

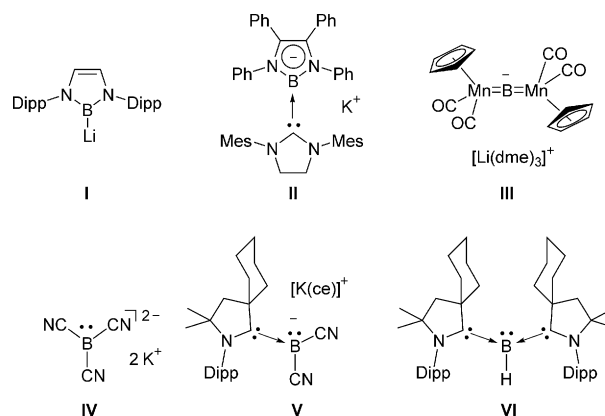


# Isolation of a Bis(oxazol-2-ylidene)–Phenylborylene Adduct and its Reactivity as a Boron-Centered Nucleophile\*\*

Lingbing Kong, Yongxin Li, Rakesh Ganguly, Dragoslav Vidovic, and Rei Kinjo\*

**Abstract:** An isolable phenylborylene species supported by two oxazol-2-ylidene ligands was synthesized and structurally characterized. Computational studies revealed the presence of lone-pair electrons on the boron atom in this molecule; therefore, there are eight electrons around the three-coordinate boron center. The nucleophilic property was confirmed by the reactions with trifluoromethanesulfonic acid and  $[(\text{thf})\text{Cr}(\text{CO})_3]$ , which gave the corresponding conjugate acid and a chromium–borylene complex, respectively.

T trivalent boron compounds are normally electrophilic because of the unoccupied 2p orbital in the valence shell of the boron atom, which enables the boron atom to accept two electrons. Accordingly, boranes behave as Lewis acids and electrophiles in general organic and inorganic reactions. Meanwhile, nucleophilic boron species have rarely been characterized as they are usually persistent only at low temperature,<sup>[1]</sup> and the isolation of such species has attracted significant attention in organoboron chemistry. Recently, several strategies for the preparation of “bottle-able” nucleophilic boron species have been developed (Figure 1).<sup>[2]</sup> In 2006, Nozaki, Yamashita et al. reported the first isolation of boryl lithium species **I**, which bears two bulky 2,6-diisopropylphenyl groups on the nitrogen atoms next to the boron atom.<sup>[3,4]</sup> Braunschweig et al. demonstrated that both N-heterocyclic carbenes (NHCs) and transition metals may effectively stabilize nucleophilic boron centers; thus, they synthesized a borole anion supported by an NHC (**II**)<sup>[5a–c]</sup> as well as dimetalloborylene **III**,<sup>[6]</sup> which readily reacted with methyl iodide to form a boron–carbon bond.<sup>[5c]</sup> Interestingly, Bernhardt et al. showed that the reaction of  $\text{K}[\text{B}(\text{CN})_4]$  with potassium yields the dianionic boron species  $\text{K}_2[\text{B}(\text{CN})_3]$  (**IV**), where the anionic charge is delocalized onto the cyanide groups.<sup>[7]</sup> Recently, Bertrand and co-workers reported the first deprotonation reaction of an adduct between a neutral borohydride and a cyclic (alkyl)(amino)carbene (CAAC),<sup>[8,9]</sup> which provided the corresponding CAAC-stabilized boryl



**Figure 1.** Structurally characterized nucleophilic boron compounds. ce = dibenzo-[18]crown-6, Dipp = 2,6-diisopropylphenyl, dme = 1,2-dimethoxyethane, Mes = 2,4,6-trimethylphenyl.

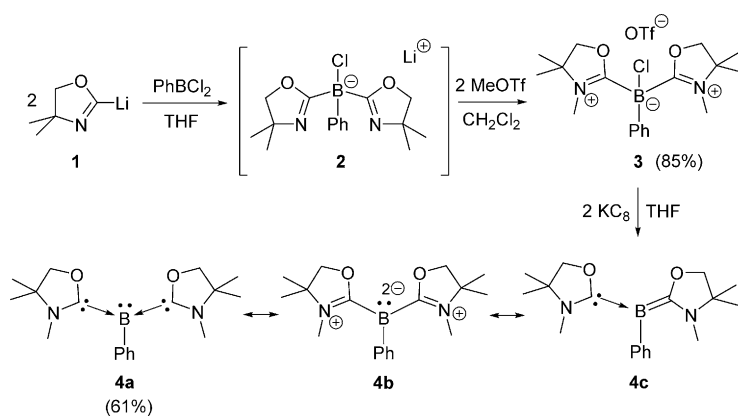
anion **V**.<sup>[10]</sup> Remarkably, by using two CAACs, Bertrand et al. also synthesized the neutral tricoordinate nucleophilic boron species **VI**, in which the strong electrophilicity of the CAACs as  $\pi$ -acceptors is critical for delocalizing and stabilizing the lone pair of the HB: fragment of **VI**.<sup>[11,12]</sup> Although **VI** is reluctant to react with most electrophiles because of steric congestion around the boron center, it readily reacted with Brønsted acids to yield the corresponding boronium ions, indicating its potential as an electron-donating ligand. Encouraged by all of these pioneering studies, we decided to investigate the preparation of a neutral tricoordinate boron ligand. Herein, we report the synthesis, single-crystal X-ray diffraction, and computational studies of a novel tricoordinate nucleophilic boron species. Its reactivity towards electrophiles is also described.

To stabilize nucleophilic tricoordinate boron atoms in a way that still allows them to react with electrophiles, ligands that feature similar  $\pi$ -acceptor capabilities to CAACs but are considerably smaller should be required. We chose oxazol-2-ylidenes, because they possess lower-energy LUMOs with respect to NHCs and are sterically less demanding because of the presence of an oxygen atom next to the carbene center.<sup>[13,14]</sup> As isolable oxazol-2-ylidenes are not available, we decided to construct oxazol-2-ylidenes by N alkylation of oxazolinyl groups attached to a boron center in the course of the synthesis. The oxazolinyl groups were installed on the boron atom by treatment of 2-lithio-4,4'-dimethyl-2-oxazolidine (**1**) with dichlorophenylborane in THF (Scheme 1). Without further purification of the crude product **2**, a subsequent reaction with two equivalents of methyl trifluoromethanesulfonate in  $\text{CH}_2\text{Cl}_2$  afforded boronium cation **3** (85% yield),

[\*] Dr. L. Kong, Dr. Y. Li, Dr. R. Ganguly, Prof. Dr. D. Vidovic, Prof. Dr. R. Kinjo  
Division of Chemistry and Biological Chemistry  
School of Physical and Mathematical Sciences  
Nanyang Technological University  
Nanyang Link 21, Singapore 637371 (Singapore)  
E-mail: rkinjo@ntu.edu.sg

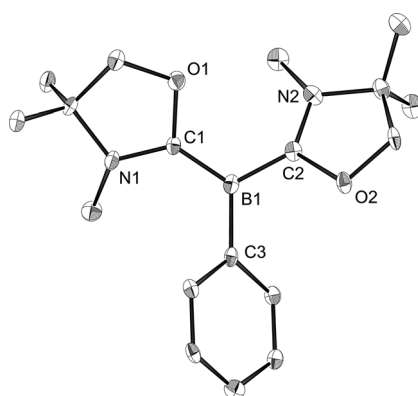
[\*\*] We gratefully acknowledge financial support from Nanyang Technological University and PSF/A\*STAR (SERC 1321202066) of Singapore.

Supporting information for this article, including complete experimental details and computational results, is available on the WWW under <http://dx.doi.org/10.1002/anie.201405201>.



**Scheme 1.** Synthesis of bis(oxazol-2-ylidene)-PhB: adduct **4** and its resonance forms. Tf = trifluoromethanesulfonyl.

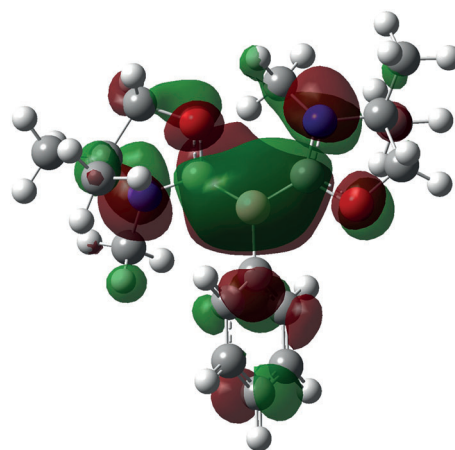
which was fully characterized by NMR spectroscopy and X-ray diffractometry.<sup>[15]</sup> By reducing **3** with two equivalents of potassium graphite, the desired product **4** was then obtained as a red solid in 21% yield. The <sup>11</sup>B NMR spectrum of **4** displays a sharp singlet at −1.1 ppm, which is shifted downfield compared to that of **3** (−9.4 ppm). Although **4** is extremely soluble in all solvents, a few single crystals were obtained from a hexane solution at room temperature, and X-ray diffraction revealed the solid-state structure of **4**.<sup>[15]</sup> There are four molecules in the unit cell, and they are nearly identical except for one, which is disordered because of the respective conformation of the two oxazol-2-ylidenes (see the Supporting Information). The C1, C2, B1, and C3 atoms are in a planar arrangement, confirming the trigonal-planar geometry of the boron center (bond-angle sum: 359.1°), which is characteristic for sp<sup>2</sup> hybridization (Figure 2). The B1–C1 (1.496 (12) Å) and B1–C2 distances (1.511(13) Å) are significantly shorter than those (1.617(19) and 1.59(2) Å) in **3** and lie between typical boron–carbon single and double bonds, suggesting the delocalization of the lone-pair electrons on



**Figure 2.** Solid-state structure of **4**, only the main conformer is shown (hydrogen atoms omitted for clarity). Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°]; values calculated at the M05-2X/6-311G(d,p) level of theory are given in square brackets: B1–C1: 1.496 (12) [1.494], B1–C2: 1.511 (13) [1.500], B1–C3: 1.570 (12) [1.587]; C1–B1–C2: 118.1 (8) [120.2], C2–B1–C3: 117.9 (8) [118.5], C1–B1–C3: 123.1 (3) [120.7].

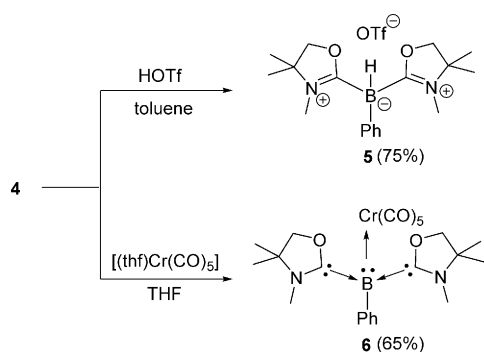
the boron atom to the carbene carbon atoms of the oxazol-2-ylidene ligands. This was confirmed by quantum chemical calculations. The optimized geometry of **4** at the M05-2X/6-311G(d,p) level of theory is in good agreement with experimental structural parameters. Natural bond order (NBO) analysis gave Wiberg bond index (WBI) values for the B–C(carbene) bonds (1.26 for B1–C1 and 1.22 for B1–C2) that support the partial B=C double-bond character. Indeed, the HOMO of **4** displays an electron lone pair on the boron atom that is delocalized onto the p orbital of the two oxazol-2-ylidene carbon atoms (Figure 3). Natural population analysis (NPA) shows an almost neutral charge at the boron center, which can be rationalized by the charge exchange that occurs through carbene→BPh σ donation and BPh→carbene π back-donation, indicating the great contribution of the resonance forms **4a**

and **4c** rather than **4b**. Note that **4a** can be viewed as a bis(oxazol-2-ylidene)-phenylborylene adduct. The IR spectrum of **4** in a THF solution displayed a signal at 1180 cm<sup>−1</sup> corresponding to the stretching of the B–C(phenyl) bond, which is in agreement with computational results (mode 74: 1195 cm<sup>−1</sup>; see the Supporting Information) and comparable to the results obtained at 10 K in a N<sub>2</sub> matrix for the free phenylborylene PhB: (1225/1215 cm<sup>−1</sup>).<sup>[16]</sup>



**Figure 3.** Plot of the HOMO (−4.80 eV) of **4** calculated at the M05-2X/6-311G(d,p) level of theory.

Under argon atmosphere at room temperature, compound **4** is stable both in the solid state and in solution for several months, but rapidly decomposes upon exposure to air. To investigate the reactivity of **4** toward Brønsted acids, we added one equivalent of trifluoromethanesulfonic acid to a solution of **4** in toluene at −30°C. After removing the solvent in vacuo, the conjugate acid **5** was obtained in 75% yield (Scheme 2). The <sup>11</sup>B NMR spectrum of **5** displays a doublet (*J*<sub>BH</sub> = 87.9 Hz) at −21.2 ppm, which is due to coupling with the hydrogen atom. The boronium nature of **5** was confirmed by single-crystal X-ray diffraction, which revealed the presence of a tetracoordinate boron center (Figure 4, top).<sup>[15]</sup> The electron-donating property of **4** to



**Scheme 2.** Reaction of **4** with HOTf and  $[(\text{thf})\text{Cr}(\text{CO})_5]$ .

Lewis acids was also confirmed by the reaction with transition metals. The reaction of **4** with a THF solution of  $[(\text{thf})\text{Cr}(\text{CO})_5]$ , which had been freshly generated by irradiation of  $[\text{Cr}(\text{CO})_6]$ , proceeded instantaneously, and after work-up, complex **6** was isolated as a yellow solid in 65% yield. It is noteworthy that the direct synthesis of borylene–transition-metal complexes through the reaction between neutral borylene species and neutral transition metals has not been reported thus far.<sup>[17]</sup> The  $^{11}\text{B}$  NMR signal of **6** appears as a singlet at  $-21.2$  ppm, which is shifted upfield from that of **4**. Single crystals of **6** were obtained from a saturated toluene solution at  $-25^\circ\text{C}$ , and X-ray diffraction analysis disclosed

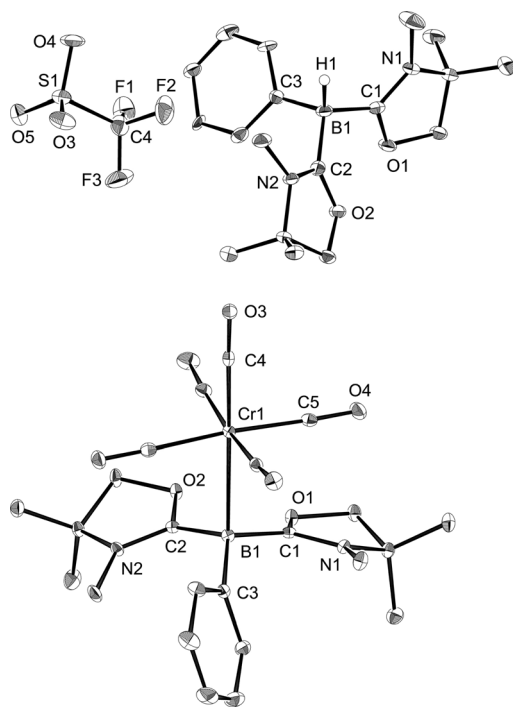
that the tetracoordinate boron atom coordinates to the chromium(0) center in an  $\eta^1$  fashion (Figure 4, bottom).<sup>[15]</sup> The B1–Cr1 distance of  $2.535(2)$  Å is significantly longer than those (ca.  $1.878$ – $1.996$  Å) reported for terminal borylene–chromium complexes  $[(\text{OC})_5\text{Cr}=\text{BR}]$ ,<sup>[18]</sup> indicating a lack of  $\text{Cr} \rightarrow \text{B}$   $\pi$ -backbonding in **6**. Consequently, the enhanced interaction between the Cr atom and the carbonyl ligands induces the shorter Cr–C distances in comparison to those found in  $[(\text{OC})_5\text{Cr}=\text{BR}]$ . This was also confirmed by the infrared CO vibration frequencies of **6** ( $1892$ ,  $1933$ ,  $1977$ , and  $2016$   $\text{cm}^{-1}$ ), which are significantly red-shifted with respect to those of  $[(\text{OC})_5\text{Cr}=\text{BR}]$ .<sup>[18]</sup>

In summary, we have demonstrated that two oxazol-2-ylidenes effectively stabilize a  $\text{PhB:}$  fragment, affording adduct **4**. X-ray diffraction and computational studies revealed the presence of a lone pair on the trigonal-planar boron center, which readily reacts with both Brønsted and Lewis acids. This result illustrates the direct preparation of borylene–transition-metal complexes using tricoordinate nucleophilic boron ligands that are synthetically available. Investigations concerning the further reactivity and ligand properties of **4** are underway in our laboratory.

Received: May 12, 2014

Published online: June 30, 2014

**Keywords:** boron · borylenes · carbenes · nucleophiles · reactive species



**Figure 4.** Solid-state structures of **5** and **6** (hydrogen atoms omitted for clarity). Thermal ellipsoids are set at the 30% probability level. Selected bond lengths [Å] and angles [°] for **5**: B1–C1:  $1.596(7)$ , B1–C2:  $1.616(7)$ , B1–C3:  $1.618(12)$ ; C1–B1–C2:  $111.8(4)$ , C2–B1–C3:  $113.2(9)$ , C1–B1–C3:  $104.0(9)$ . For **6**: B1–Cr1:  $2.535(2)$ , B1–C1:  $1.561(3)$ , B1–C2:  $1.568(3)$ , B1–C3:  $1.614(3)$ , Cr1–C4:  $1.831(2)$ , Cr1–C5:  $1.886(2)$ ; C1–B1–C2:  $112.56(16)$ , C2–B1–C3:  $115.50(17)$ , C1–B1–C3:  $113.63(16)$ .

- [1] a) D. P. Curran, A. Solovyev, M. Makhlof Brahmi, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem.* **2011**, *123*, 10476–10500; *Angew. Chem. Int. Ed.* **2011**, *50*, 10294–10317; b) J. Monot, A. Solovyev, H. Bonin-Dubarle, É. Derat, D. P. Curran, M. Robert, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem.* **2010**, *122*, 9352–9355; *Angew. Chem. Int. Ed.* **2010**, *49*, 9166–9169; c) L. Dang, Z. Lin, T. B. Marder, *Chem. Commun.* **2009**, 3987–3995; d) T. Imamoto, T. Hikosaka, *J. Org. Chem.* **1994**, *59*, 6753–6759; e) T. D. Parsons, J. M. Self, L. H. Schaad, *J. Am. Chem. Soc.* **1967**, *89*, 3446–3448.
- [2] For reviews, see: a) J. Cid, H. Gulyás, J. J. Carbó, E. Fernández, *Chem. Soc. Rev.* **2012**, *41*, 3558–3570; b) L. Weber, *Eur. J. Inorg. Chem.* **2012**, 5595–5609; c) H. Gulyás, A. Bonet, C. Pubill-Ulldemolins, C. Solé, J. Cid, E. Fernández, *Pure Appl. Chem.* **2012**, *84*, 2219–2231; d) M. Yamashita, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 983–999; e) M. Yamashita, K. Nozaki, *J. Synth. Org. Chem. Jpn.* **2010**, *68*, 359–369; f) Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079; g) M. Yamashita, K. Nozaki, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1377–1392.
- [3] Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113–115.
- [4] For recent reports, see: a) A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birj Kumar, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *Nat. Chem.* **2014**, *6*, 315–319; b) N. Dettenrieder, C. Schädle, C. Maichle-Mössmer, P. Sirsch, R. Anwander, *J. Am. Chem. Soc.* **2014**, *136*, 886–889; c) N. Dettenrieder, Y. Aramaki, B. M. Wolf, C. Maichle-Mössmer, X. Zhao, M. Yamashita, K. Nozaki, R. Anwander, *Angew. Chem.* **2014**, *126*, 6373–6377; *Angew. Chem. Int. Ed.* **2014**, *53*, 6259–6262; d) A. V. Protchenko, K. H. Birj Kumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge,

- J. Am. Chem. Soc.* **2012**, *134*, 6500–6503; e) N. Dettenrieder, H. M. Dietrich, C. Schaedle, C. Maichle-Mössmer, K. W. Törnroos, R. Anwender, *Angew. Chem.* **2012**, *124*, 4537–4541; *Angew. Chem. Int. Ed.* **2012**, *51*, 4461–4465; f) Y. Okuno, M. Yamashita, K. Nozaki, *Eur. J. Org. Chem.* **2011**, 3951–3958; g) M. S. Cheung, T. B. Marder, Z. Lin, *Organometallics* **2011**, *30*, 3018–3028; h) Y. Okuno, M. Yamashita, K. Nozaki, *Angew. Chem.* **2011**, *123*, 950–953; *Angew. Chem. Int. Ed.* **2011**, *50*, 920–923; i) S. Li, J. Cheng, Y. Chen, M. Nishiura, Z. Hou, *Angew. Chem.* **2011**, *123*, 6484–6487; *Angew. Chem. Int. Ed.* **2011**, *50*, 6360–6363; j) Y. Hayashi, Y. Segawa, M. Yamashita, K. Nozaki, *Chem. Commun.* **2011**, 47, 5888–5890; k) L. M. A. Saleh, K. H. Birjkumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis, P. Mountford, *J. Am. Chem. Soc.* **2011**, *133*, 3836–3839; l) K. Nozaki, Y. Aramaki, M. Yamashita, S.-H. Ueng, M. Malacria, E. Lacôte, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 11449–11451; m) T. Terabayashi, T. Kajiwar, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14162–14163; n) T. Kajiwar, T. Terabayashi, M. Yamashita, K. Nozaki, *Angew. Chem.* **2008**, *120*, 6708–6712; *Angew. Chem. Int. Ed.* **2008**, *47*, 6606–6610; o) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *J. Am. Chem. Soc.* **2007**, *129*, 9570–9571; p) Y. Segawa, M. Yamashita, K. Nozaki, *Angew. Chem.* **2007**, *119*, 6830–6833; *Angew. Chem. Int. Ed.* **2007**, *46*, 6710–6713.
- [5] a) H. Braunschweig, C.-W. Chiu, T. Kupfer, K. Radacki, *Inorg. Chem.* **2011**, *50*, 4247–4249; b) H. Braunschweig, C.-W. Chiu, K. Radacki, T. Kupfer, *Angew. Chem.* **2010**, *122*, 2085–2088; *Angew. Chem. Int. Ed.* **2010**, *49*, 2041–2044. Significantly, a recent report revealed that the reaction of **II** with heavier triorganyltetrel halides may proceed by a stepwise radical process through single electron transfer; see: c) R. Bertermann, H. Braunschweig, R. D. Dewhurst, C. Hörl, T. Kramer, I. Krummenacher, *Angew. Chem.* **2014**, *126*, 5557–5561; *Angew. Chem. Int. Ed.* **2014**, *53*, 5453–5457.
- [6] a) H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kramer, S. Östreicher, K. Radacki, A. Vargas, *J. Am. Chem. Soc.* **2013**, *135*, 2313–2320; b) H. Braunschweig, P. Brenner, R. D. Dewhurst, M. Kaupp, R. Müller, S. Östreicher, *Angew. Chem.* **2009**, *121*, 9916–9919; *Angew. Chem. Int. Ed.* **2009**, *48*, 9735–9738; c) H. Braunschweig, M. Burzler, R. D. Dewhurst, K. Radacki, *Angew. Chem.* **2008**, *120*, 5732–5735; *Angew. Chem. Int. Ed.* **2008**, *47*, 5650–5653.
- [7] E. Bernhardt, V. Bernhardt-Pitchougina, H. Willner, N. Ignatiev, *Angew. Chem.* **2011**, *123*, 12291–12294; *Angew. Chem. Int. Ed.* **2011**, *50*, 12085–12088.
- [8] a) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304–5313; b) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992–9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; c) R. Jazzar, R. D. Dewhurst, J.-B. Bourg, B. Donnadieu, Y. Canac, G. Bertrand, *Angew. Chem.* **2007**, *119*, 2957–2960; *Angew. Chem. Int. Ed.* **2007**, *46*, 2899–2902; d) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851–5855; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709.
- [9] a) O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem.* **2013**, *125*, 3011–3015; *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943; b) G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2007**, *316*, 439–441; c) V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Angew. Chem.* **2006**, *118*, 3568–3571; *Angew. Chem. Int. Ed.* **2006**, *45*, 3488–3491.
- [10] D. A. Ruiz, G. Ung, M. Melaimi, G. Bertrand, *Angew. Chem.* **2013**, *125*, 7739–7742; *Angew. Chem. Int. Ed.* **2013**, *52*, 7590–7592.
- [11] R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking, G. Bertrand, *Science* **2011**, *333*, 610–613.
- [12] For examples of (RB)<sub>2</sub> fragments stabilized with NHCs, see: a) P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, A. Vargas, *Angew. Chem.* **2012**, *124*, 10069–10073; *Angew. Chem. Int. Ed.* **2012**, *51*, 9931–9934; b) Y. Wang, B. Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 3298–3299; c) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412–12413.
- [13] Z. Kelemen, O. Hollóczki, J. Oláh, L. Nyulászi, *RSC Adv.* **2013**, *3*, 7970–7978.
- [14] For theoretical results showing the energy level of the frontier orbital of model carbenes, see the Supporting Information.
- [15] CCDC 1002423 (**3**), 1002424 (**4**), 1002425 (**5**), and 1002426 (**6**) 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](http://www.ccdc.cam.ac.uk/data_request/cif).
- [16] H. F. Bettinger, *J. Am. Chem. Soc.* **2006**, *128*, 2534–2535.
- [17] For reviews, see: a) H. Braunschweig, R. D. Dewhurst, V. H. Gessner, *Chem. Soc. Rev.* **2013**, *42*, 3197–3208; b) H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924–3957; c) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535–559.
- [18] a) H. Braunschweig, R. D. Dewhurst, C. Hörl, K. Radacki, C. W. Tate, A. Vargas, Q. Ye, *Angew. Chem.* **2013**, *125*, 10307–10310; *Angew. Chem. Int. Ed.* **2013**, *52*, 10120–10123; b) H. Braunschweig, M. Colling, C. Kollann, H. G. Stämmler, B. Neumann, *Angew. Chem.* **2001**, *113*, 2359–2361; *Angew. Chem. Int. Ed.* **2001**, *40*, 2298–2300; c) H. Braunschweig, M. Colling, C. Kollann, K. Merz, K. Radacki, *Angew. Chem.* **2001**, *113*, 4327–4329; *Angew. Chem. Int. Ed.* **2001**, *40*, 4198–4200; d) B. Blank, M. Colling-Hendelkens, C. Kollann, K. Radacki, D. Rais, K. Uttinger, G. R. Whittell, H. Braunschweig, *Chem. Eur. J.* **2007**, *13*, 4770–4781.