

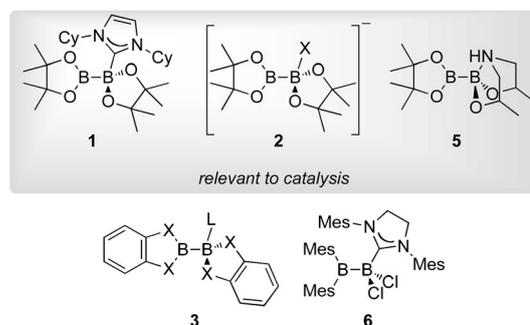
Phosphine Adducts of 1,2-Dibromo-1,2-dimesityldiborane(4): Between Bridging Halides and Rearrangement Processes**

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Modern organic chemistry and the production of high-value chemicals strongly rely on the possibility to incorporate a manifold of different functionalities into the organic framework. In this regard, the boryl group has been established a long time ago, combining versatile accessibility with a unique chemical diversity. Valuable secondary products include for example alkenes, alcohols, and ketones. Of equal importance is their outstanding significance as reagents in Suzuki–Miyaura-type coupling reactions.

Various synthetic approaches, such as salt elimination, hydroboration, or diboration reactions, have been developed to enable a convenient introduction of the boryl group. In particular, the diboration has been of great interest in facilitating the simultaneous generation of two reactive sites from commercially available diborane(4) reagents, that is, B_2cat_2 (cat = catecholato) and B_2pin_2 (pin = pinacolato).^[1] One major drawback of this approach is the requirement of transition-metal catalysis in almost all cases, except for highly reactive diborane(4) derivatives.^[2] The first example of such diboration reactivity was published back in 1954 for B_2Cl_4 , which readily adds to the double bond of ethylene in the absence of any additive.^[2a] However, catalytic processes are by far predominant, for which reason current research focuses on alternative metal-free systems.

Hoveyda et al. recently reported the efficient metal-free β -boration of α,β -unsaturated ketones promoted by an *N*-heterocyclic carbene (NHC).^[3] A neutral 1:1 NHC adduct of B_2pin_2 (**1**; Scheme 1) was proposed as the catalytically active species, even though its exact structure remained unknown at that time. Nevertheless, these findings stimulated research in this area and other metal-free systems for the borylation of organic substrates have been developed based on both neutral and anionic sp^2 – sp^3 diboron compounds.^[4] As a result, more detailed information on the actual composition of the organic catalyst is now available, which clearly emphasizes the high relevance of sp^2 – sp^3 diboranes as intermediates in both transition-metal^[5] and organocatalyzed^[4] borylation reac-



Scheme 1. Known sp^2 – sp^3 diboron compounds (Cy = cyclohexyl, Mes = mesityl).

tions. Elegant spectroscopic and theoretical studies by Marder et al. eventually verified the existence of the neutral NHC adduct **1** both in solution and in the solid state.^[6] Furthermore, Kleeberg et al. recently succeeded in the isolation of related anionic species $B_2pin_2X^-$ (**2**; $X^- = OMe^-, OtBu^-, 4-tBu-C_6H_4O^-, F^-$; Scheme 1), which showed a high potential in the metal-free borylation of organic electrophiles.^[7]

With these fundamental developments in mind, it appears rather surprising that simple 1:1 adducts of diboranes(4) with Lewis bases have been neglected for a long time. Accordingly, the number of fully characterized sp^2 – sp^3 diboron compounds is still comparatively small. Initially, Marder and Norman studied the reactivity of B_2cat_2 and $B_2(1,2-S_2C_6H_4)$ towards nitrogen and phosphorus donors to afford the corresponding mono- and bis-adducts $B_2(1,2-E_2C_6H_4)L$ (**3**; E = O, S; L = 4-picoline, PMe_2Ph , PEt_3 ; Scheme 1) and $B_2(1,2-E_2C_6H_4)L_2$ (**4**).^[8] Later on, intramolecular Lewis base coordination was established for pinacolato(diiisopropanolaminato)diboron (**5**; PDIPA-diboron; Scheme 1), which was shown to be a highly useful sp^2 – sp^3 diboron reagent in the copper-catalyzed β -boration of α,β -unsaturated substrates.^[9]

Together with the more recently published derivatives **1** and **2**, it becomes evident that the few known sp^2 – sp^3 diboranes are exclusively derived from oxo- and sulfur-based diborane(4) precursors. We became interested in the coordination chemistry of more reactive halide-substituted diboranes(4), that is, $X_2B_2Mes_2$ (X = Cl, Br), as part of our ongoing efforts to generate unusual low-coordinate boron species. Coordination of the NHC SIMes (1,3-dimesitylimidazolin-2-ylidene) to $Cl_2B_2Mes_2$ entailed a carbene-induced rearrangement process to afford the asymmetric sp^2 – sp^3 diborane **6**.^[10] As such 1,2-aryl migrations are rare in diborane chemistry (limited to an early report by Berndt et al.

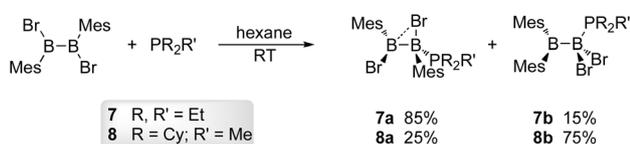
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from 1991),^[11] we began to elucidate whether this rather uncommon transformation depends on the nature of the Lewis base. Thus, the coordination of simple phosphines to Lewis-acidic diborane(4) $\text{Br}_2\text{B}_2\text{Mes}_2$ results in the formation of two constitutional isomers of $\text{Br}_2\text{B}_2\text{Mes}_2(\text{PR}_2\text{R}')$ (**7**: $\text{R}, \text{R}' = \text{Et}$; **8**: $\text{R} = \text{Cy}, \text{R}' = \text{Me}$), the ratio of which is related to the size of the Lewis base. A non-rearranged structure featuring a rare B–Br–B bridge is found for PET_3 , while the increased steric bulk of PMeCy_2 obviously favors the rearrangement event. Herein, we present the results of these studies along with X-ray diffraction data on the two major isomers **7a** and **8b**.

Reaction of $\text{Br}_2\text{B}_2\text{Mes}_2$ with one equivalent of PET_3 in C_6D_6 was fast and occurred spontaneously at room temperature within seconds.^[12] Examination of the reaction mixture by ^{31}P NMR spectroscopy indicated quantitative conversion of the starting materials to afford the phosphine adduct $\text{Br}_2\text{B}_2\text{Mes}_2(\text{PET}_3)$ (**7**), which was eventually obtained as a colorless solid in 76% yield (Scheme 2). Initially, we were



Scheme 2. Synthesis of $\text{sp}^2\text{-sp}^3$ diboron compounds **7** and **8**.

puzzled by the appearance of four well-separated signals in the room-temperature ^{11}B NMR spectrum of **7** ($\delta = 91.0, 58.1, -1.6, -7.9$) and a rather complex ^1H NMR spectrum, which was not consistent with the observation of one broad ^{31}P NMR resonance ($\delta = 0.19$) and the formation of a single species. However, the ^{31}P NMR signal readily splits into two distinct resonances below -35°C in CD_2Cl_2 ($\delta = -0.69$ (**7a**), 0.15 (**7b**); at room temperature: $\delta = 0.21$ (**7**)), which eventually verified the presence of two constitutional isomers **7a** and **7b** in solution. With this in mind, all of the ^1H NMR and ^{11}B NMR signals could clearly be assigned to the different isomers, while integration of the former revealed a ratio **7a**/**7b** of 85:15. It should also be noted that the ratio does not change with temperature (-80°C to 70°C), which precludes any interconversion between **7a** and **7b** and suggests that this reactivity is driven by thermodynamics. Evidence for the structural nature of the isomers comes from ^{11}B NMR spectroscopy. Thus, adduct formation is substantiated for both species by upfield-shifted ^{11}B NMR signals at $\delta = -1.6$ (**7a**) and $\delta = -7.9$ (**7b**), which appear in the typical region for four-coordinate boron centers. Together with the pronounced downfield shift of the second ^{11}B NMR signal of the minor isomer **7b** ($\delta = 91.0$), it becomes obvious that the major isomer **7a** is a normal 1:1 adduct between $\text{Br}_2\text{B}_2\text{Mes}_2$ and PET_3 , while **7b** features a rearranged structure resulting from a phosphine-induced 1,2-migration of one mesityl and one bromide ligand. Also, the ^{11}B NMR signal of the main product **7a** ($\delta = 58.1$) is shifted upfield by 28 ppm with respect to $\text{Br}_2\text{B}_2\text{Mes}_2$ ($\delta = 86$), which suggests some kind of additional electron donation to the sp^2 boron center in solution.

X-ray diffraction served to validate the non-rearranged structure of the $\text{sp}^2\text{-sp}^3$ diborane **7a** in the solid state (Figure 1).^[19] The most exciting structural feature of **7a** is the coordination mode of the bromide ligand Br2, which

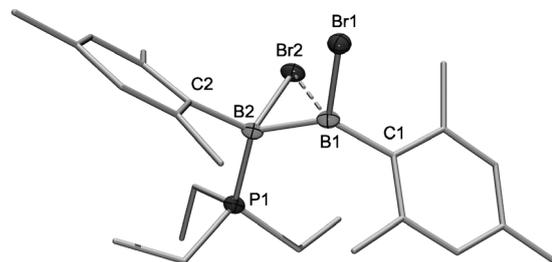
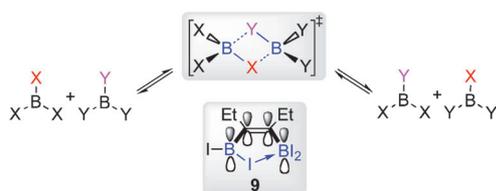


Figure 1. Molecular structure of **7a** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

adopts a bridging position between the two boron center B1 and B2. As a result of this interaction, the two faces of B1 (sp^2) become diastereotopic, making the formation of **7a** a highly stereoselective process. Only diastereoisomer **7a** with both mesityl ligands in “*trans*” position is formed, while the corresponding “*cis*” diastereoisomer has not been observed at any time, which is presumably due to steric congestion. Even though the B1–Br2 distance (2.437(2) Å) in **7a** is considerably elongated by 21.8% and 11.8% with respect to the “normal” B1–Br1 (2.004(2) Å) and B2–Br2 bonds (2.178(2) Å), respectively, the presence of a dative bonding interaction is clearly indicated by an extremely small value for the B1–B2–Br2 angle (76.55(12)°). All of the B–Br bonds are longer than those of the diborane(4) precursor $\text{Br}_2\text{B}_2\text{Mes}_2$ (1.928(4) Å, 1.932(4) Å),^[13] which is most likely due to the increased electron density at B2 after adduct formation. Consequently, electron density is also enhanced at Br2, which now facilitates a dative bonding interaction to the highly electrophilic $\text{B}(\text{Mes})(\text{Br})$ fragment. With this interaction in mind, the unusual upfield shift of the ^{11}B BMR signal of B1 observed in solution is also readily rationalized.

The presence of a bridging bromide strongly affects the geometries at B1 and B2, which deviate significantly from ideal trigonal-planar ($\text{sp}^2\text{-B1}$) and tetrahedral ($\text{sp}^3\text{-B2}$), respectively. By contrast, the effect of adduct formation on the B–B bond lengths is rather marginal, and an elongation of only 4 pm is observed with respect to $\text{Br}_2\text{B}_2\text{Mes}_2$ (1.673(6) Å),^[13] which is thus much smaller than in the related NHC $\text{sp}^2\text{-sp}^3$ diboranes **1** (1.743(2) Å)^[6] and **6** (1.774(3) Å).^[10]

The observation of a dative bonding interaction between a halide and an sp^2 boron center in a neutral diborane species is of exceeding significance with respect to the chemistry of simple boron trihalides. It is well-known that halide redistribution reactions readily occur between most mixtures of boron trihalides to afford rapidly established equilibria.^[14] Even though the kinetics of these processes have been studied theoretically and by different spectroscopic methods, mechanistic details are still rare.^[15] Halide redistribution most likely proceeds by an associative mechanism involving



Scheme 3. Halide redistribution equilibria in mixtures of boron halides (top) and the dative B–I bonding interaction in **9** (bottom).

a halide-bridged, four-center transition state dimer (Scheme 3).

Conclusive experimental evidence for the existence of such dimeric species is however limited to few matrix isolation experiments with BF_3 in krypton and argon matrices at 20 K.^[16] In fact, we are only aware of one single example in which a related dative B–Hal interaction could be verified.^[17] A rather short B–I separation distance (2.383(4) Å) between the two boryl fragments in *cis*-3,4-bis(diiodoboryl)hex-3-ene (**9**) clearly substantiated the presence of a dative B–I bond (compare with other B–I bonds: 2.107(4)–2.231(4) Å). Here, the *cis* configuration and conjugation of the π system with the empty p_z orbitals at boron already create the geometrical preconditions for an effective B–I dative bonding interaction, which is clearly not the case in **7a**, making its bonding situation somewhat unique. All efforts to further substantiate the nature of the minor reaction product **7b** failed, as we were not able to separate **7b** from the reaction mixture.

The reaction of $Br_2B_2Mes_2$ with $PMeCy_2$ was used to elucidate the steric influence of the Lewis base on the observed reactivity patterns and the ratio of the resulting two isomeric products. Again, adduct formation was fast and proceeded quantitatively within seconds to afford sp^2 – sp^3 diborane $Br_2B_2Mes_2(PMeCy_2)$ (**8**) as a colorless substance in 88% yields.^[12] Examination of the NMR spectroscopic parameters in solution indicated the presence of two constitutional isomers **8a** and **8b** in a ratio of 1:3, as evidenced by their characteristic ^{11}B NMR data (C_6D_6 : **8a** $\delta = -0.4, 60.3$; **8b** $\delta = -6.4, 95.5$ ppm) and ^{31}P NMR chemical shifts (C_6D_6 : **8a** $\delta = 1.45$; **8b** $\delta = -4.76$; CD_2Cl_2 : **8a** $\delta = -1.97$; **8b** $\delta = -4.35$ ppm). However, coordination of the more bulky $PMeCy_2$ obviously favors the formation of the 1,2-shifted product **8b**, which is now the major component of the reaction mixture. These findings clearly imply that the size of the phosphine ligand exerts a strong influence on the strength of the dative B–Br bonding interaction. Thus, the larger $PMeCy_2$ most likely prevents any effective B–Br interaction stabilizing a “normal” adduct structure (**8a**), for which reason the phosphine-induced rearrangement pathway becomes more favorable (**8b**).

This scenario is further supported by DFT calculations on **7** and **8** at the PBE level of theory.^[18] To this end, geometry optimizations were performed on both isomers **7a/7b** and **8a/8b** without symmetry restraints. In any case, adduct formation is an exothermic process regardless of the product nature ($\Delta E = -34.83$ to -63.14 kJ mol⁻¹). Consistent with our experimental results, reaction with PEt_3 energetically favors the “normal” adduct structure **7a_{cal}** over **7b_{cal}** by approximately 6 kJ mol⁻¹ (Figure 2), while for $PMeCy_2$ the rearranged

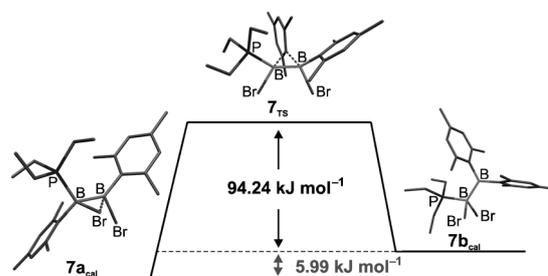


Figure 2. Calculated parameters for the interconversion of constitutional isomers **7a_{cal}** and **7b_{cal}** via transition state **7_{TS}**.

structure **8b_{cal}** is 17 kJ mol⁻¹ lower in energy than **8a_{cal}**. We were able to locate the transition states for the interconversion of the two isomeric species **7a_{cal}/7b_{cal}** (Figure 2) and **8a_{cal}/8b_{cal}**. Accordingly, activation barriers for the interconversion of the two constitutional isomers are high ($\Delta E = 84.24$ – 101.34 kJ mol⁻¹), which is in agreement with our experimental findings that such a process is not accessible under ambient conditions. Furthermore, the transition-state structures **7_{TS}** and **8_{TS}** suggest that the rearrangement event proceeds via an initial 1,2-shift of one mesityl ligand.

Determination of the molecular structure of **8b** eventually confirmed the phosphine-induced rearrangement upon addition of the bulky $PMeCy_2$ to $Br_2B_2Mes_2$. Again, isolation and structural characterization was only successful in the case of the major isomer **8b** (Figure 3).^[19] Most of the geometrical parameters are not affected by the 1,2-shift of the mesityl and

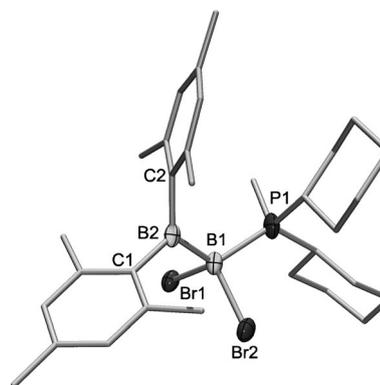
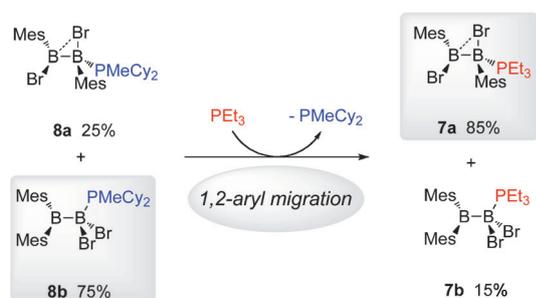


Figure 3. Molecular structure of **8b** in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.

bromine ligands. Thus, the B–B (1.749(3) Å), B–P (1.988(2) Å), and B–C bond lengths (1.595(3) Å, 1.602(3) Å) lie in a similar region to those of **7a** featuring a “normal” adduct structure. Notable structural differences to **7a**, such as the B–Br distances (2.067(3) Å, 2.053(2) Å; compare with **7a**: B2–Br2 2.178(2) Å; B2–Br1 2.437(2) Å), clearly result from the absence of a bridging halide in rearranged **8b**, which is also highlighted by a regular trigonal-planar geometry at B2 ($\Sigma B2 = 360.0^\circ$). Deviations from the tetrahedral coordination sphere at B1 are caused by the larger size of the $PMeCy_2$ ligand. These findings imply that

the steric requirements of the phosphine ligand play a critical role in determining the nature of the product.

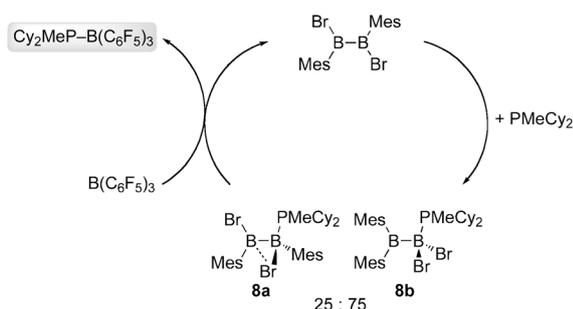
Similar conclusions come from the following displacement experiment. Reaction of a benzene solution of **8** as its thermodynamic mixture (**8a**/**8b** = 1:3) with the smaller and more Lewis-basic PEt_3 results in the spontaneous exchange of the phosphine donor, as readily evidenced by the appearance of characteristic signals for **7** and free PMeCy_2 in the ^{31}P NMR spectrum of the reaction mixture (Scheme 4). However, the



Scheme 4. Ligand-exchange reaction and rearrangement of **8** by the reaction with PEt_3 .

initial isomer ratio of 1:3 for **8a**/**8b** is not retained at all. Instead, the above-mentioned 85:15 ratio for **7a** and **7b** demanded by thermodynamics is established immediately.

We next tried to remove the phosphine ligand in **8b**, aiming at the generation and isolation of the unsymmetrical diborane(4) $\text{Mes}_2\text{B}-\text{BBR}_2$. When a reaction mixture containing **8** was treated with $\text{B}(\text{C}_6\text{F}_5)_3$, the new phosphine-borane adduct $\text{Cy}_2\text{MeP}-\text{B}(\text{C}_6\text{F}_5)_3$ was formed quantitatively within seconds (Scheme 5). However, no spectroscopic evidence for the existence of $\text{Mes}_2\text{B}-\text{BBR}_2$ could be obtained, and the



Scheme 5. Removal of PMeCy_2 in **8** by adduct formation with $\text{B}(\text{C}_6\text{F}_5)_3$.

diborane(4) starting material $\text{Br}_2\text{B}_2\text{Mes}_2$ was cleanly regenerated. Obviously $\text{Mes}_2\text{B}-\text{BBR}_2$ requires the electronic stabilization by an electron donor (phosphine, NHC) to prevent its rearrangement. We also elucidated the possibility of a thermal equilibrium between $\text{Br}_2\text{B}_2\text{Mes}_2$ and its constitutional isomer in the absence of any Lewis base by VT NMR spectroscopy on $\text{Br}_2\text{B}_2\text{Mes}_2$. Again, free $\text{Mes}_2\text{B}-\text{BBR}_2$ could not be detected at any time, for which reason a mechanism for the formation of **7b** and **8b** involving initial rearrangement of $\text{Br}_2\text{B}_2\text{Mes}_2$

and subsequent Lewis base coordination appears very unlikely.

In conclusion, we have demonstrated that coordination of simple phosphines (PEt_3 , PMeCy_2) to electrophilic $\text{Br}_2\text{B}_2\text{Mes}_2$ results in mixtures of two different types of sp^2-sp^3 diboron species, the relative ratio of which strongly depends on the size of the Lewis base. Thus, reaction with the more bulky PMeCy_2 afforded **8b** as the major component formed by phosphine-induced 1,2-rearrangement of mesityl and bromine ligands. By contrast, the “normal” adduct structure **7a** was strongly favored when the smaller PEt_3 was chosen as reagent. Examination of the molecular structure of **7a** by X-ray diffraction revealed a B-B-B bridge and the presence of a dative B-Hal bonding interaction to the sp^2 boron center. Such interactions have been suggested to be involved in halide rearrangement processes observed for mixtures of boron trihalides, while conclusive evidence for their existence has remained exceedingly rare and limited to a few studies to date. Furthermore, theoretical calculations showed that adduct formation is an exothermic process in all cases and that any interconversion of the constitutional isomers has to be considered unlikely owing to large activation barriers, results that are consistent with experimental findings.

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- [1] a) T. Ishiyama, N. Matsuda, N. Miyaura, A. Suzuki, *J. Am. Chem. Soc.* **1993**, *115*, 11018; b) T. Ishiyama, N. Matsuda, M. Murata, F. Ozawa, A. Suzuki, N. Miyaura, *Organometallics* **1996**, *15*, 713; c) G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685; d) T. B. Marder, N. C. Norman, *Top. Catal.* **1998**, *5*, 63; e) T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2000**, *611*, 392; f) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1; g) H. Braunschweig, T. Kupfer, M. Lutz, K. Radacki, F. Seeler, R. Sigritz, *Angew. Chem.* **2006**, *118*, 8217; *Angew. Chem. Int. Ed.* **2006**, *45*, 8048.
- [2] a) G. Urry, J. Kerrigan, T. D. Parsons, H. I. Schlesinger, *J. Am. Chem. Soc.* **1954**, *76*, 5299; b) W. Siebert, *Z. Naturforsch. B* **1989**, *44*, 1179.
- [3] K.-s. Lee, A. R. Zhugralin, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 7253.
- [4] a) F. Mo, Y. Jiang, D. Qiu, Y. Zhang, J. Yang, *Angew. Chem.* **2010**, *122*, 1890; *Angew. Chem. Int. Ed.* **2010**, *49*, 1846; b) A. Bonet, H. Gulyás, E. Fernández, *Angew. Chem.* **2010**, *122*, 5256; *Angew. Chem. Int. Ed.* **2010**, *49*, 5130; c) A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyás, E. Fernández, *Angew. Chem.* **2011**, *123*, 7296; *Angew. Chem. Int. Ed.* **2011**, *50*, 7158; d) C. Pubill-Ulldemolins, A. Bonet, C. Bo, H. Gulyás, E. Fernández, *Chem. Eur. J.* **2012**, *18*, 1121; e) H. Li, L. Wang, Y. Zhang, J. Wang, *Angew. Chem.* **2012**, *124*, 2997; *Angew. Chem. Int. Ed.* **2012**, *51*, 2943.
- [5] a) H. Ito, H. Yamanaka, J. Tateiwa, A. Hosomi, *Tetrahedron Lett.* **2000**, *41*, 6821; b) K. Takahashi, T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2001**, *625*, 47; c) K. Takahashi, T. Ishiyama, N. Miyaura, *Chem. Lett.* **2000**, 982; d) J. E. Lee, J. Yun, *Angew. Chem.* **2008**, *120*, 151; *Angew. Chem. Int. Ed.* **2008**, *47*, 145;

- e) J. E. Lee, J. Kwon, J. Yun, *Chem. Commun.* **2008**, 733; f) H.-S. Sim, X. Feng, J. Yun, *Chem. Eur. J.* **2009**, *15*, 1939.
- [6] C. Kleeberg, A. G. Crawford, A. S. Batsanov, P. Hodgkinson, D. C. Apperley, M. S. Cheung, Z. Lin, T. B. Marder, *J. Org. Chem.* **2012**, *77*, 785.
- [7] C. Kleeberg, *IMEBoron XIV Conference 2011*, Niagara Falls, Canada.
- [8] a) W. Haubold, J. Hrebicek, G. Sawitzki, *Z. Naturforsch. B* **1984**, *39*, 1027; b) P. Nguyen, C. Dai, N. J. Taylor, W. P. Power, T. B. Marder, N. L. Pickett, N. C. Norman, *Inorg. Chem.* **1995**, *34*, 4290; c) W. Clegg, C. Dai, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, N. L. Pickett, W. P. Power, A. J. Scott, *J. Chem. Soc. Dalton Trans.* **1997**, 83; d) W. J. Grigsby, P. P. Power, *Chem. Eur. J.* **1997**, *3*, 368.
- [9] M. Gao, S. B. Thorpe, C. Kleeberg, C. Slebodnick, T. B. Marder, W. L. Santos, *J. Org. Chem.* **2011**, *76*, 3997.
- [10] P. Bissinger, H. Braunschweig, A. Damme, R. D. Dewhurst, T. Kupfer, K. Radacki, K. Wagner, *J. Am. Chem. Soc.* **2011**, *133*, 19044.
- [11] A. Höfner, B. Ziegler, R. Hunold, P. Willershausen, W. Massa, A. Berndt, *Angew. Chem.* **1991**, *103*, 580; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 594.
- [12] Experimental details are provided in the Supporting Information.
- [13] H. Hommer, J. Knizek, H. Nöth, W. Ponikwar, H. Schwenk-Kircher, *Eur. J. Inorg. Chem.* **1998**, 1519.
- [14] a) M. F. Lappert, *Chem. Rev.* **1956**, *56*, 959; b) J. C. Lockhart, *Chem. Rev.* **1965**, *65*, 131; c) K. Moedritzer, *Adv. Organomet. Chem.* **1968**, *6*, 171; d) N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, **1997**.
- [15] a) L. H. Long, D. Dollimore, *J. Chem. Soc.* **1954**, 4457; b) J. Goubeau, D. E. Richter, H. J. Becher, *Z. Anorg. Allg. Chem.* **1955**, *278*, 12; c) L. P. Lindeman, M. K. Wilson, *J. Chem. Phys.* **1956**, *24*, 242; d) R. F. Porter, D. R. Bidinosti, K. R. Watterson, *J. Chem. Phys.* **1962**, *36*, 2104; e) T. D. Coyle, F. G. A. Stone, *J. Chem. Phys.* **1960**, *32*, 1892; f) P. N. Gates, E. F. Mooney, D. C. Smith, *J. Chem. Soc.* **1964**, 3511; g) M. F. Lappert, M. R. Litgow, J. B. Pedley, T. R. Spalding, H. Nöth, *J. Chem. Soc. A* **1971**, 383; h) M. F. Lappert, M. R. Litgow, J. B. Pedley, A. Tweedale, *J. Chem. Soc. A* **1971**, 2426; i) P. D. W. Boyd, M. J. Taylor, *Inorg. Chim. Acta* **1992**, *193*, 1.
- [16] J. M. Bassler, P. L. Timms, J. L. Margrave, *J. Chem. Phys.* **1966**, *45*, 2704.
- [17] Y. Nie, H. Pritzkow, S. Schwiegk, W. Siebert, *Eur. J. Inorg. Chem.* **2004**, 1630.
- [18] Details on the theoretical calculations are provided in the Supporting Information.
- [19] CCDC 869358 (**7a**) and CCDC 869359 (**8b**) 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.