ORGANOMETALLICS
Communication
pubs.acs.org/Organometallics

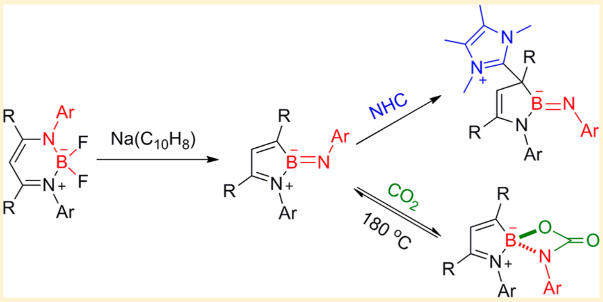
Synthesis and Reactions of π-Conjugated Iminoboranes Stabilized by Intramolecular Imine Groups

Liang Xie, Jianying Zhang, Hongfan Hu, and Chunming Cui*

State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Collaborative Innovation Center of Chemical Science and Technology (Tianjin), Tianjin 300071, People's Republic of China

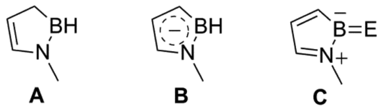
Ⓢ *Supporting Information*

ABSTRACT: Reduction of the boron difluorides HC[(CBu^t)(NAr)]$_2$BF$_2$ led to C−N bond cleavage to give the iminoborane [C(Bu^t)CHC(Bu^t)NAr]B═NAr (**2**, Ar = 2,6-Me$_2$C$_6$H$_3$; **2′**, Ar = 2,6-Pr$^i_2$C$_6$H$_3$) stabilized by an intramolecular imine group. Reaction of **2** with NHC resulted in nucleophilic attack on the α-carbon atom to give [C(Bu^t)(NHC)CHC(Bu^t)NAr]B═NAr (**3**). **2** reacted with CO$_2$ to give [C(Bu^t)CHC(Bu^t)NAr]B(CO$_2$)NAr (**4**).



Recent research has revealed that conjugated B−N heterocycles possess unique chemical and physical features due to the nitrogen lone-pair interaction with the boron empty p orbital.[1] Azaboroles (Chart1, **A**) are an attractive class of π-conjugated boracycles that have been employed as luminescent materials and for the generation of azaborolyl anions (**B**) as the analogues of ubiquitous cyclopentadienyl ligands.[2] Although a number of azaboroles and azaborolyl anions have been reported, there are no examples of an azaborole framework featuring an exocyclic B═E (E = C, N, P) double bond (**C**) that have been prepared. Herein, we report on the synthesis of a type **C** boracycle featuring an exocyclic B═N double bond.

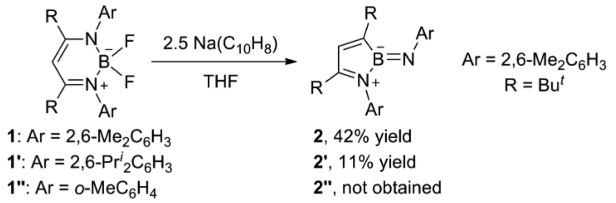
Chart 1



The synthesis of stable borylenes is one of the focuses in main-group chemistry.[3] Very recently, the parent borylene (BH) stabilized by two carbene ligands was reported by the Bertrand group,[3a] while N-heterocyclic anionic boryls, isoelectronic with NHCs, have been studied by Nozaki group.[3b,c] Our approaches to this end have focused on the hitherto unknown neutral N-heterocyclic borylenes supported by β-diketiminato ligands. It has been shown that this family of ligands is particularly effective for the stabilization of heavy group 13 carbene analogues.[4] We recently reported the synthesis of oxoboranes and their heavy analogues stabilized by bulky β-diketiminato ligands featuring β-methyl groups.[5a,b] To avoid the C−H bond cleavage of the β-methyl group on the ligand backbone as observed in these studies,[5a,b] three ligands of the type HC[(CBu^t)(NAr)]$_2$ (L, Ar = 2,6-Me$_2$C$_6$H$_3$;[5c] L′, Ar = 2,6-Pr$^i_2$C$_6$H$_3$; L″, Ar = *o*-MeC$_6$H$_4$) with β-*tert*-butyl groups at the ligand backbone have been prepared with the expectation of the stabilization of the elusive borylenes. It is noted that the six-membered ring boryl radical [L′BF]$^•$, prepared by the partial reduction of L′BF$_2$, has been recently reported by Nozaki and co-workers.[6]

The three boron difluorides LBF$_2$ (**1**), L′BF$_2$ (**1′**), and L″BF$_2$ (**1″**) were similarly prepared by the reaction of HC[(CBu^t)(NAr)]$_2$Li with BF$_3$·Et$_2$O in diethyl ether. Reduction of **1** and **1′** (Scheme 1) with 2.5 equiv of Na/naphthalene in THF at low temperature yielded a blue solution, from which compounds **2** and **2′** were isolated as blue crystals in ca. 42 and 11% yields, respectively.[6] In contrast, reduction of **1″** under the same conditions led to a complicated mixture, which cannot be separated and identified definitely. **2** and **2′** have been characterized by multiple NMR spectra, IR spectra, and elemental analysis. The ^{11}B NMR spectra of **2** and **2′** exhibit a broad resonance at δ 23.5 and 23.7 ppm, respectively, which are comparable to those reported for N-silyl-substituted iminoboranes but are shifted significantly to low field relative

Scheme 1. Reduction of the Three Difluorides LBF$_2$, L′BF$_2$, and L″BF$_2$



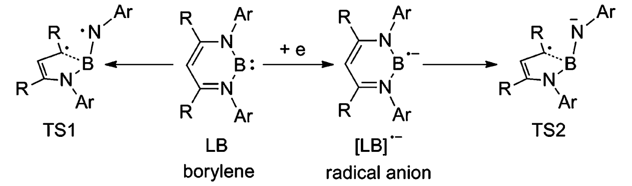
Received: August 20, 2013
Published: November 11, 2013

© 2013 American Chemical Society

to those for N-aryl-substituted iminoboranes (δ 10.6−12.2 ppm).[7,8] It has been shown that donor-supported iminoboranes are not easily accessible, since linear iminoboranes are resistant to nitrogen-based Lewis bases.[8] The formation of **2** and **2′** may be attributed to the unique electronic structure of the conjugated BC_3N framework. They apparently resulted from the C−N bond cleavage during the reduction process. This type of C−N bond cleavage arising from alkali-metal reduction has been recently reported by several groups.[9] Furthermore, C−N bond cleavage has also been observed in the reaction of the aluminum(I) species $HC[(CBu^t)(NAr)]_2Al$ with an isocyanide and NHCs.[9f,g]

The molecular formula of **2** is identical with that of borylene LB, which is shown in Scheme 2. Thus, **2** is very likely formed through isomerization of the borylene intermediate generated by reduction of **1** with 2 equiv of Na/naphthalene. However, attempts to isolate and trap these intermediates were unsuccessful. In order to have an insight into this transformation, DFT calculations have been performed. Calculations on the borylene LB at the UB3LYP/6-31G(d) level disclosed the singlet ground state and the very small singlet and triplet energy gap of 3.09 kcal/mol (see the optimized structures in Figure 1). The cleavage of the C−N bond of the singlet state to form **2** is predicted to be exothermic (52.83 kcal/mol) at the UB3LYP/6-31G(d) level. The transition state (TS1 in Scheme 2) for the transformation was optimized and further verified by frequency calculations. The activation barrier for the C−N cleavage via this transition state is predicted to be very high (36.42 kcal/mol; see Figure 1), indicating that this mechanism may not be operative. It is reasonable to assume that LB could be further reduced to form the radical anion $[LB]^{\bullet-}$ as long as Na/naphthalene is not completely consumed (Scheme 2). Thus, the geometries of the radical anion, TS2, and the resulting five-membered ring radical anion have been optimized at the 6-31+G(d) level and subsequently verified by frequency analysis. The cleavage of the C−N bond to form the five-membered radical anion via TS2 is predicted to be much more favorable (69.90 kcal/mol; see Figure 2 for the optimized structures and relative potential energies) with a very small activation barrier of 4.89 kcal/mol. We reasoned that the resulting radical anion with a five-membered ring may participate in the reduction process, such as single-electron reduction of the LB intermediate, to yield **2**. Unfortunately, we were unable to isolate and detect the radical anion due to the complicated reduction process that involves some very reactive intermediates. We have previously observed that the univalent aluminum species $HC[(CBu^t)(NAr)]_2Al$ underwent a similar C−N bond cleavage in the presence of NHCs and isocyanides.[9f,g] It is apparent that the increased electron density on the central atom facilitates its nucleophilic attack at the β-carbon atom of the ligand, leading to the C−N bond cleavage.

Scheme 2. Predicted Transition States for the C−N Cleavage[a]



[a]See Figures 1 and 2 for the optimized structures of these intermediates and transition states and relative potential energies corrected by zero-point energies.

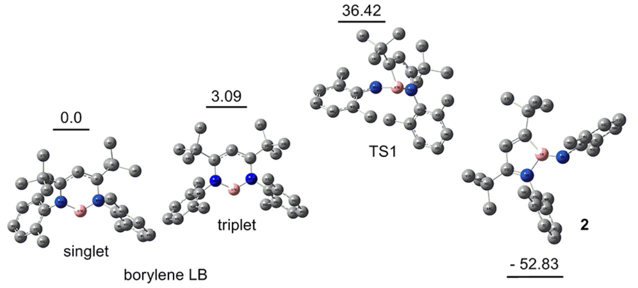


Figure 1. Optimized structures for the C−N bond cleavage of the borylene LB to form **2** via the transition state TS1 at the UB3LYP/6-31G(d) level.

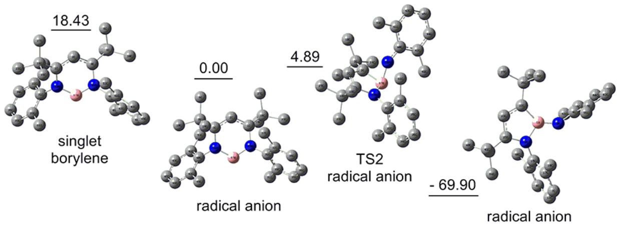


Figure 2. Optimized structures for the C−N bond cleavage of the singly reduced borylene $[LB]^{\bullet-}$ to form the five-membered ring radical anion via the transition state TS2 at the UB3LYP/6-31+G(d) level.

To investigate whether the radical species isolated by Nozaki group[6] could be an intermediate toward the borylene LB, reduction of **1** with 1 equiv of Na/naphthalene was performed at −78 °C. However, this still resulted in the formation of **2** along with unreacted **1**, which was due to the homogeneous nature of Na/naphthalene in THF. Moreover, further reduction of the radical featuring 2,6-dimethylphenyl groups similarly prepared according to Nozaki's method[6] was studied, with an equivalent amount of Na/naphthalene, but no blue product was obtained. In light of the above results, the reported radical might not be generated in the pathway of the formation of the borylene intermediate.

The structure of **2** has been confirmed by an X-ray single-crystal analysis and is shown in Figure 3. **2** features a planar BC_3N core with an exocyclic B1−N2 double-bond length of 1.3396(19) Å, which is much shorter than a typical B−N bond in the three-coordinate aminoboranes (ca. 1.40 Å), in which the B−N bonds have been considered to possess π character to some extent. The short B−N bond indicates a strong π-bonding character. However, it is longer than those in the linear iminoboranes (1.22−1.25 Å).[7,8,10] The geometry of the three-coordinate boron atom is essentially planar (the sum of the angles is 360.0°) with B1−N1 and B1−C1 single-bond lengths of 1.5690(19) and 1.596(2) Å, respectively. The relatively long C2−C3 distance of 1.465(2) Å and short C1−C2 and N1−C3 distances of 1.3478(19) and 1.3109(17) Å indicate a small degree of electron delocalization in the ring system. Both the X-ray and NMR data indicate the existence of only one isomer (*E* isomer) in the solid state and in solution.

The molecular structure of **2** predicted at the B3LYP/6-31G(d) level is in good agreement with that determined by X-ray analysis (Figure S2 in the Supporting Information). Natural

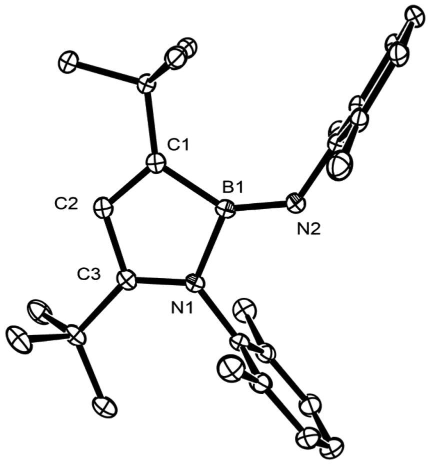


Figure 3. Ortep drawing of **2** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1−N2 = 1.3396(19), B1−N1 = 1.5690(19), B1−C1 = 1.596(2), N1−C3 = 1.3109(17), C1−C2 = 1.3478(19), C2−C3 = 1.465(2); N1−B1−N2 = 117.65(12), N2−B1−C1 = 141.23(13), N1−B1−C1 = 101.14(11).

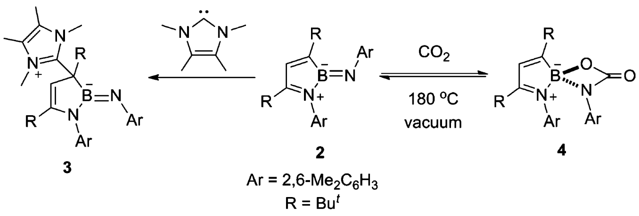
bond order (NBO) analysis of **2** indicates that the B−N π bond is formed by the boron p orbital with the nitrogen p orbital and is strongly polarized toward the nitrogen atom (70.86%). In addition, NBO analysis, according to second-order perturbation theory, discloses some donor−acceptor interactions (stabilization energies 4.54, 4.73, 6.38, 9.67, 10.58, 30.23 kcal/mol) among the B−N$_{exo}$, C−C, and C−N π and π* orbitals (see Table S2 in the Supporting Information), indicating some degree of the π-conjugated system. The LUMO of **2** is mostly contributed by the π* orbitals of the central N2−B1−C1−C2−C3−N1 framework.

In order to elucidate why **2** only exists as the *E* isomer, DFT calculations on the *Z* isomer (N1 atom and Ar ring on the N2 atom at the same side of the B═N bond) at the B3LYP/6-31G(d) level have been performed. The optimization led to the isomerization to the *E* isomer, indicating that the *Z* isomer is not stable. DFT calculations on the parent molecule [(CH)$_3$NH]B═NH (the Ar and Bu^t groups in **2** are replaced by hydrogen atoms) predicted that the *E* and *Z* isomers are both energy minima, with the *E* isomer being only 2.45 kcal/mol more stable than the *Z* isomer. Furthermore, calculations on the model compound of **2** (two Ar groups in **2** are replaced by two C$_6$H$_5$ groups) revealed that both isomers are stable and the *E* isomer is more stable than the *Z* isomer by only 0.18 kcal/mol. Therefore, it can be concluded that the steric effects of Ar groups lead to there being only one stable isomer of **2**.

The UV−vis absorption spectrum of **2** displays a weak absorption maximum at 668 nm (broad, ε = 147 mol^{-1} cm^{-1} dm^3) in the visible region (Figure S4 in the Supporting Information), which is comparable to those of reported blue compounds.[11] As the observed maximum at 668 nm indicates absorption of red light, compound **2** exhibits the complementary blue color.

Interestingly, reaction of **2** with 1 equiv of 1,3,4,5-tetramethylimidazol-2-ylidene at room temperature led to the disappearance of the blue color of **2** and yielded compound **3** as colorless crystals (Scheme 3) in good yield. In this case, the NHC attacks the unsaturated carbon atom bonded to the boron atom rather than the boron atom itself. **3** has been fully characterized by standard spectroscopic methods, elemental analysis, and X-ray single-crystal analysis. The ^{11}B NMR spectrum of **3** displays a singlet at δ 24.1 ppm, which is shifted only slightly to low field in comparison to that for **2**, indicating their similar coordination environments. The ^{13}C NMR spectrum exhibits 17 signals at low field and 12 at high field, respectively, which is mainly attributed to the restricted rotation of the two Ar groups.

Scheme 3. Reactions of 2 with NHC and CO$_2$



The molecular structure of **3** (Figure 4) reveals the three-coordinate, planar boron atom (the sum of the angles is 359.7°). The B1−N2 bond length (1.353(2) Å) is only marginally longer than that in **2**, and the B1−C1 (1.683(2) Å) and B1−N1 (1.504(2) Å) bond lengths are noticeably lengthened and shortened, respectively, relative to those in **2**. The C2−C3 bond length of 1.338(2) Å indicates a C═C double bond, while the C1−C2 and N1−C3 bond lengths are in the range for a single bond. Thus, **3** can be viewed as a donor-stabilized amino(iminoborane), in which the C1 atom in the ylidic C1−C28 alkene fragment serves as a donor rather than the nitrogen atom as observed in **2**.[12]

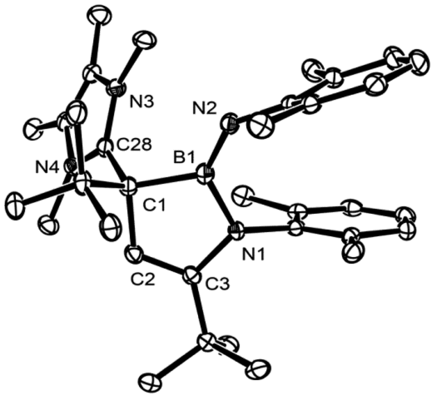


Figure 4. Ortep drawing of **3** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1−N2 = 1.353(2), B1−N1 = 1.504(2), B1−C1 = 1.683(2), C1−C2 = 1.527(2), C2−C3 = 1.338(2), N1−C3 = 1.4124(18), C1−C28 = 1.531(2); N1−B1−N2 = 129.38(13), C1−B1−N1 = 104.31(12), C1−B1−N2 = 126.04(14).

Treatment of **2** with CO$_2$ at room temperature resulted in intermolecular [2 + 2] cycloaddition, affording **4** as bright yellow crystals in 72% yield (Scheme 3), which unexpectedly regenerated **2** quantitatively upon heating to 180 °C under vacuum (see Figure S1 in the Supporting Information for ^{1}H NMR information). It is noted that this kind of decomposition behavior was distinct from that concerning the cycloaddition product of CO$_2$ with the iminoborane TMPB═NBu^t (TMP = 2,2,6,6-tetramethylpiperidine), which led to the formation of (TMPBO)$_2$ and Bu^{t}NCO.[13] Compound **4** has been characterized by ^{1}H, ^{11}B, and ^{13}C NMR, elemental analysis, and EI mass spectroscopy. The ^{11}B resonance observed at δ 6.8 ppm corresponds to a four-coordinate boron atom, revealing no multiple bonds connected to it. The molecular structure of **4** has been determined by X-ray single-crystal analysis, which is shown in Figure 5. The newly formed B1−O1−C4−N2 four-membered ring in **4** is practically planar (the sum of the angles is 359.9°) and is perpendicular to the BC_3N backbone. The B1−N2 bond (1.543(2) Å) is remarkably lengthened in comparison to that in **2** (1.3396(19) Å) into the range for a single bond, illustrating the participation of the B−N π bond in this reaction.

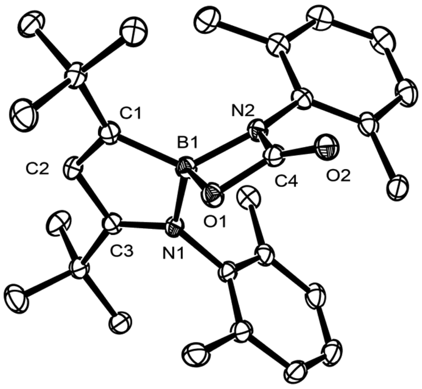


Figure 5. Ortep drawing of **4** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1−N2 = 1.543(2), B1−O1 = 1.505(2), C4−O1 = 1.3598(18), C4−N2 = 1.368(2), C4−O2 = 1.2119(18), B1−N1 = 1.597(2), B1−C1 = 1.601(2), N1−C3 = 1.3058(19), C1−C2 = 1.346(2), C2−C3 = 1.463(2); N2−B1−O1 = 85.79(11), B1−O1−C4 = 88.49(11), O1−C4−N2 = 98.98(12), B1−N2−C4 = 86.63(11), N1−B1−C1 = 99.46(12).

In summary, the first intramolecular donor stabilized π-conjugated iminoboranes **2** and **2′** have been prepared and structurally characterized. Reactions of **2** with NHC yielded **3**, indicating an electrophilic α-carbon atom in **2**. **4** was isolated by [2 + 2] cycloaddition of **2** with CO_2, which underwent CO_2 elimination at high temperature. DFT calculations on **2** strongly support the interaction of the exocyclic B═N double bond with the cyclic π-conjugated system. Further reactivity studies of **2** are currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving synthetic procedures and characterization data for compounds **1**−**4**, crystallographic data for compounds **2**−**4**, and DFT calculations on **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for C.C.: cmcui@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China and the 973 program (Grant No. 2012CB821600) for financial support.

■ REFERENCES

(1) For selected references, see: (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Bosdet, M. J. D.; Piers, W. E. *Can. J. Chem.* **2009**, *87*, 8. (c) Wakamiya, A.; Taniguchi, T.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 3170. (d) Yoshino, J.; Kano, N.; Kawashima, T. *Chem. Commun.* **2007**, 559. (e) Ishida, N.; Moriya, T.; Goya, T.; Murakami, M. *J. Org. Chem.* **2010**, *75*, 8709.

(2) For leading references, see: (a) Rao, Y. L.; Amarne, H.; Zhao, S.-B.; McCormick, T. M.; Martic, S.; Sun, Y.; Wang, R.-Y.; Wang, S. *J. Am. Chem. Soc.* **2008**, *130*, 12898. (b) Baik, C.; Hudson, Z. M.; Amarne, H.; Wang, S. *J. Am. Chem. Soc.* **2009**, *131*, 14549. (c) Amarne, H.; Baik, C.; Murphy, S. K.; Wang, S. *Chem. Eur. J.* **2010**, *16*, 4750. (d) Baik, C.; Murphy, S. K.; Wang, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8224. (e) Schmid, G.; Schütz, M. *Organometallics* **1992**, *11*, 1789. (f) Liu, S.-Y.; Lo, M. M.-C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 174. (g) Fang, X.; Assoud, J. *Organometallics* **2008**, *27*, 2408. (h) Fang, X.; Li, X.; Hou, Z.; Assoud, J.; Zhao, R. *Organometallics* **2009**, *28*, 517. (i) Ly, H. V.; Moilanen, J.; Tuononen, H. M.; Parvez, M.; Roesler, R. *Chem. Commun.* **2011**, *47*, 8391.

(3) (a) Kinjo, R.; Donnadieu, B.; Celik, M. A.; Frenking, G.; Bertrand, G. *Science* **2011**, *333*, 610. (b) Segawa, Y.; Yamashita, M.; Nozaki, K. *Science* **2006**, *314*, 113. (c) Segawa, Y.; Suzuki, Y.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 16069. (d) Bissinger, P.; Braunschweig, H.; Kraft, K.; Kupfer, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 4704. (e) Braunschweig, H.; Chiu, C.-W.; Radacki, K.; Kupfer, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 2041. (f) Bissinger, P.; Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Kupfer, T.; Radacki, K.; Wagner, K. *J. Am. Chem. Soc.* **2011**, *133*, 19044. (g) Curran, D. P.; Boussonnière, A.; Geib, S. J.; Lacôte, E. *Angew. Chem., Int. Ed.* **2012**, *51*, 1602.

(4) (a) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274. (b) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, 1991. (c) Hill, M. S.; Hitchcock, P. B. *Chem. Commun.* **2004**, 1818.

(5) (a) Wang, H.; Zhang, J.; Hu, H.; Cui, C. *J. Am. Chem. Soc.* **2010**, *132*, 10998. (b) Wang, Y.; Hu, H.; Zhang, J.; Cui, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 2816. (c) Xie, L.; Hu, H.; Cui, C. *Organometallics* **2012**, *31*, 4405.

(6) Prior to the following publication, we discussed the reduction chemistry of $L'BF_2$ with Prof. Nozaki, and our group focused on the chemistry of the five-membered iminoboranes while the Nozaki group studied the six-membered ring radical thereafter. See: Aramaki, Y.; Omiya, H.; Yamashita, M.; Nakabayashi, K.; Ohkoshi, S.-I.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 19989.

(7) (a) Haase, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 324. (b) Luthin, W.; Elter, G.; Heine, A.; Stalke, D.; Sheldrick, G. M.; Meller, A. *Z. Anorg. Allg. Chem.* **1992**, *608*, 147.

(8) Rivard, E.; Merrill, W. A.; Fettinger, J. C.; Wolf, R.; Spikes, G. H.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 2971.

(9) (a) Tomson, N. C.; Arnold, J.; Bergman, R. G. *Organometallics* **2010**, *29*, 5010. (b) Woodul, W. D.; Richards, A. F.; Stasch, A.; Driess, M.; Jones, C. *Organometallics* **2010**, *29*, 3655. (c) Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chim. Acta* **2007**, *360*, 246. (d) Bailey, B. C.; Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2006**, *25*, 3963. (e) Basuli, F.; Kilgore, U. J.; Brown, D.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2004**, *23*, 6166. (f) Li, X.; Cheng, X.; Song, H.; Cui, C. *Organometallics* **2007**, *26*, 1039. (g) Li, J.; Li, X.; Huang, W.; Hu, H.; Zhang, J.; Cui, C. *Chem. Eur. J.* **2012**, *18*, 15263.

(10) Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 162.

(11) (a) Rodríguez-Méndez, M. L.; Souto, J.; de Saja, J. A.; Aroca, R. *J. Mater. Chem.* **1995**, *5*, 639. (b) Steinert, M.; Acker, J.; Krause, M.; Oswald, S.; Wetzig, K. *J. Phys. Chem. B* **2006**, *110*, 11377. (c) Guo, Z.; Kim, G.-H.; Shin, I.; Yoon, J. *Biomaterials* **2012**, *33*, 7818. (d) Zhou, Y.; Yang, Z.; Xu, M. *Anal. Methods* **2012**, *4*, 2711.

(12) Fürstner, A.; Alcarazo, M.; Goddard, R.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 3210.

(13) Männig, D.; Narula, C. K.; Nöth, H.; Wietelmann, U. *Chem. Ber.* **1985**, *118*, 3748.