c) Tang, H.; Wu, C. *ChemSusChem* **2013**, *6*, 1050.

(16) (a) Huynh, K.; Vignolle, J.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2009**, *48*, 2835. (b) Iida, A.; Sekioka, A.; Yamaguchi, S. *Chem. Sci.* **2012**, *3*, 1461.

(17) The $\sigma^1\pi^0$ configuration features: (a) a spin density in the sp^2-σ orbital direction (in the plane of the molecule ring) and (b) a large spin population on boron (>0.8 e). The $\sigma^0\pi^1$ structure features: (a) the spin density in the p_z-π orbital direction (perpendicular to the ring plane and delocalized) and (b) a moderate to small spin population on boron (<0.7 e). However, there is no strict quantitative definition to distinguish the two configurations.

(18) (a) Clar, E. *Polycyclic Hydrocarbons*; AP: London, 1964. (b) For a recent review on Clar's rule, see: Solà, M. *Front. Chem.* **2013**, *1*, 22.