Unsymmetrical, Cyclic Diborenes and Thermal Rearrangement to a Borylborylene

Tom E. Stennett,[a] James D. Mattock,[b] Ivonne Vollert,[a] Alfredo Vargas*[b] and Holger Braunschweig*[a]

Abstract: Cyclic diboranes(4) based on a chelating monoanionic benzylphosphine linker were prepared by boron-silicon exchange between arylsilanes and B_2Br_4. Coordination of Lewis bases to the remaining sp^2 boron atom yielded unsymmetrical sp^3-sp^3 diboranes, which were reduced with KC_8 to their corresponding *trans*-diborenes. These compounds were studied by a combination of spectroscopic methods, X-ray diffraction and DFT calculations. PMe_3-stabilized diborene **6** was found to undergo thermal rearrangement to *gem*-diborene **8**. DFT calculations on **8** reveal a polar boron-boron bond, and indicate that the compound is best described as a borylborylene.

Since the report of the first neutral diborene by Robinson and co-workers, which was prepared in low yields via a radical hydrogen scavenging process,[1] the preparation of compounds bearing boron-boron double bonds[2] has been extended by three rational and selective synthetic routes – the reductive coupling of two N-heterocyclic carbene (NHC)-stabilized aryldihaloboranes,[2b, 3] the reduction of $B_2X_2R_2$ species in the presence of stabilizing phosphine ligands,[4] and the stoichiometric reduction of carbene adducts of B_2Br_4.[5] A very recent development in this field has been the realization of the first unsymmetrical diborenes,[5b, 6] which promise to reveal more information about the fundamental nature of the boron-boron π-bond, and also allow investigation of the effect of a polarised B-B bond on the species' behaviour.

We are currently especially interested in the reactivity of phosphine-stabilized diborenes. Whereas carbenes typically remain bound to boron during the course of the reactions of diborenes with small molecules,[3b, 5b, 7] phosphine donors can dissociate under UV light and their diborenes display markedly different reactivity.[8] A drawback of the currently known examples of phosphine-stabilized diborenes is that they are mostly prepared from 1,2-dihalo-1,2-diarylboranes, $B_2X_2R_2$, the syntheses of which are limited in terms of substituent scope.[9] With convenient routes now available to all of the tetrahalodiboranes(4),[10] we are therefore keen to develop milder and better-yielding routes for the direct functionalization of B_2X_4 species.

Substituted monoboranes (RBX_2) can in many cases be conveniently prepared by silicon-boron exchange of the corresponding R-$SiMe_3$ species with trihaloboranes,[11] but equivalent reactions with diboranes(4) are limited to just a handful of examples. In the early 1980s, Haubold et al. prepared bridged sp^2-sp^3 diboranes by reaction of B_2Cl_4 with 2-silylamino-

and 2-siloxypyridines, forming B-N and B-O bonds, respectively, by Me_3SiCl elimination (Scheme 1).[12] The group of Siebert later succeeded in transferring a Cp* group to B_2Cl_4 via chlorosilane elimination, with a rearrangement giving a cyclopentadienylborylene-borane adduct as the final product.[13] Inspired by these studies, we selected a readily prepared arylsilane containing a phosphine donor group, with the goal of generating new diboranes capable of being reduced to B-B multiply-bonded compounds. From this starting point, we present a rational synthesis of unsymmetrical diborenes and rearrangement of one of these compounds to its *gem* isomer.
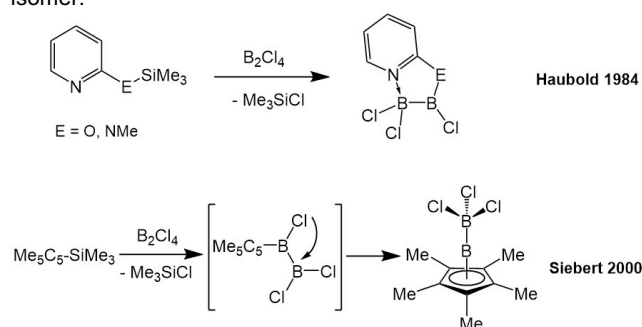
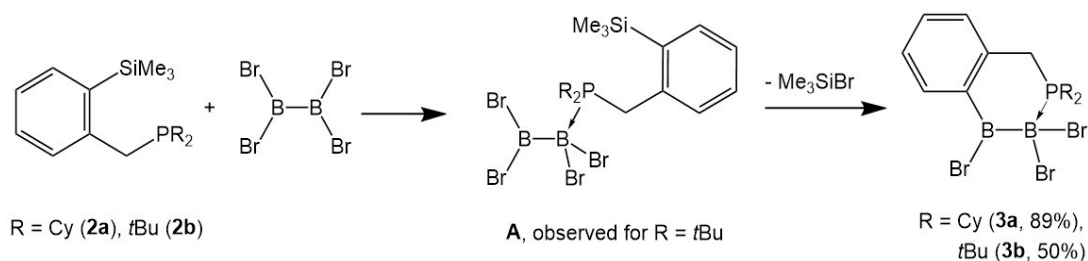**Scheme 1.** Formation of B-E bonds via silyl halide elimination

Reaction of 2-trimethylsilylbenzyl(dicyclohexyl)phosphine (**2a**), prepared in quantitative yield by treating the corresponding aryllithium compound, 2-$LiC_6H_4CH_2PCy_2$.Et_2O (**1**), with Me_3SiCl,[14] with B_2Br_4 at 0 °C led to the formation of sp^2-sp^3 diborane **3a** in high yield (89%; Scheme 2). The ^{11}B NMR spectrum of **3a** shows the low- and high-field signals expected for the sp^2 (73.3 ppm) and sp^3 (–10.5 ppm) boron atoms, respectively. A broad ^{31}P NMR signal at 2.6 ppm is also indicative of coordination to boron. X-ray diffraction provided confirmation of the expected structure (Figure 1), with the B-B bond length of 1.678(9) Å slightly shorter than published sp^2-sp^3 diboranes,[15] possibly as a result of steric constraints imposed by the chelating benzylphosphine group. Addition of a further equivalent of **2a** to **3a** resulted in no reaction at room temperature, while higher temperatures (80 °C) resulted in slow, unselective conversion to several species, none of which could be identified. The corresponding reaction with 2-trimethylsilylbenzyl(di-*tert*-butyl)phosphine (**2b**) also yields the equivalent sp^2-sp^3 diborane, **3b**. In this case, an intermediate species is observed when the reaction is performed at room temperature; observation of signals in the ^{11}B NMR spectrum at 68.6 and –5.7 ppm, a broad ^{31}P signal at 21.6 ppm and a signal at 0.31 ppm in the ^1H NMR spectrum for the $SiMe_3$ group indicate formation of adduct **A**, which can be completely converted to **3b** by heating to 60 °C for 2 h. This observation explains the regioselectivity of the formation of **3a** and **3b**. Silicon-boron exchange reactions of haloboranes are, to the best of our knowledge, limited to sp^2-hybridized boranes, hence the selective formation of the 1,2-isomer.[16] The structure of **3b** was also determined by X-ray crystallography (Figure 1), with the B-B bond length (1.681(9) Å) and other parameters not differing significantly from those in **3a**.

[a]   Dr. T. E. Stennett, I. Vollert, Prof. Dr. H. Braunschweig
       Institute for Inorganic Chemistry
       Julius-Maximilians-Universität Würzburg
       Am Hubland, 97074 Würzburg (Germany)
       and
       Institute for Sustainable Chemistry & Catalysis with Boron
       Julius-Maximilians-Universität Würzburg
       Am Hubland, 97074 Würzburg (Germany)
       E-mail: h.braunschweig@uni-wuerzburg.de
[b]   J. D. Mattock, Dr. A. Vargas
       Department of Chemistry, School of Life Sciences
       University of Sussex
       Brighton, BN1 9QJ, Sussex (UK)
       E-mail: alfredo.vargas@sussex.ac.uk

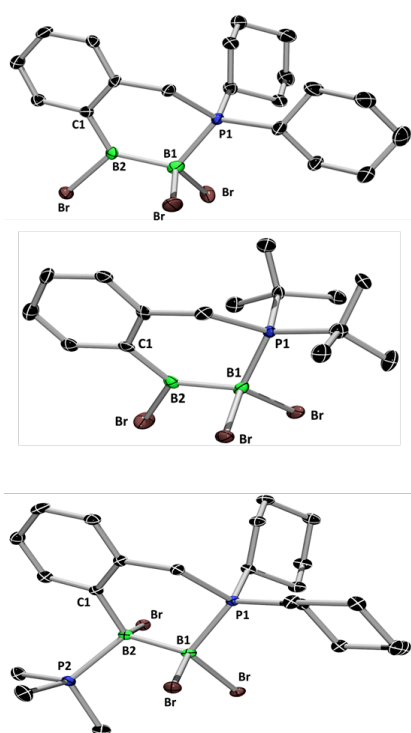   Supporting information for this article is given via a link at the end of the document.

Figure 1. Crystal structures of **3a** (top), **3b** (middle) and **4** (bottom) with atomic displacement ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths in Å: **3a**: B1-B2 1.678(9), P1-B1 1.954(8), C1-B2 1.54(1). **3b**: B1-B2 1.681(9), P1-B1 1.956(7), C1-B2 1.563(9). **4**: B1-B2 1.737(3), P1-B1 1.952(2), P2-B1 1.986(2), C1-B2 1.630(3).

Treatment of **3a** with small Lewis bases, L, led to their coordination to the remaining sp^2 boron atom and formation of sp^3-sp^3 diboranes (L = PMe₃ (**4**), N,N-di*iso*propylimidazol-2-ylidene (I'Pr) (**5**), Scheme 3), as indicated by a shift of the low-field resonance for the sp^2 boron atom to high field. The ^{31}P NMR spectrum of **4** shows two broad, mutually coupled doublets at –7.9 and –12.4 ppm ($^3J_{PP}$ ≈ 40 Hz), whereas the sole signal of

5 appears at –10.5 ppm. The structure of **4** was confirmed by X-ray diffraction (Figure 1). The B-B bond length displays the expected slight elongation, to 1.737(3) Å, with the structural parameters being otherwise unremarkable.
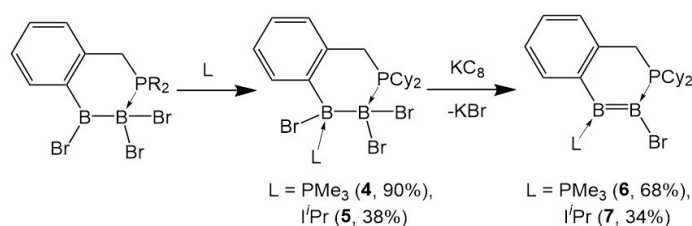
Scheme 3. Synthesis of unsymmetrical diborenes **6** and **7**.

Reaction of **4** with KC₈ in benzene gave a stark color change to dark yellow and formation of a new species with a single, broad signal in its ^{11}B NMR spectrum at 20.4 ppm, within the range of known diborenes. After two days conversion was complete, and after workup diborene **6** was isolated as a yellow solid in 68% yield. Single crystals suitable for X-ray diffraction were grown from hexane, allowing confirmation of the formation of **6** (Figure 2, Table 1). At 1.563(3) Å, the B-B distance is in the expected range for a boron-boron double bond, while the P-B bonds are both contracted by roughly 0.07 Å compared to **4**. Interestingly, the benzylphosphine chelate appears to cause a distortion of the substituents from ideal double-bond geometry, as the P1-B1-B2-C1 unit has a torsion angle of 17.3°. A similar procedure resulted in the reduction of **5** to diborene **7**, isolated as an orange solid in 34% yield, which is the first reported non-allenic diborene stabilized by two different classes of Lewis base – a phosphine and an NHC. In this case, the ^{11}B NMR signals at 30.0 and 12.5 ppm are at the extreme ends of the range for previously reported diborenes, and therefore suggest a reasonable degree of polarity of the B-B bond. The structure of **7** was also confirmed by X-ray diffraction (Figure 2), and the B-B double bond (1.562(6) Å) found to be the same length as that in **6**, within error.
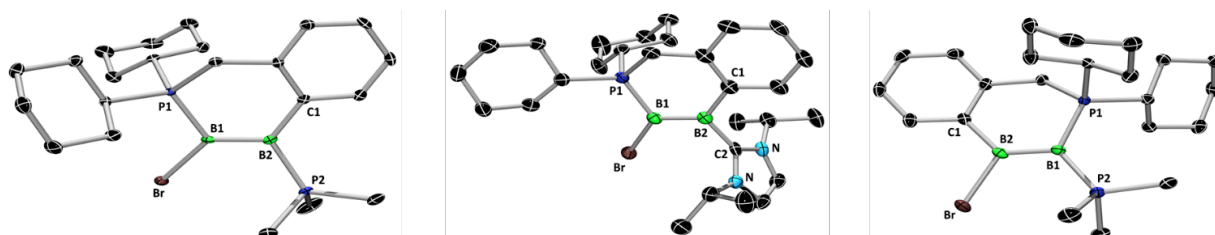
Figure 2. Crystal structures of **6**, **7** and **8** with atomic displacement ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Key bond lengths are displayed in Table 1.

d/Å	6	7	8
B1-B2	1.563(3)	1.562(6)	1.558(7)
P1-B1	1.879(2)	1.863(5)	1.853(4)
P2-B	1.909(2)	-	1.869(4)
C1-B2	1.587(3)	1.573(5)	1.576(6)
C2-B2	-	1.582(6)	-

Table 1. Selected bond lengths (Å) for compounds **6-8**.

Calculations based on the Kohn-Sham Density Functional Theory (DFT) at the OLYP/TZ2P level were conducted to further understand the observed results and the underlying rationales. Figure 3 shows the frontier orbitals of **6** and **7** and Table 2 displays the calculated bond lengths, bond orders and partial charges of the two structures in the gas phase. While both species largely display diborene characteristics in terms of electronic structure, as shown by their frontier orbitals and the B-B bond length, the phosphine-stabilized compound **6** exhibits a slightly higher B-B bond order than **7**, and a less polarized B-B unit. In addition, this unequal charge distribution is inversed in one compared to the other, i.e. in **6** the B1 centre carries the lesser negative charge, in contrast to the situation in **7**. These observations suggest that there is a higher C:→B2→B1 charge flow compared to the P:→B2→B1 path. The LUMO of both compounds has a large contribution from the π-system of the arene moiety, which is held close to the B=B plane by the chelate. This conjugation is noteworthy as homoarene substituents in previously reported diborenes sit exclusively perpendicular to the B=B bond. Both the HOMO and LUMO are found to be at lower energies in phosphine derivative **6** than in **7** due to the higher σ-donor strength of the NHC.

	6	7
d(BB)/Å	1.593	1.595
d(B2-C1)/Å	1.588	1.576
Bond order(BB)	1.52	1.48
q(B1)	−0.129	−0.149
q(B2)	−0.155	−0.113
q(Br)	−0.141	−0.153

Table 2. Calculated properties of compounds **6** and **7**.
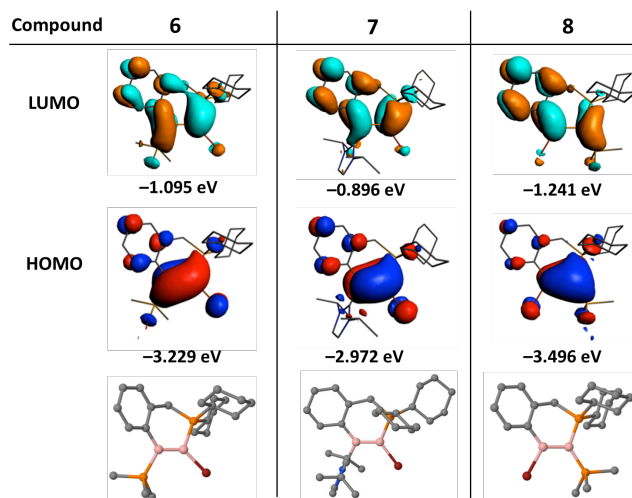

Figure 3. Frontier molecular orbitals of compounds **6-8**.

Unsymmetrical diborenes remain very much a novelty, with the only reported examples coming from the group of Kinjo in the past year,[5b, 6] and their behavior is as yet largely unexplored. We initially tested the thermal stability of **6** and **7**. Heating **6** to 80 °C in benzene led to a slow conversion to a new species displaying a broad signal at 52.2 ppm and a pseudo-triplet at −21.1 ppm in the ^{11}B NMR spectrum. Broad multiplets at 23.3 ppm and −11.9 ppm in the ^{31}P NMR spectrum indicated that both phosphines remained coordinated to boron. After 2 d at this temperature conversion was complete, and single crystals were grown by concentration of the reaction solution. X-ray diffraction revealed the product to be **8** (Scheme 4, Figure 2), in which an exchange of the diborene substituents had occurred, with both phosphines now bonded to the same boron atom. The B-B bond distance of 1.558(7) Å remains in the range for a boron-boron double bond, unchanged from **6**, while the B-P distances are slightly shorter than those in **6**. Heating compound **7** in benzene resulted in an even slower, unselective reaction, with no NMR signals comparable to those for **8** observed. As yet we have been unable to identify any of the products.
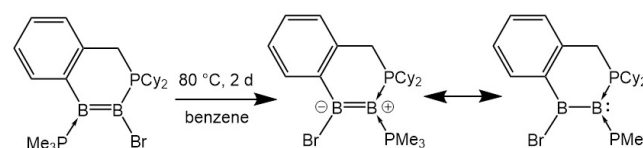
Scheme 4. Thermal rearrangement of **6** into **8**.

The nature of the boron-boron bond in **8** is not immediately clear; a classical π-bond would necessitate a formal negative charge on B2 and a positive charge on B1 (Scheme 4). Alternatively, the compound can be viewed as a boryl-substituted borylene, in which the monovalent B1 boron atom carries a lone pair of electrons. Although borylenes were formerly merely postulated as fleeting intermediates, isolable, metal-free borylene compounds stabilized by two (or one) neutral donors are now firmly established.[17] A recent computational study by Ghorai and Jemmis predicted that a simplified diborene, $B_2Br_2(PH_3)_2$, would be more stable as its *gem* isomer than as its *cis* and *trans* isomers (derivatives of both of which have been realized experimentally), while its NHC

derivative favors the *trans* conformation.[18] The authors proposed a borylborylene type structure, involving a large donor-acceptor contribution to the boron-boron bond, from the P_2B unit to the BBr_2 boron atom. Having isolated such a compound, we again turned to DFT for more insight into the formation and structure of **8**.

The calculated thermal conversion of **6** to **8** corresponds to a stabilization by 3.90 kcal/mol in terms of total electronic energy in the gas phase, and by 5.08 kcal/mol in toluene (within the conductor-like screening model). The more pronounced lowering in energy in the presence of a polarizable medium suggests the formation of a highly polarized B-B core in the product **8**. Table 3 shows the comparison of **6** and **8** in terms of selected parameters. The B-B bond order is somewhat lower in **8** (1.406) than in **6** (1.544), but nevertheless indicates significant double-bond character. Close inspection of the calculated partial charges (q_{B1} = –0.243, q_{B2} = –0.038) indicates a highly charge-separated state in **8**, in which the polarity is inversed with respect to **6** and the negative charge localized on B1. This analysis favors the borylborylene configuration proposed by Jemmis,[18] where B1 carries a lone pair. Furthermore, the frontier molecular orbitals shown in Figure 3 indicate a marked difference in the HOMO compared to the *trans*-diborenes. While in both compounds **6** and **7**, the HOMO describes a typical (albeit slightly distorted) diborene π-system, in compound **8** the HOMO, though still bearing an overall π symmetry, is more centered on the P1-B1-P2 unit. The LUMO is of boron-boron π-antibonding character with significant delocalization into the arene π-system. While the HOMO-LUMO gaps of the compounds are of similar magnitude, both of these orbitals are stabilized by the rearrangement, the HOMO to a slightly greater extent. The HOMO-1 of all three compounds represents the B-B sigma bonding interaction. Compound **8** bears some resemblance to a diboraallene compound recently reported by Kinjo and co-workers;[6] however, in that case, the HOMO is localized on the B=C double bond, with the lower-lying HOMO-1 describing the boron-boron π-interaction.

Additionally, the B-B interaction in **6** and **8** was estimated within the Energy Decomposition Analysis formalism (EDA) under the assumption that the bond energies between B1 and P1 in **6** and **8** are the same. Table 4 gives the values of the different bonding components. The total interaction energy is of slightly larger magnitude in **6**. Both the orbital interactions and repulsive Pauli components of the interaction are larger in **8** – this can be ascribed to borylene lone pair donation to the boryl centre, resulting in significant π-π interactions. The electrostatic component is larger in **8**, reflecting the more polar nature of the diboron unit. Furthermore, the deformation densities (Figure 4), which depict the charge flow upon interaction of B1 in **6** and **8** with the rest of the corresponding molecule, indicate significant similarities and differences between the two isomers. In both **6** and **8**, the main deformation density Δρ1 shows charge accumulation towards the boron atom stabilized by PMe_3. However, in **8**, one can see that charge flows to B1 not only from B1-P1 (dative) but also from B2 (covalent) – confirming the borylene-like nature of B1. The B2→B1 flow in **6** is only a secondary deformation density (Δρ2) and is of π-like symmetry, as expected for diborenes; in **8**, there is also some charge flow (Δρ2) towards the B2-B1 bond of σ-like character, further supporting the assignment of B1 as a doubly dative-stabilized borylene.

	8 (gas)	**6** (gas)
E_{el}	–363.77	–282.71
E_{orb}	–612.09	–406.69
E_{Pauli}	810.15	498.72
E_{int}	–165.70	–190.68

Table 4. The interaction energy decomposition (kcal/mol) in **6** (fragment 1 = B1-Br) and **8** (fragment 1 = B1-PMe_3) with fragment 2 = rest of the molecule.

To summarize, we have used boron-silicon metathesis at B_2Br_4 to develop a route to unsymmetrical diborenes based upon a chelating benzylphosphine linker, with either a phosphine or an N-heterocyclic carbene as the second stabilizing ligand. DFT calculations confirm the slight polarity of these compounds. We have also reported thermodynamic rearrangement of one of these unsymmetrical *trans*-diborenes to an unprecedented *gem*-diborene containing a polar boron-boron bond. On the basis of DFT calculations, which reveal large electrostatic and orbital contributions to the bonding, we propose that the compound is best described as a borylborylene.

Acknowledgements

	8 (gas)	**6** (gas)	**8** (solv)	**6** (solv)
d(BB)	1.618	1.593	1.612	1.593
Bond order(BB)	1.349	1.526	1.406	1.544
q(B1)	–0.243	–0.129	–0.240	–0.133
q(B2)	–0.019	–0.155	–0.038	–0.156
q(Br)	–0.131	–0.141	–0.169	–0.167

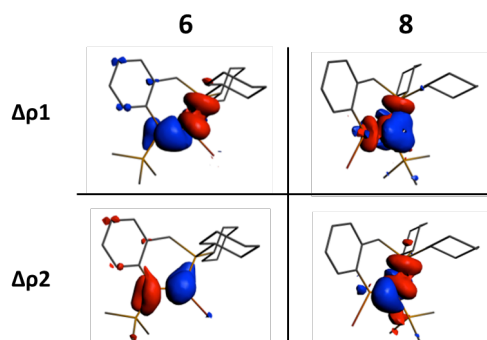**Table 3.** Calculated properties of compounds **6** and **8**.

6   **8**

Δρ1

Δρ2

Figure 4. The first two deformation densities of compounds **6** and **8,** with negative charge flow depicted from red lobes to blue.

[1]   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.

[2]   a) M. Arrowsmith, H. Braunschweig, T. E. Stennett, *Angew. Chem. Int. Ed.* **2017**, *56*, 96-115; b) P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, A. Vargas, *Angew. Chem. Int. Ed.* **2012**, *51*,

9931-9934; c) H. Braunschweig, R. D. Dewhurst, *Organometallics* **2014**, *33*, 6271-6277.

[3]   a) H. Braunschweig, I. Krummenacher, C. Lichtenberg, J. D. Mattock, M. Schafer, U. Schmidt, C. Schneider, T. Steffenhagen, S. Ullrich, A. Vargas, *Angew. Chem. Int. Ed.* **2017**, *56*, 889-892; b) H. Braunschweig, R. D. Dewhurst, C. Hoerl, A. K. Phukan, F. Pinzner, S. Ullrich, *Angew. Chem. Int. Ed.* **2014**, *53*, 3241-3244.

[4]   a) P. Bissinger, H. Braunschweig, M. A. Celik, C. Claes, R. D. Dewhurst, S. Endres, H. Kelch, T. Kramer, I. Krummenacher, C. Schneider, *Chem. Commun.* **2015**, *51*, 15917-15920; b) P. Bissinger, H. Braunschweig, A. Damme, T. Kupfer, I. Krummenacher, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 5689-5693.

[5]   a) H. Braunschweig, R. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, *Abstracts of Papers of the American Chemical Society* **2013**, *336*, 1420-1422; b) W. Lu, Y. X. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.* **2017**, *139*, 5047-5050.

[6]   W. Lu, Y. X. Li, R. Ganguly, R. Kinjo, *Angew. Chem. Int. Ed.* **2017**, *56*, 9829-9832.

[7]   H. Braunschweig, T. Dellermann, W. C. Ewing, T. Kramer, C. Schneider, S. Ullrich, *Angew. Chem. Int. Ed.* **2015**, *54*, 10271-10275.

[8]   M. Arrowsmith, J. Böhnke, H. Braunschweig, M. Celik, C. Claes, W. Ewing, I. Krummenacher, K. Lubitz, C. Schneider, *Angew. Chem. Int. Ed.* **2016**, *55*, 11271-11275.

[9]   H. Klusik, A. Berndt, *J. Organomet. Chem.* **1982**, *234*, C17-C19.

[10]   a) M. Arrowsmith, J. Böhnke, H. Braunschweig, A. Deissenberger, R. D. Dewhurst, W. C. Ewing, C. Hörl, J. Mies, J. H. Muessig, *Chem. Commun.* **2017**, *53*, 8265-8267; b) H. Nöth, H. Pommerening, *Chem. Ber.-Recueil* **1981**, *114*, 398-399.

[11]   a) W. Haubold, J. Herdtle, W. Gollinger, W. Einholz, *J. Organomet. Chem.* **1986**, *315*, 1-8; b) D. Kaufmann, *Chem. Ber.-Recueil* **1987**, *120*, 853-854; c) D. Kaufmann, *Chem. Ber.-Recueil* **1987**, *120*, 901-905.

[12]   W. Haubold, J. Hrebicek, G. Sawitzki, *Z. Naturforsch. B.* **1984**, *39*, 1027-1031.

[13]   P. Greiwe, A. Bethauser, H. Pritzkow, T. Kuhler, P. Jutzi, A. Siebert, *Eur. J. Inorg. Chem.* **2000**, 1927-1929.

[14]   H. P. Abicht, K. Issleib, *Z. Anorg. Allg. Chem.* **1976**, *422*, 237-242.

[15]   a) H. Braunschweig, A. Damme, J. O. C. Jiménez-Halla, T. Kupfer, K. Radacki, *Angew. Chem. Int. Ed.* **2012**, *51*, 6267-6271; b) R. D. Dewhurst, E. C. Neeve, H. Braunschweig, T. B. Marder, *Chem. Commun.* **2015**, *51*, 9594-9607; c) S. Pietsch, E. C. Neeve, D. C. Apperley, R. Bertermann, F. Y. Mo, D. Qiu, M. S. Cheung, L. Dang, J. B. Wang, U. Radius, Z. Y. Lin, C. Kleeberg, T. B. Marder, *Chem. Eur. J.* **2015**, *21*, 7082-7098.

[16]   a) D. A. Singleton, S. W. Leung, *J. Organomet. Chem.* **1997**, *544*, 157-161; b) A. Boussonnière, X. C. Pan, S. J. Geib, D. P. Curran, *Organometallics* **2013**, *32*, 7445-7450.

[17]   a) R. Kinjo, B. Donnadieu, M. A. Celik, G. Frenking, G. Bertrand, *Science* **2011**, *333*, 610-613; b) M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2017**, *56*, 10282-10292; c) H. Braunschweig, R. D. Dewhurst, F. Hupp, M. Nutz, K. Radacki, C. W. Tate, A. Vargas, Q. Ye, *Nature* **2015**, *522*, 327-330; d) M. Arrowsmith, D. Auerhammer, R. Bertermann, H. Braunschweig, G. Bringmann, M. A. Celik, R. D. Dewhurst, M. Finze, M. Grune, M. Hailmann, T. Hertle, I. Krummenacher, *Angew. Chem. Int. Ed.* **2016**, *55*, 14462-14466.

[18]   S. Ghorai, E. D. Jemmis, *Chem. Eur. J.* **2017**, *23*, 9746-9751.