Boracumulene Complexes

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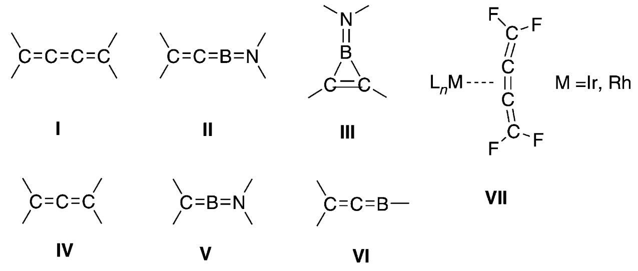
Synthesis of 1-Aza-2-borabutatriene Rhodium Complexes by Thermal Borylene Transfer from $[(OC)_5Mo{=}BN(SiMe_3)_2]$**

Holger Braunschweig, Qing Ye, Alexander Damme, Thomas Kupfer, Krzysztof Radacki, and Justin Wolf*

Since the first reports of allenes more than a century ago[1] compounds with cumulated double bonds have attracted interest owing to their highly unsaturated structure. [3]-Cumulene, or butatriene (**I**), consists of three cumulated carbon–carbon double bonds that can potentially ligate to a transition-metal center. However, they coordinate mostly in an η^2-π fashion through the central C=C bond.[2] As reported by the groups of Hughes and Lentz, the highly reactive molecule tetrafluorobutatriene (which decomposes slowly even at −80 °C) can be trapped and stabilized by transition-metal coordination (**VII**).[3] In 2002, Suzuki et al. reported the coordination of a butatriene to low-valent zirconocene in a novel κ^2-σ,σ bonding mode, the first example of a five-membered metallacycloalkyne.[4]



As boron-based π systems have attracted much attention owing to their interesting photophysical properties,[5] we turned our attention to boron-containing cumulene systems. Amino(methylene)boranes (**V**), isoelectronic to allenes (**IV**), can be isolated when the kinetically unstable B=C bond is sterically protected by bulky substituents. Structural characterization revealed that such amino(methylene)boranes adopt an allene-like structure with a linear N=B=C skeleton.[6] Furthermore, there are a few examples of boron-containing ionic allene analogues such as the 1,3-borataallene dianion and the 2-borataallene anion.[7] The attempt to synthesize 1-boraallene (**VI**) by the reaction of an alkynylfluoroborane with *tert*-butyllithium at −120 °C afforded the corresponding boraallene only as an intermediate, which promptly underwent a hydroalkylation reaction at the B=C bond.[8]

B-amino-1-boraallenes (**II**) are isoelectronic to butatriene (**I**) and might represent boron-containing [3]-cumulene systems when the boron–nitrogen π interaction is taken into account. Currently, very little is known about this class of compounds, and no successful synthetic approach has been reported. Ab initio calculations on the parent compound **II** and its constitutional isomer aminoborirene **III** have been carried out[9] suggesting that **II** is 12.9 kcal mol^{-1} higher in energy than **III**, which is surprising given the borirene's 2π-electron aromatic stabilization.[10] Ever since a facile synthetic route to Group 6 terminal borylene complexes was developed,[11] they have proven excellent sources for the borylene fragment.[12] This borylene transfer method has developed quickly in the past decade and has been applied to the synthesis of borirenes,[13] new transition-metal borylene complexes,[12,14] metathesis reactions,[15] and the insertion of the :B−R fragment into olefinic C−H bonds.[16]

One particularly intriguing and unexplored area of transition-metal borylene chemistry is their reactivity with (and perhaps transfer to) metal–carbon multiple bonds. Given this paucity and our motivation towards the synthesis of *B*-amino-1-boraallenes (**II**), we decided to investigate the behavior of terminal Group 6 metal borylenes with vinylidenerhodium complexes. Herein, we report our preliminary results of the borylene transfer to vinylidenerhodium complexes which leads to 1-aza-2-borabutatriene rhodium complexes in good yields.

When the vinylidenerhodium complex **2** was added to an equimolar amount of $[(OC)_5Mo{=}B{=}N(SiMe_3)_2]$ (**1**) in benzene and slightly warmed to 40 °C, NMR spectroscopy revealed a gradual consumption of the starting materials and the formation of a mixture of the title compound **6** and the rhodium monocarbonyl complex $[(\eta^5\text{-}C_5H_5)Rh(CO)(P\mathit{i}Pr_3)]$ (**4**)[17] in a ratio of approximately 2:1 (^{1}H NMR spectroscopy). The $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **6** feature signals at $\delta_B = 67.9$ ppm and at $\delta_P = 66.4$ ppm ($^1J_{\text{Rh-P}} = 202.5$ Hz), respectively, which are both shifted upfield relative to the signals for the starting materials **1** ($\delta_B = 89.1$ ppm)[18] and **2** ($\delta_P = 73.5$ ppm, $^1J_{\text{Rh-P}} = 209.0$ Hz). In the ^{1}H NMR spectrum of **6**, a new set of signals is present in the expected ratio for one C_5H_5 ligand and two Me_3Si groups, thus confirming its constitution in solution. Most notably, the observation of two broad signals for trimethylsilyl groups at $\delta = 0.30$ and 0.62 ppm in a 1:1 ratio and two signals for olefinic

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[*] Prof. Dr. H. Braunschweig, Q. Ye, A. Damme, Dr. T. Kupfer, Dr. K. Radacki, Dr. J. Wolf
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
E-mail: h.braunschweig@mail.uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/braunschweig/index.html

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protons at $\delta = 7.31$ (dd, $^{3}J_{\text{Rh-H}} = 4.1$ Hz, $^{4}J_{\text{P-H}} = 1.1$ Hz) and 6.48 ppm (dd, $^{3}J_{\text{Rh-H}} = 2.9$ Hz, $^{4}J_{\text{P-H}} = 2.2$ Hz) suggests both a considerable rotational barrier of the nitrogen boron double bond and the asymmetry of the product, which is in good accordance with the proposed structure. This coupling pattern of olefinic protons is confirmed by comparison with a ^{1}H{^{31}P} NMR spectrum, which features doublet instead of doublet-of-doublet signals and thus geminal H–H coupling is excluded. The assignment of the resonances for *endo*- and *exo*-H or *endo*- and *exo*-SiMe$_3$ is based on the NOESY correlation with protons of the P*i*Pr$_3$ ligand. Unfortunately, as a result of its oily consistency, single crystals of **6** suitable for X-ray diffraction could not be obtained.

To probe the versatility of the synthetic method and to structurally characterize the target compound, we synthesized the sterically more demanding PCy$_3$-substituted rhodium vinylidene **3**. The reaction of [(OC)$_5$Mo=B=N(SiMe$_3$)$_2$] (**1**) with **3** was carried out under analogous conditions to those applied for the synthesis of compound **6** and was monitored by NMR spectroscopy. The formation of **7** was indicated by a new resonance signal at $\delta = 68.7$ ppm in the ^{11}B{^{1}H} NMR spectrum and at $\delta = 56.6$ ppm ($^{1}J_{\text{Rh-P}} = 201.9$ Hz) in the ^{31}P{^{1}H} NMR spectrum. Resembling that of **6**, the ^{1}H NMR spectrum is characterized by two signals for trimethylsilyl groups at $\delta = 0.33$ and 0.64 ppm and two signals for olefinic protons at $\delta = 7.37$ (d, $^{3}J_{\text{Rh-H}} = 3.5$ Hz) and 6.55 ppm (d, $^{3}J_{\text{Rh-H}} = 2.9$ Hz). Notably, and in contrast to the common behavior of aminoboranes,[19] the amino group in the title compound shows no rotation about the B=N bond up to 80 °C, as judged by variable-temperature NMR experiments in C$_6$D$_6$, thus suggesting a significant double bond character. Complex **5**, analogous to [(η^5-C$_5$H$_5$)Rh(CO)(P*i*Pr$_3$)] (**4**), was detected as a byproduct in a ratio of 1:2 relative to **7**, as indicated by the resonance signal at $\delta_{\text{P}} = 68.7$ ppm ($^{1}J_{\text{Rh-P}} = 189.6$ Hz) and $\delta_{\text{H}} = 5.32$ ppm (s, C$_5$H$_5$) in the ^{31}P{^{1}H} NMR and ^{1}H NMR spectra, respectively. Moreover, the reaction is accompanied by the concomitant formation of [Mo(CO)$_6$] as indicated by a resonance at $\delta = 201.49$ ppm in the ^{13}C NMR spectrum, which is in accordance with the reported results on borylene transfer reactions of Group 6 carbonyl species.[14d] Both of the title compounds (**6** and **7**) possess considerable stability. No sign of decomposition in solution at ambient temperature was observed. The complexes were also stable towards chromatography at room temperature without significant loss of material. Complex **7** was isolated in the form of pale yellow crystals by crystallization from hexane at −30 °C. The result of X-ray diffraction analysis of **7** is displayed in Figure 1.

Complex **7** crystallizes in the monoclinic space group *P*2$_1$/*c*. The coordinated B–C bond (1.489(12) Å) is ca. 6% longer than the B=C bonds in non-coordinated amino(methylene)boranes **V** (e.g. 1.391(4)[6b] and 1.424(3) Å[6c]) and approximately 3% shorter than the B–C single bond found between two-coordinate boron and four-coordinate carbon atoms (1.531(11) Å).[20] This finding indicates considerable back-bonding from rhodium to an antibonding π^* orbital of the ligand; a bonding situation, which was also found for the butatriene complex **VII**. In particular, a similar increase by around 10% for the coordinated C–C double bond in comparison to the free tetrafluorobutatriene was observed for **VII**.[3] In the case of **7**, coordination of the 1-aza-2-bora-butatriene is accompanied by significant bending. The N1-B1-C1 angle of 142.1(7)° is comparable to the values of corresponding C-C-C angles (137.5–145.5°) in **VII**,[3] while the B1-C1-C2 angle of 152.9(7)° is widened by more than 5% compared to those values, thus suggesting some boron–carbon double bond character. The B1–N1 (1.400(10) Å) and C1–C2 (1.331(10) Å) distances are both slightly elongated in comparison to those of amino(methylene)borane (e.g. 1.363(4) Å)[6b] and free triene (1.3162(3) Å)[3]), which can be explained by a decrease of the s character in the B–C σ-bond orbitals upon bending of the [3]-boracumulene. Comparison of the structural characteristics of **7** with those of free amino(methylene)boranes (**V**), butatrienes (**I**), and butatriene complexes (**VII**) suggests an overall bonding situation to which both mesomeric forms **A** and **B** contribute (Scheme 1).

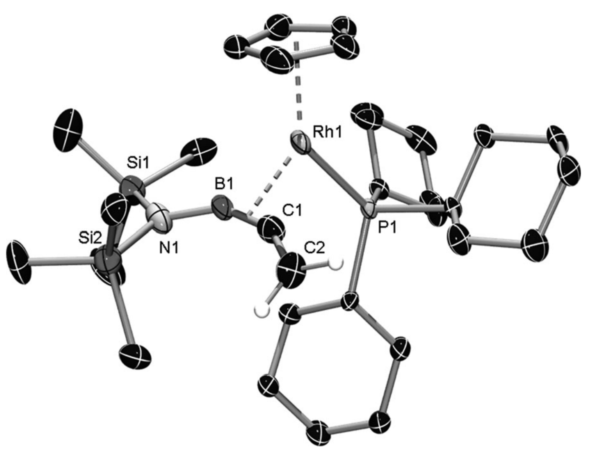
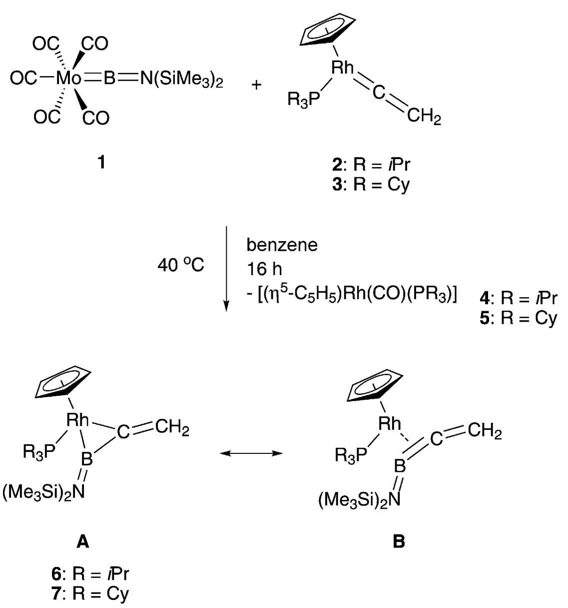


Figure 1. Molecular structure of **7**. Except for the two olefinic protons, hydrogen atoms have been omitted for clarity. Ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: N1–B1 1.400(10), B1–C1 1.489(12), C1–C2 1.331(10), Rh1–B1 2.027(8), Rh1–C1 2.056(7), N1–Si1 1.769(6), N1–Si2 1.765(6), Rh1–P1 2.2799(17); N1-B1-C1 142.1(7), B1-C1-C2 152.9(7).

To provide further insight into the electronic structure of **7**, DFT calculations were performed. We studied two model species by geometry optimization at the B3LYP level of theory – one with side-on coordination of the B=C bond derived from the crystal structure of **7** (**BC**), and a hypothetical isomer with side-on coordination of the C=C bond (**CC**; Figure 2). The calculations indicated a distinct preference for the observed B=C coordination mode, that is, **BC** is more stable than **CC** by 65.06 kJ mol^{-1} (Figure 2).

The relevant Wiberg bond indices (WBI, Table 1) for **BC** and **CC** are in accordance with a preference for the B=C over the C=C coordination mode. Thus, the WBIs in **BC** for the Rh1–B1 and Rh1–C1 linkages are slightly higher than the corresponding WBIs in **CC**, that is, Rh1–C1 and Rh1–C2.

The major MO contribution to the unprecedented side-on coordination of a boron–carbon double bond is represented by the HOMO+2 in the case of **BC**, which comprises an interaction of the p$_z$-orbital of the B–C bond with the d_{z^2} and $d_{x^2-y^2}$ orbitals of the rhodium center (Figure 3).



Scheme 1. Synthesis of 1-aza-2-bora-butatriene rhodium complexes **6** and **7** by borylene transfer to **2** and **3**, respectively.

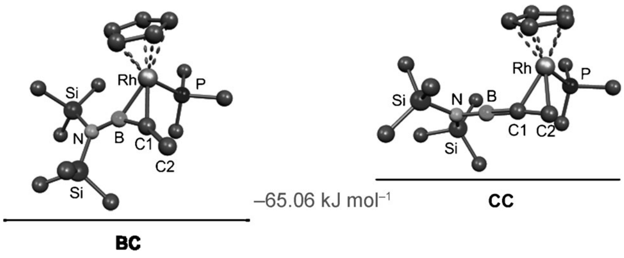


Figure 2. Energy difference between hypothetical isomers **BC** and **CC**.

Table 1: Calculated relevant WBIs for complexes **BC** and **CC**.

Comp.	Rh1–B1	Rh1–C1	Rh1–C2	B1–C1	C1–C2
BC	0.6024	0.5648	0.0900	1.0982	1.8788
CC	0.0966	0.3977	0.5010	1.7788	1.3135

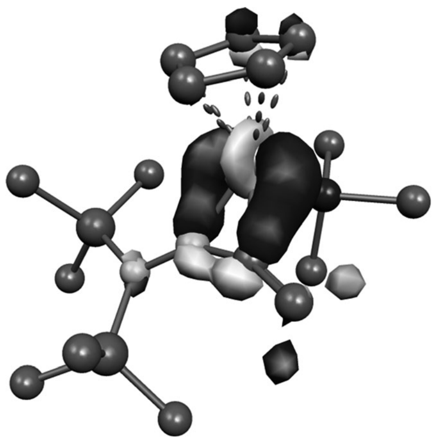
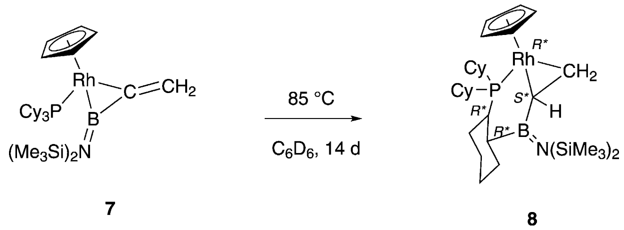


Figure 3. Graphical representation of HOMO+2 of **BC**.

After demonstrating the facile synthetic route to the novel 1-aza-2-bora-butatriene-rhodium complexes, we addressed the question, whether a ligand-exchange process would occur in the presence of CO to afford the free monocarbonyl complexes and the free *B*-amino 1-boraallene species. Owing to the poor steric protection, the *B*-amino 1-boraallene species is expected to be labile and might undergo secondary reactions. However, in stark contrast to butatriene rhodium complexes,[2c,e] 1-aza-2-bora-butatriene complex **7** proved to be stable in the presence of CO at ambient temperature, even under photolytic conditions. However, upon warming to 85 °C, NMR spectroscopy revealed a gradual and almost quantitative transformation of the starting material, as indicated by $^{11}B\{^1H\}$ ($\delta_B = 42.7$ ppm) and $^{31}P\{^1H\}$ NMR ($\delta_P = 74.3$ ppm, $^1J_{Rh\text{-}P} = 187.8$ Hz) spectra. Unexpectedly, neither $^{31}P\{^1H\}$ NMR nor $^{13}C\{^1H\}$ NMR spectra suggested the formation of the corresponding carbonyl complex. Moreover, the significant upfield shift of the ^{11}B NMR resonance by 26 ppm implies a change from B–C to C–C coordination, which could obviously take place without CO as well. Thus, an analogous experiment in the absence of CO was carried out, which confirmed our assumption.

Complete conversion of **7** required two weeks at 85 °C. After workup, single crystals were obtained from a hexane solution at ambient temperature. The product **8** (Scheme 2) crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit, both featuring very similar structural parameters. The results of X-ray diffraction analysis partially confirm our proposed structure. As shown in Figure 4, the C═C bond coordinates in a η2-fashion to the rhodium center. Despite the presence of the $N(SiMe_3)_2$ group that provides both steric shielding and π-electron donation, the released B═C bond is highly reactive and undergoes an addition reaction with the C4–H bond of one cyclohexyl group of the PCy_3ligand, affording the Rh1-C1-B1-C4-C3-P1 six-membered ring. The C1–C2 bond (1.417(6) Å) is elongated by approximately 6 % as a result of the side-on coordination, which is comparable to that observed for the B═C bond in **7**. The B1–C1 (1.533(7) Å) and B1–C4 (1.615(8) Å) separations fall within the expected range for the corresponding single bonds.[20] The elongation of the B1–C4 in comparison to the B1–C1 bond can be attributed to a lower amount of s-character in C4. Both boron and nitrogen atoms adopt a trigonal-planar geometry as indicated by the sum of angles of 359.1 and 359.9, respectively. The Si2-N1-B1-



Scheme 2. Quantitative formation of **8** (*RSRR/SRSS*) by a thermally induced change of coordination mode from B–C to C–C and subsequent C–H activation by the B═C bond.

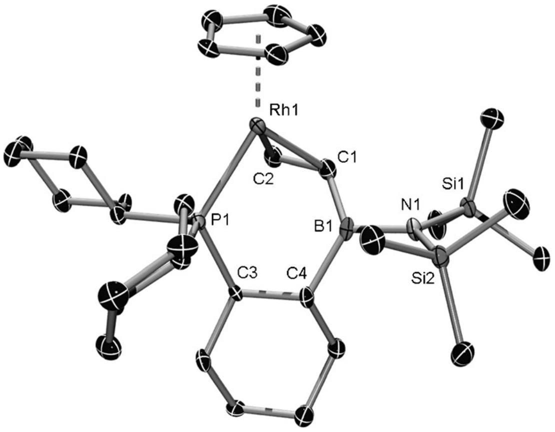


Figure 4. Molecular structure of **8** (R_{Rh},S_{C1},R_{C3},R_{C4}). Hydrogen atoms, the co-crystallized solvent molecules and the second independent molecule (S_{Rh},R_{C1},S_{C3},S_{C4}) in asymmetric unit have been omitted for clarity. Ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: C1–C2 1.417(6), C1–B1 1.533(7), B1–C4 1.615(8), C3–C4 1.546(6), P1–Rh1 2.2631(13), B1–N1 1.492(6); C2-C1-B1 131.6(5), C1-B1-C4 125.1(4), C1-B1-N1 116.6(4), N1-B1-C4 117.4(4), B1-N1-Si1 115.9(3), B1-N1-Si2 123.2(3), Si1-N1-Si2 120.8(2).

C4 torsion angle of 51.76° suggests a reduced B=N π-contribution, which corresponds to the significant elongation of the B1–N1 bond (1.492(6) Å) in comparison to that of **7** (1.400(10) Å) and is presumably a result of the pronounced steric congestion imposed by the bulky $N(SiMe_3)_2$, Cp, and Cy substituents bound to boron.

While complex **8** exists as a racemate (as the R_{Rh},S_{C1},R_{C3},R_{C4}-**8** and S_{Rh},R_{C1},S_{C3},S_{C4}-**8** enantiomers), remarkably, no other diastereomers were detected in the material. Since the two carbon atoms on the P-CH-CH-B system are both chiral centers, as are the Rh center and the Rh-bound CH atom, there are eight possible sets of enantiomers for **8**. If we assume that the olefin ligand is coordinatively labile, the Rh and adjacent CH atoms would then be configurationally unstable, reducing the possible products to two sets of enantiomers. However, careful examination of the ^{1}H and ^{13}C NMR spectra of the reaction mixture and isolated material showed no indication of diastereomers other than the R_{Rh}*,S_{C1}*,R_{C3}*,R_{C4}*-**8** racemate. Therefore, the C–H insertion reaction must proceed with a high degree of stereoselectivity.

Finally, we studied the reactivity of the bound 1-aza-2-borabutatriene ligand towards unsaturated substrates. Diphenylacetylene and benzophenone were chosen as representative non-polar and polar reagents, respectively, to investigate the propensity of the *B*-amino-1-boraallene species to undergo [2+2]cycloaddition reactions. However, no reaction was observed at ambient temperature, even upon irradiation. Under more forcing thermal conditions, the aforementioned intramolecular C–H addition with formation of **8** was again observed.

In conclusion, augmenting the ability of $[(OC)_5Mo{=}B{=}N(SiMe_3)_2]$ as a convenient source of borylene fragments under standard conditions, we have presented the first example of borylene transfer to a metal–carbon double bond. Moreover, the borylene-based functionalization of vinylidene rhodium complexes allows straightforward access to novel η^2-1-aza-2-borabutatriene rhodium complexes in satisfactory yields. Preliminary reactivity studies revealed a thermally induced B–C to C–C coordination mode shift with subsequent highly stereoselective C–H activation by the B=C bond.

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[1] a) G. Gustavson, N. Demjanov, *J. Prakt. Chem.* **1888**, *38*, 201–207; b) L. M. Morton, A. A. Noyes, *Am. Chem. J.* **1888**, *10*, 430–433.

[2] a) U. Schubert, J. Grönen, *Chem. Ber.* **1989**, *122*, 1237–1245; b) P. J. Stang, M. R. White, G. Maas, *Organometallics* **1983**, *2*, 720–725; c) H. Werner, M. Laubender, R. Wiedemann, B. Windmüller, *Angew. Chem.* **1996**, *108*, 1330–1332; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1237–1239; d) J.-D. van Loon, P. Seiler, F. Diederich, *Angew. Chem.* **1993**, *105*, 1235–1238; *Angew. Chem. Int. Ed.* **1993**, *32*, 1187–1189; e) H. Werner, R. Wiedemann, M. Laubender, B. Windmüller, P. Steinert, O. Gevert, J. Wolf, *J. Am. Chem. Soc.* **2002**, *124*, 6966–6980; for a recent Review, see: f) N. Suzuki, D. Hashizume, *Coord. Chem. Rev.* **2010**, *254*, 1307–1326.

[3] a) R. P. Hughes, R. B. Laritchev, L. N. Zakharov, A. L. Rheingold, *J. Am. Chem. Soc.* **2004**, *126*, 2308–2309; b) F. A. Akkerman, D. Lentz, *Angew. Chem.* **2007**, *119*, 4989–4991; *Angew. Chem. Int. Ed.* **2007**, *46*, 4902–4904.

[4] N. Suzuki, M. Nishiura, Y. Wakatsuki, *Science* **2002**, *295*, 660–663.

[5] a) C. D. Entwistle, T. B. Marder, *Angew. Chem.* **2002**, *114*, 3051–3056; *Angew. Chem. Int. Ed.* **2002**, *41*, 2927–2931; b) F. Jäkle, *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 293–307.

[6] a) B. Glaser, H. Nöth, *Angew. Chem.* **1985**, *97*, 424–425; *Angew. Chem. Int. Ed.* **1985**, *24*, 416–417; b) R. Boese, P. Paetzold, A. Tapper, *Chem. Ber.* **1987**, *120*, 1069–1071; c) B. Glaser, E. Hanecker, H. Nöth, H. Wagner, *Chem. Ber.* **1987**, *120*, 659–667.

[7] A. Berndt, *Angew. Chem.* **1993**, *105*, 1034–1058; *Angew. Chem. Int. Ed.* **1993**, *32*, 985–1009.

[8] M. Brock, Dissertation, Universität Marburg, **1990**.

[9] N. Metzler, H. Nöth, *Chem. Ber.* **1995**, *128*, 711–717.

[10] a) M. E. Volpin, Y. D. Koreshkov, V. G. Dulova, D. N. Kursanov, *Tetrahedron* **1962**, *18*, 107–122; for INDO calculations, see: b) C. U. Pittman, A. Kress, T. B. Patterson, P. Walton, L. D. Kispert, *J. Org. Chem.* **1974**, *39*, 373–378; c) N. L. Allinger, J. H. Siefert, *J. Am. Chem. Soc.* **1975**, *97*, 752–760; for ab-initio calculations, see: d) K. Krogh-Jespersen, D. Cremer, J. D. Dill, J. A. Pople, P. von R. Schleyer, *J. Am. Chem. Soc.* **1981**, *103*, 2589–2594.

[11] H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355–3357; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179–3180.

[12] H. Braunschweig, M. Colling, C. Kollann, B. Neumann, H.-G. Stammler, *Angew. Chem.* **2001**, *113*, 2359–2361; *Angew. Chem. Int. Ed.* **2001**, *40*, 2298–2300.

[13] a) H. Braunschweig, T. Herbst, D. Rais, S. Ghosh, T. Kupfer, K. Radacki, A. Crawford, R. Ward, T. Marder, I. Fernández, G. Frenking, *J. Am. Chem. Soc.* **2009**, *131*, 8989–8999; b) H. Braunschweig, I. Fernández, G. Frenking, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 5307–5310; *Angew. Chem. Int. Ed.* **2007**, *46*, 5215–5218; c) H. Braunschweig, Q. Ye, K. Radacki, *Chem. Commun.* **2009**, 6979–6981; d) H. Braunschweig, Q. Ye,

K. Radacki, P. Brenner, G. Frenking, S. De, *Inorg. Chem.* **2011**, *50*, 62–71.

[14] a) H. Braunschweig, M. Colling, C. Hu, K. Radacki, *Angew. Chem.* **2003**, *115*, 215–218; *Angew. Chem. Int. Ed.* **2003**, *42*, 205–208; b) H. Braunschweig, M. Forster, K. Radacki, *Angew. Chem.* **2006**, *118*, 2187–2189; *Angew. Chem. Int. Ed.* **2006**, *45*, 2132–2134; c) H. Braunschweig, M. Forster, K. Radacki, F. Seeler, G. Whittell, *Angew. Chem.* **2007**, *119*, 5304–5306; *Angew. Chem. Int. Ed.* **2007**, *46*, 5212–5214; d) H. Braunschweig, M. Forster, T. Kupfer, F. Seeler, *Angew. Chem.* **2008**, *120*, 6070–6072; *Angew. Chem. Int. Ed.* **2008**, *47*, 5981–5983.

[15] a) D. L. Kays née Coombs, J. K. Day, L.-L. Ooi, S. Aldridge, *Angew. Chem.* **2005**, *117*, 7623–7626; *Angew. Chem. Int. Ed.* **2005**, *44*, 7457–7460; b) H. Braunschweig, M. Burzler, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 8217–8219; *Angew. Chem. Int. Ed.* **2007**, *46*, 8071–8073; c) G. A. Pierce, S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, N. D. Coombs, D. J. Willock, *Angew. Chem.* **2007**, *119*, 2089–2092; *Angew. Chem. Int. Ed.* **2007**, *46*, 2043–2046; d) S. De, G. A. Pierce, D. Vidovic, D. L. Kays, N. D. Coombs, E. D. Jemmis, S. Aldridge, *Organometallics* **2009**, *28*, 2961–2975.

[16] H. Braunschweig, R. D. Dewhurst, T. Herbst, K. Radacki, *Angew. Chem.* **2008**, *120*, 6067–6069; *Angew. Chem. Int. Ed.* **2008**, *47*, 5978–5980.

[17] T. E. Bitterwolf, *Inorg. Chim. Acta* **1986**, *122*, 175–184.

[18] B. Blank, H. Braunschweig, M. Colling-Hendelkens, C. Kollann, K. Radacki, D. Rais, K. Uttinger, G. Whittell, *Chem. Eur. J.* **2007**, *13*, 4770–4781.

[19] C. Brown, R. H. Cragg, T. J. Miller, D. O. Smith, *J. Organomet. Chem.* **1983**, *244*, 209–215.

[20] H. Braunschweig, M. Burzler, T. Kupfer, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 7932–7934; *Angew. Chem. Int. Ed.* **2007**, *46*, 7785–7787.