Multiple Bonds

Deutsche Ausgabe: DOI: 10.1002/ange.201608994
Internationale Ausgabe: DOI: 10.1002/anie.201608994

Azaborabutadienes: Synthesis by Metal-Free Carboboration of Nitriles and Utility as Building Blocks for B,N-Heterocycles

*Lingbing Kong, Wei Lu, Yongxin Li, Rakesh Ganguly, and Rei Kinjo**

Abstract: *Metal-free regioselective carboboration of arylnitriles with L_2PhB: (**1**: L = oxazol-2-ylidene) catalyzed by Et_3B afforded the unprecedented acyclic 2-aza-4-borabutadienes **2**, thus demonstrating a new strategy to construct a B,C,N-mixed π-system involving B=C and C=N bonds. Thermal isomerization of **2** gave C-borylimines (**3**), and diverse reactivity of **2a** towards several substrates, such as H^+, F^+, O_2, S, Se, and isonitriles, allowed construction of boron-containing heterocycles with various ring sizes, thus illustrating the utility of **2** as a synthetic building block.*

Construction of multiple bonds involving boron is of paramount importance not only for fundamental studies and in-depth understanding of the intrinsic chemical bonding, but their potential utility as synthetic building blocks for organoboranes.[1] Among them, methyleneboranes, which contain B–C units with multiple bonds featuring a dicoordinated boron atom, and borataalkene, which is a B=C bonded species with an anionic tricoordinate boron, have been extensively studied.[2] The reported methyleneborane derivatives can be classified into three types: boraalkene (**A**), borataallene (**B**), and borataalkyne (**C**; Figure 1a).[2c] Seminal works by Berndt and co-workers,[3] and Nöth et al. and Paetzold et al.[4] pioneered this field in 1980s (Figure 1b, **Aa**–**c**). The anionic methyleneboranes **B** and **C**, and the borataalkene **D**, involving nucleophilic carbon centers, were developed subsequently.[5]

In sharp contrast to a large number of the isolated methyleneboranes and borataalkenes, only a few reports on acyclic compounds having a B=C bond and an extended π-system have been described by Berndt[6,7] and Siebert et al.[8] (Figure 1c, **E**–**G**). Meanwhile, Braunschweig et al. revealed that the borylene transfer from an iron bis(borylene) complex to alkynes produced 1,4-dibora-1,3-butadiene iron complexes (**Ha–c**)[9] Given that oxygen- and nitrogen-containing compounds are ubiquitous in naturally occurring compounds as well as pharmaceuticals,[10] the potential applications of the extended boron π-system involving heteroatoms (O, N) are versatile. Nevertheless, although the relevant bis(boraketene) **I** and bis(boraketenimine) **J** have been reported recently,[11] the azaborabutadiene framework (e.g. **K**; Figure 1d), as another type of B-containing butadiene analogue, is only seen in the aromatic cyclic systems.[12] As far as we are aware, the neutral acyclic azaborabutadiene has not been reported thus far.

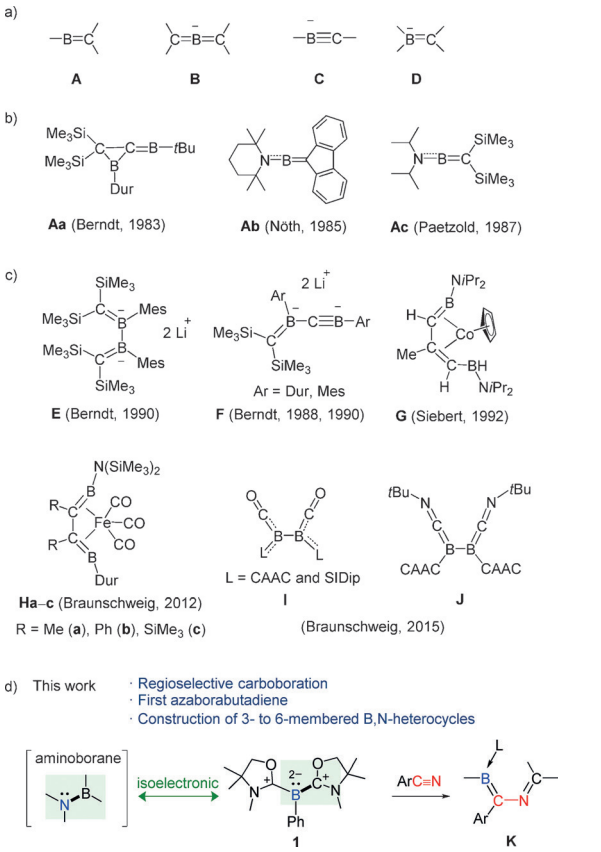


Figure 1. a) Three types of methyleneboranes (**A**–**C**) and a borataalkene (**D**). b) Selected examples of methyleneboranes (**Aa-c**) in an early study. c) Reported methyleneborane derivatives with an extended π system. d) Present work. CAAC = 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene, Dur = 2,3,5,6-tetramethylphenyl, Mes = 2,4,6-trimethylphenyl, SIDip = 1,3-bis(diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene.

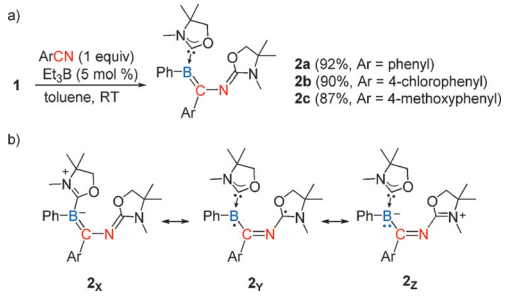
1,2-Addition of boron–element σ-bonds (B–E where E = H,C,B,Si,Sn,S,Cl,Br, or I) to C–C π-bonds is one of the most useful methods for forming B–C and C–E bonds simultaneously.[13] While most of the conventional reactions involve activation of the B–E σ-bonds by transition metals, it has been elegantly demonstrated by Blum et al. that aminoboration of alkynes can be achieved by activation of alkynes instead of the N–B σ-bonds in aminoboranes.[14] Recently, we reported the isolation of a tricoordinate organoboron species **1** (Figure 1d) involving a boron atom formally surrounded by eight

[*] Dr. L. Kong, Dr. W. Lu, Dr. Y. Li, Dr. R. Ganguly, 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.sga

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201608994.

electrons.[15] Considering the isoelectronic relationship between one of the resonance forms of **1** and aminoborane, we envisaged that **1** would undergo carboboration with activated unsaturated bonds which could be applied to construct hitherto unknown azaborabutadiene derivatives. Herein, we report the synthesis of neutral 2-aza-4-borabutadienes (**K**) by metal-free regioselective carboboration of nitriles with **1**. We also describe their thermal isomerization and reactivity towards H^+ and F^+, as well as small molecules including O_2, S_8, Se, and isonitrile.

To a toluene solution of **1**, in the presence of a stoichiometric amount of benzonitrile, triethylborane (1M in hexanes; 5 mol%) was added as a C≡N bond activator,[16] and the mixture was stirred at ambient temperature. The color of the solution turned immediately from orange to deep red, and a crimson solid gradually precipitated. After work up, **2a** was obtained in 92% yield (Scheme 1a). In the ^{1}H NMR spectrum, two sets of peaks (major/minor = 100:14) were observed, thus indicating the existence of two geometric isomers of **2a** in solution. The structure of the minor isomer is not clear at present. In the ^{11}B NMR spectrum of **2a**, a broad singlet appeared at $\delta = 17.3$ ppm, and is significantly shifted downfield compared with that of **1** ($\delta = -1.1$ ppm).[15a] When *para*-substituted benzonitriles with electron-withdrawing (Cl) and electron-donating (OMe) groups were employed under the same reaction conditions, the corresponding derivatives **2b**,**c** were obtained in 90 and 87% yields, respectively, and these products presented a broad ^{11}B NMR shift at $\delta =$ 17.7 ppm (**2b**) and $\delta = 16.6$ ppm (**2c**). Because of the π-conjugation system, the compounds **2a**–**c** can be represented by several canonical forms involving $\mathbf{2_X}$, $\mathbf{2_Y}$, and $\mathbf{2_Z}$ (Scheme 1b).



Scheme 1. a) Synthesis of **2a**–**c**. b) Selected resonance forms of **2**.

The structural properties of **2a**–**c** became apparent upon an X-ray diffraction analysis, which confirmed (*Z*,*Z*)-2-aza-4-borabutadiene structures featuring an oxazol-2-ylidene at the B center (Figure 2). The six atoms B1, C1, C7, C13, C14, and N2 in **2a** are nearly coplanar (average deviation from the plane = 0.0815 Å). The two phenyl groups at B1 and C13 are substituted on the same side with respect to the B=C bond. The B1C13N2C20 butadiene skeleton displays non-coplanar conformation with a torsion angle of 56.5°. The B1–C13 distance [1.469(5) Å] is within the range of reported of B=C bonds (1.31–1.49 Å).[2c] The C13–N2 distance [1.439(4) Å] is significantly longer than the C20–N2 distances [1.256(4) Å], thus indicting their single- and double-bond characters, respectively. The B1–C1 distance [1.573(5) Å] and B1–C7 distance [1.563(8) Å] are similar, and typical of a B–C bond. These geometric features reveal the considerable contribution of the 1,3-diene form $\mathbf{2_X}$ (Scheme 1b) to the electronic nature of **2a**, and $\mathbf{2_Y}$ and $\mathbf{2_Z}$ are less likely in the solid state. The compounds **2b**,**c** exhibit metric parameters similar to those of **2a**.

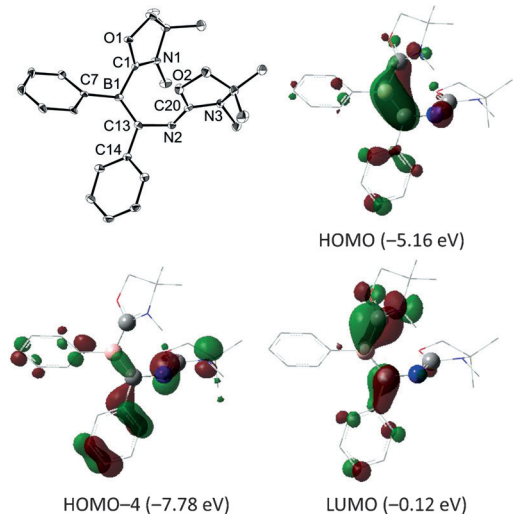


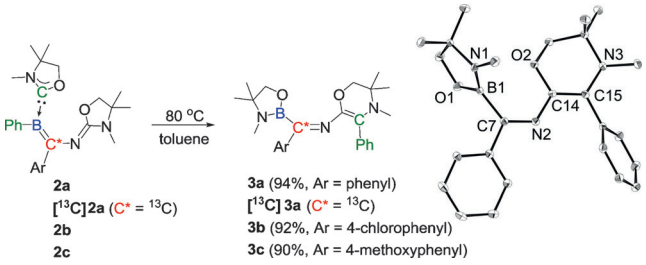
Figure 2. Solid-state structure of **2a**.[30] Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms are omitted for clarity, and plots of the frontier orbitals calculated at the M05-2X/6-311G(d,p) level of theory (hydrogen atoms are omitted for clarity).

We performed quantum chemical calculations to investigate the intrinsic electronic properties of **2a**. The crystal structure of **2a** is well reproduced by the optimized structure. The HOMO is mainly the B1–C13 π-bonding orbital whereas the LUMO is the B1–C13 π*-orbital which exhibits bonding conjugation with the p-orbital at C1 in the oxazol-2-ylidene unit (Figure 2). The C20–N2 π-orbital is found in the HOMO−4, which involves the B1–C13 σ-bonding. The 1,3-diene-type π-system is reflected in the Wiberg bond index (WBI) values of the B1–C13 (1.45), C13–N2 (1.02), and C20–N2 bonds (1.71). Natural bond orbital (NBO) analysis of **2a** indicates highly filled σ (1.95 *e*) and π orbitals (1.70 *e*) for the B1=C13 bond, with the π orbital being partially polarized toward the carbon atom (62.08%). The B1–C13 σ bond is formed by the $sp^{1.67}$ hybrid orbital of the boron and the $sp^{1.26}$ hybrid orbital of the carbon atom. In the UV/Vis spectrum of **2a**, a strong absorption band with $\lambda_{max} = 465$ nm was observed, and corresponds to the π–π* transition based on TDDFT calculations (see the Supporting Information).

Preliminary control experiments showed that neither PhC≡N nor Et_3B reacted with **1** (see the Supporting Information). Hence, it is reasonable to envisage that the reaction is initiated by interaction between nitriles and Et_3B.[16a,b] The entire process can be viewed as a regioselective carboboration of nitriles concomitant with the formation of both B=C and N=C bonds. Note that carboboration of nitriles is extremely rare,[17] and the reported examples exclusively resulted in the formation of the B–N and C–C bonds, which is contrary to our results. It is also salient to mention that the

conventional method to access Lewis base methyleneborane adducts is confined to the direct complexation between isolated methyleneboranes and Lewis bases.[2a,18]

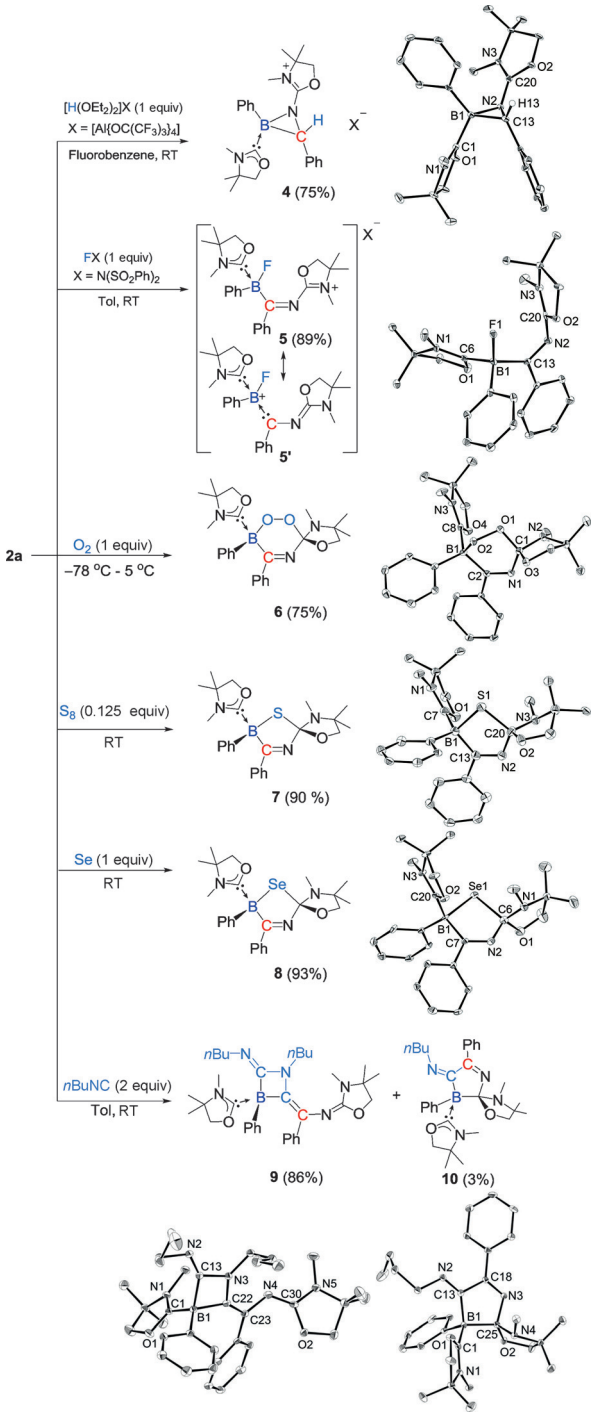
Transient methyleneboranes easily dimerize and oligomerize, and undergo isomerization[19] and cycloaddition.[2a,9] These studies prompted us to investigate the thermal stabilities of **2a–c**. A C_6D_6 solution of **2a** in a sealed NMR tube was heated at 80 °C. The color of the solution slowly changed from red to light yellow. After 12 hours, the ^{1}H NMR spectrum showed an almost quantitative conversion of **2a** into a new product (**3a**; Scheme 2). Under the same reaction



Scheme 2. Thermal isomerization of **2a–c**. For X-ray structure the thermal ellipsoids are set at the 30% probability level.[30]

conditions, **2b** and **2c** were also converted into similar products, **3b** and **3c**, respectively, in excellent yields as determined by NMR spectroscopy. Yellow single crystals of **3a–c** were obtained by recrystallization from a saturated *n*-hexane solution, and their solid-state structures were determined by single-crystal X-ray diffraction studies. **3a–c** involve an *E*-imine skeleton with a five-membered B,N,O-heterocyclic ring at the imine carbon atom and a dihydro-1,4-oxazine unit on the imine nitrogen atom. Structural parameters of **3a–c** are nearly identical. Formation of **3a–c** demonstrates a novel strategy to prepare C-borylimines.[20] To gain information about the reaction pathways for the formation of **3a–c** from **2a–c**, we performed a ^{13}C-labeling experiment. With ^{13}C-labeled benzonitrile, [^{13}C]**2a** was synthesized by the procedure described in Scheme 1 a. The ^{13}C NMR spectrum of [^{13}C]**2a** displays an additional broad peak at $\delta = 151.1$ ppm compared with those of **2a**, and can be assigned to the C* next to B in the 1,3-diene skeleton. Thermal isomerization of [^{13}C]**2a** afforded [^{13}C]**3a** smoothly, and its ^{13}C NMR spectrum displayed a broad singlet for the ^{13}C-labeled carbon atom at $\delta = 160.9$ ppm, which was assigned to the imine carbon atom. This result indicates the ^{13}C–N bond in [^{13}C]**2a** is not cleaved during the isomerization to [^{13}C]**3a**, and a plausible mechanism may involve two ring expansions (see the Supporting Information).[21]

The B=C units in **2a–c** are supported by a strong σ-donating oxazol-2-ylidene and a (2σ,4π)-electron-donating iminato ligand,[22] thus implying the peculiar electron-rich nature of the boron centers. Therefore, we next investigated the reactivity of **2a** towards various substrates (Scheme 3). Note that study on the reactivity of borabutadiene derivatives (**E** and **F**), and even their metal complexes (**G** and **H**), towards electrophiles is exceedingly limited to a handful of reports to date.[5e] Treatment of **2a** with [H(OEt$_2$)$_2$][Al{OC(CF$_3$)$_3$}$_4$] generated a cationic azaboracyclopropane species (**4**)[4h,23] while the reaction with FN(SO$_2$Ph)$_2$[24] afforded the boronium species **5** featuring a B–F bond, thus illustrating the formal umpolung nature of the B=C π-bond. Although **2a** did not react with H_2, CO, CO_2, and ethylene, it readily reacted to capture triplet O_2 at low temperature, and furnished the novel boron peroxide **6** featuring a BC_2NO_2 six-membered ring. Note that only six boron peroxides have been structurally



Scheme 3. Reactions of **2a** with [H(OEt$_2$)$_2$][Al{OC(CF$_3$)$_3$}$_4$], FN(SO$_2$Ph)$_2$, O_2, S, Se, and *n*BuNC. For X-ray structures the thermal ellipsoids are set at the 30% probability level.[30]

characterized thus far.[25] Because **2a** has a singlet–triplet gap of 13.3 kcal mol^{-1} (see the Supporting Information), which is small in comparison to that (50.4 kcal mol^{-1}) of 1,3-butadiene (C_4H_6),[26] a mechanism involving radical coupling between **2a** and $^3O_2$ might be possible, although there is no evidence for the generation of a biradical species, such as $\mathbf{2_Y}$ (Scheme 1b), during the reaction. Alternatively, electron transfer from **2a** to $^3O_2$ followed by the B–O bond formation could also be feasible for the formation of **6**. Indeed, cyclic voltammetric measurement of **2a** in THF revealed that **2a** is susceptible to oxidation with the low oxidation potential at −0.95 V relative to ferrocene/ferrocenium (Fc/Fc^+) (see the Supporting Information). In addition, reactions of **2a** with S_8 and Se produced the cyclic boron sulfide **7** and selenide **8**, respectively, which include the BC_2NE (E = S, Se) five-membered ring.[27] Insertion and cyclization reactions of isonitriles with unsaturated substrates are effective routes for the construction of heterocyclic compounds.[28] Reactions between methyleneboranes and isonitriles have been previously described by Nöth and Paetzold et al.[4a,29] Contrary to their reports, in the reaction of **2a** with *n*BuNC, a complete cleavage of the B=C bond of **2a** was observed and the azaboracyclobutane **9**, bearing a BC_2N four-membered ring, as well as the azaboracyclopentene **10**, with a BC_3N five-membered ring, were isolated as the major and minor products, respectively. These results demonstrate the utility of azaborabutadienes as synthetic building blocks.

Since **2a** does not react with H_2, CO, CO_2, and ethylene, small-molecule capture/activation by **2a** is substrate specific. Moreover, the progress of the reactions between **2a** and other molecules is accompanied by the fading of the deep red color of **2a**. Thus, the collective results suggest a potential utility of azaborabutadiene as a colorimetric sensor. Investigation on the reactivity of **2a–c** towards other substrates is currently underway in our laboratory.

Acknowledgments

We are grateful to the Singapore Ministry of Education (MOE2015-T2-2-032) and Nanyang Technological University (NTU) for financial support.

Keywords: boron · carboboration · heterocycles · multiple bonds · structure elucidation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 14718–14722
Angew. Chem. **2016**, *128*, 14938–14942

[1] a) H. Braunschweig, R. D. Dewhurst, *Organometallics* **2014**, *33*, 6271; b) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2014**, *53*, 11815; c) J. Brand, H. Braunschweig, S. S. Sen, *Acc. Chem. Res.* **2014**, *47*, 180; d) H. Braunschweig, R. D. Dewhurst, *Angew. Chem. Int. Ed.* **2013**, *52*, 3574; *Angew. Chem.* **2013**, *125*, 3658; e) D. J. D. Wilson, J. L. Dutton, *Chem. Eur. J.* **2013**, *19*, 13626; f) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877; g) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201.

[2] a) P. Paetzold, U. Englert, R. Finger, T. Schmitz, A. Tapper, R. Ziembinski, *Z. Anorg. Allg. Chem.* **2004**, *630*, 508; b) J. J. Eisch, *Adv. Organomet. Chem.* **1996**, *39*, 355; c) A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 985; *Angew. Chem.* **1993**, *105*, 1034.

[3] a) M. Pilz, H. Michel, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 401; *Angew. Chem.* **1990**, *102*, 438; b) R. Hunold, M. Pilz, J. Allwohn, M. Stadler, W. Massa, P. von R. Schleyer, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 781; *Angew. Chem.* **1989**, *101*, 759; c) M. Pilz, M. Stadler, R. Hunold, J. Allwohn, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 784; *Angew. Chem.* **1989**, *101*, 761; d) H. Klusik, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 877; *Angew. Chem.* **1983**, *95*, 895.

[4] a) A. Tapper, T. Schmitz, P. Paetzold, *Chem. Ber.* **1989**, *122*, 595; b) S. Helm, H. Nöth, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1331; *Angew. Chem.* **1988**, *100*, 1378; c) I. Manners, P. Paetzold, *J. Chem. Soc. Chem. Commun.* **1988**, 183; d) R. Boese, P. Paetzold, A. Tapper, *Chem. Ber.* **1987**, *120*, 1069; e) B. Glaser, H. Nöth, *Chem. Ber.* **1987**, *120*, 345; f) B. Glaser, E. Hanecker, H. Nöth, H. Wagner, *Chem. Ber.* **1987**, *120*, 659; g) B. Glaser, H. Nöth, *Chem. Ber.* **1986**, *119*, 3856; h) B. Glaser, H. Nöth, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 416; *Angew. Chem.* **1985**, *97*, 424.

[5] Selected examples: a) P.-Y. Feng, Y.-H. Liu, T.-S. Lin, S.-M. Peng, C.-W. Chiu, *Angew. Chem. Int. Ed.* **2014**, *53*, 6237; *Angew. Chem.* **2014**, *126*, 6351; b) J. Möbus, G. Kehr, C. G. Daniliuc, R. Fröhlich, G. Erker, *Dalton Trans.* **2014**, *43*, 632; c) C.-W. Chiu, F. P. Gabbaï, *Angew. Chem. Int. Ed.* **2007**, *46*, 6878; *Angew. Chem.* **2007**, *119*, 7002; d) P. Willershausen, C. Kybart, N. Stamatis, W. Massa, M. Bühl, P. von R. Schleyer, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1238; *Angew. Chem.* **1992**, *104*, 1278; e) R. Hunold, J. Allwohn, G. Baum, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 961; *Angew. Chem.* **1988**, *100*, 961; f) M. M. Olmstead, P. P. Power, K. J. Weese, R. J. Doedens, *J. Am. Chem. Soc.* **1987**, *109*, 2541.

[6] M. Pilz, J. Allwohn, P. Willershausen, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1030; *Angew. Chem.* **1990**, *102*, 1084.

[7] J. Allwohn, M. Pilz, R. Hunold, W. Massa, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1032; *Angew. Chem.* **1990**, *102*, 1084.

[8] G. Gabbert, W. Weinmann, H. Pritzkow, W. Siebert, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1603; *Angew. Chem.* **1992**, *104*, 1670.

[9] a) H. Braunschweig, Q. Ye, M. A. Celik, R. D. Dewhurst, K. Radacki, *Angew. Chem. Int. Ed.* **2015**, *54*, 5065; *Angew. Chem.* **2015**, *127*, 5154; b) H. Braunschweig, Q. Ye, K. Radacki, A. Damme, *Angew. Chem. Int. Ed.* **2012**, *51*, 7839; *Angew. Chem.* **2012**, *124*, 7959.

[10] a) *Bioactive Heterocyclic Compound Classes: Pharmaceuticals* (Eds.: C. Lamberth, J. Dinges), Wiley-VCH, Weinheim, **2012**; b) *Heterocycles in Natural Product Synthesis* (Eds.: K. C. Majumdar, S. K. Chattopadhyay), Wiley-VCH, Weinheim, **2011**; c) S. A. Lawrence, *Amines: Synthesis Properties, and Applications*, Cambridge University Press, New York, **2004**; d) D. O'Hagan, *Nat. Prod. Rep.* **2000**, *17*, 435.

[11] a) J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, K. Hammond, J. O. C. Jimenez-Halla, T. Kramer, J. Mies, *Angew. Chem. Int. Ed.* **2015**, *54*, 13801; *Angew. Chem.* **2015**, *127*, 14006; b) J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, T. Kramer, I. Krummenacher, A. Vargas, *Angew. Chem. Int. Ed.* **2015**, *54*, 4469; *Angew. Chem.* **2015**, *127*, 4551. See also: c) H. Braunschweig, Q. Ye, A. Vargas, R. D. Dewhurst, K. Radacki, A. Damme, *Nat. Chem.* **2012**, *4*, 563.

[12] For selected recent examples, see: a) S. M. McDonald, S. K. Mellerup, J. Peng, D. Yang, Q.-S. Li, S. Wang, *Chem. Eur. J.* **2015**, *21*, 13961; b) B. Neue, J. F. Araneda, W. E. Piers, M. Parvez, *Angew. Chem. Int. Ed.* **2013**, *52*, 9966; *Angew. Chem.* **2013**, *125*, 10150; c) H. Braunschweig, A. Damme, J. O. C. Jimenez-Halla, B. Pfaffinger, K. Radacki, J. Wolf, *Angew. Chem. Int. Ed.* **2012**,

51, 10034; *Angew. Chem.* **2012**, *124*, 10177; d) S. Xu, T. C. Mikulas, L. N. Zakharov, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 7527; *Angew. Chem.* **2013**, *125*, 7675; e) S. Xu, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 20152.

[13] a) M. Suginome, *Chem. Rec.* **2010**, *10*, 348; b) M. Suginome, M. Shirakura, A. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 14438; c) A.-M. Carroll, T. P. O'Sullivan, P. J. Guiry, *Adv. Synth. Catal.* **2005**, *347*, 609; d) M. Suginome, A. Yamamoto, M. Murakami, *J. Am. Chem. Soc.* **2003**, *125*, 6358; e) C. M. Crudden, D. Edwards, *Eur. J. Org. Chem.* **2003**, 4695; f) "Hydroboration, Diboration, Silylboration, and Stannylboration": N. Miyaura in *Catalytic Heterofunctionalization* (Eds.: A. Togni, H. Grützmacher), Wiley-VCH, Weinheim, **2001**, pp. 1 – 45; g) T. B. Marder, N. C. Norman, *Top. Catal.* **1998**, *5*, 63; h) M. Suginome, H. Nakamura, Y. Ito, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2516; *Angew. Chem.* **1997**, *109*, 2626; i) S. Onozawa, Y. Hatanaka, T. Sakakura, S. Shimada, M. Tanaka, *Organometallics* **1996**, *15*, 5450; j) M. Suginome, H. Nakamura, Y. Ito, *Chem. Commun.* **1996**, 2777; k) T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 11018; l) T. Ishiyama, K. Nishijima, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 7219; m) D. Männig, H. Nöth, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 878; *Angew. Chem.* **1985**, *97*, 854; n) S. Hara, H. Dojo, S. Takinami, A. Suzuki, *Tetrahedron Lett.* **1983**, *24*, 731; o) M. F. Lappert, B. Prokai, *J. Organomet. Chem.* **1964**, *1*, 384.

[14] E. Chong, S. A. Blum, *J. Am. Chem. Soc.* **2015**, *137*, 10144.

[15] a) L. Kong, Y. Li, R. Ganguly, D. Vidovic, R. Kinjo, *Angew. Chem. Int. Ed.* **2014**, *53*, 9280; *Angew. Chem.* **2014**, *126*, 9434; b) L. Kong, R. Ganguly, Y. Li, R. Kinjo, *Chem. Sci.* **2015**, *6*, 2893; c) L. Kong, W. Lu, Y. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.* **2016**, *138*, 8623.

[16] a) F. Focante, P. Mercandelli, A. Sironi, L. Resconi, *Coord. Chem. Rev.* **2006**, *250*, 170; b) R. Choukroun, C. Lorber, B. Donnadieu, *Chem. Eur. J.* **2002**, *8*, 2700. See also: c) M. M. Hansmann, R. L. Melen, F. Rominger, A. S. K. Hashmi, D. W. Stephan, *J. Am. Chem. Soc.* **2014**, *136*, 777.

[17] Yu. N. Bubnov, B. M. Mikhailov, *Izv. Akad. Nauk SSSR Ser. Khim.* **1967**, *2*, 472.

[18] a) H. Lukasch, G. Schmidt-Lukasch, U. Lippold, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 960; *Angew. Chem.* **1988**, *100*, 959. See also: b) Y. Katsuma, H. Asakawa, K.-H. Lee, Z. Lin, M. Yamashita, *Organometallics* **2016**, *35*, 2563; c) H. Asakawa, K.-H. Lee, Z. Lin, M. Yamashita, *Nat. Commun.* **2014**, *5*, 4245.

[19] Selected examples: a) P. Paetzold, T. Schmitz, A. Tapper, R. Ziembinski, *Chem. Ber.* **1990**, *123*, 747; b) R. Boese, P. Paetzold, A. Tapper, R. Ziembinski, *Chem. Ber.* **1989**, *122*, 1057.

[20] a) H. Braunschweig, M. A. Celik, R. D. Dewhurst, K. Ferkinghoff, A. Hermann, J. O. C. Jimenez-Halla, T. Kramer, K. Radacki, R. Shang, E. Siedler, F. Weißenberger, C. Werner, *Chem. Eur. J.* **2016**, *22*, 11736; b) A. Ansorge, D. J. Brauer, S. Buchheim-Spiegel, H. Bürger, T. Hagen, G. Pawelke, *J. Organomet. Chem.* **1995**, *501*, 347; c) S. Luckert, E. Eversheim, M. Müller, B. Redenz-Stormanns, U. Englert, P. Paetzold, *Chem. Ber.* **1995**, *128*, 1029; d) U. Sicker, A. Meller, W. Maringgele, *J. Organomet. Chem.* **1982**, *231*, 191; e) W. Maringgele, A. Meller, *Z. Anorg. Allg. Chem.* **1977**, *433*, 94; f) A. Grote, A. Haag, G. Hesse, *Justus Liebigs Ann. Chem.* **1972**, *755*, 67; g) J. Casanova, Jr., R. E. Schuster, *Tetrahedron Lett.* **1964**, *5*, 405.

[21] a) K. J. Iversen, D. J. D. Wilson, J. L. Dutton, *Organometallics* **2013**, *32*, 6209; b) D. Schmidt, J. H. J. Berthel, S. Pietsch, U. Radius, *Angew. Chem. Int. Ed.* **2012**, *51*, 8881; *Angew. Chem.* **2012**, *124*, 9011; c) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, *Angew. Chem. Int. Ed.* **2012**, *51*, 2098; *Angew. Chem.* **2012**, *124*, 2140; d) S. M. Ibrahim Al-Rafia, R. McDonald, M. J. Ferguson, E. Rivard, *Chem. Eur. J.* **2012**, *18*, 13810.

[22] T. Ochiai, D. Franz, S. Inoue, *Chem. Soc. Rev.* **2016**, DOI: 10.1039/C6CS00163G.

[23] a) H. Braunschweig, P. Paetzol, T. P. Spaniol, *Chem. Ber.* **1993**, *126*, 1565. See also: b) D. J. Brauer, H. Bürger, S. Buchheim-Spiegel, G. Pawelke, *Eur. J. Inorg. Chem.* **1999**, 255; c) A. Ansorge, D. J. Brauer, H. Bürger, T. Hagen, G. Pawelke, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 384; *Angew. Chem.* **1993**, *105*, 429.

[24] J. Baudoux, D. Cahard, *Org. React.* **2007**, *69*, 347.

[25] a) E. Tsurumaki, J. Sung, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2016**, *55*, 2596; *Angew. Chem.* **2016**, *128*, 2642; b) J. T. Henthorn, S. Lin, T. Agapie, *J. Am. Chem. Soc.* **2015**, *137*, 1458; c) J. T. Henthorn, T. Agapie, *Angew. Chem. Int. Ed.* **2014**, *53*, 12893; *Angew. Chem.* **2014**, *126*, 13107; d) S. Porcel, G. Bouhadir, N. Saffon, L. Maron, D. Bourissou, *Angew. Chem. Int. Ed.* **2010**, *49*, 6186; *Angew. Chem.* **2010**, *122*, 6322; e) T. K. Wood, W. E. Piers, B. A. Keay, M. Parvez, *Angew. Chem. Int. Ed.* **2009**, *48*, 4009; *Angew. Chem.* **2009**, *121*, 4069; f) M. Ahijado, T. Braun, *Angew. Chem. Int. Ed.* **2008**, *47*, 2954; *Angew. Chem.* **2008**, *120*, 2996.

[26] S. V. Bondarchuk, B. F. Minaev, *Chem. Phys. Lett.* **2014**, *607*, 75.

[27] A. Z. Rys, E. K. V. Schultz, D. N. Harpp, *J. Sulfur Chem.* **2010**, *31*, 351, and references therein.

[28] a) V. P. Boyarskiy, N. A. Bokach, K. V. Luzyanin, V. Y. Kukushkin, *Chem. Rev.* **2015**, *115*, 2698; b) M. A. Mironov, *Isocyanide Chemistry*, Wiley-VCH, Weinheim, **2012**, p. 35; c) S. Sadjadi, M. M. Heravi, *Tetrahedron* **2011**, *67*, 2707; d) A. V. Lygin, A. de Meijere, *Angew. Chem. Int. Ed.* **2010**, *49*, 9094; *Angew. Chem.* **2010**, *122*, 9280.

[29] E. P. Mayer, H. Nöth, *Chem. Ber.* **1993**, *126*, 1551.

[30] CCDC 1503050 (**2a**), 1503053 (**3a**), 1503056 (**4**), 1503057 (**5**), 1503058 (**6**), 1503059 (**7**), 1503060 (**8**), 1503061 (**9**), and 1503062 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: September 14, 2016
Revised: October 6, 2016
Published online: October 24, 2016

