Boron Ligands

DOI: 10.1002/anie.201302828

An Electron-Precise, Tetrahedral μ_3 Boride Complex**

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Recent research into the transition-metal chemistry of boron has unveiled a remarkable ability of boron-based ligands to adopt a wide diversity of different coordination modes (Figure 1). Classifications have been made by the number of substituents at boron and by the number of transition metals attached to the boron center.[1] Experimental and theoretical studies clearly identified a classical bonding situation with two-center–two-electron (2c2e) bonds for most borane (**I**) and boryl (**II**) complexes. By contrast, borders between electron-precise and non-classical structures tend to become blurred moving to borylene (**III**–**V**) or boride (**VI**) ligands.

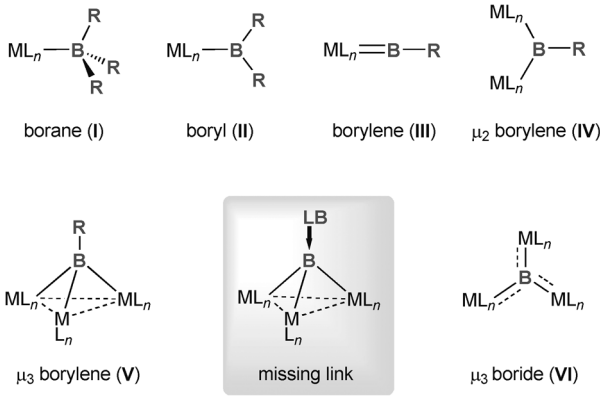
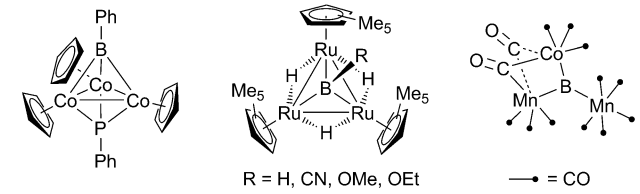


Figure 1. Coordination modes of boron-based ligands (LB = Lewis base).

Various synthetic strategies have enabled the isolation of terminal (mono-) and μ_2/μ_3 bridging (di- and trinuclear) borylene complexes, which usually require kinetic stabilization by sterically demanding ligands at the transition-metal center, or by bulky and/or electron-donating substituents at boron.[2] Trinuclear μ_3 bridging borylene complexes still remain rather exotic species, and only few examples have been structurally authenticated so far. Thus, Fehlner and Rheingold reported on the synthesis of a phosphacobaltaborane (**1**; Scheme 1) featuring a μ_3-BPh ligand.[3] Later on, Suzuki et al. succeeded in the generation of the trinuclear ruthenium species **2** (R = H, CN), albeit without structural



Scheme 1. Examples of boron coordinated to three transition metals.

authentication by X-ray diffraction.[4] Reaction of the B-H derivative with protic reagents (MeOH, EtOH) resulted in the loss of H_2 and formation of the corresponding alkoxyborylenes **2** (R = OMe, OEt), which implies a hydridic nature of the B–H moiety. Consequently, homotrimetallic borylenes **2** might also be regarded as trimetalloborate complexes, thus emphasizing the difficulties associated with the exact description of such uncommon species. However, the borylene ligands in **1** and **2** always act as two-electron donors within a non-classical cluster structure. Therefore, an electron-precise bonding situation is only amenable in the absence of any covalently bound exohedral ligand at the boron center of the M_3B core.

At best, this is achieved by formal removal of the B-bound substituent R resulting in trinuclear μ_3 boride complexes in which boron is exclusively coordinated to transition-metal fragments. Several examples for this family of compounds have been realized to date, featuring varying structures (T-shaped, Y-shaped, trigonal) with variable degrees of metal–boron bonding.[1,5] However, the transition from μ_3 borylene to μ_3 boride complexes involves rehybridization of the boron center from sp^3 to either sp (T-shaped, Y-shaped) or sp^2 (trigonal) and loss of the tetrahedral M_3B structure. For instance, trinuclear **3**, which closely approaches an ideal trimetalloboride structure with an electron-precise bonding situation, is essentially trigonal-planar (sum of angles: 359.3°).[5e]

These results clearly imply that saturation of the fourth valence at boron by a non-covalent interaction is required to make a tetrahedral, electron-precise μ_3 boride complex feasible. Thus, the missing link between tetrahedral μ_3 borylenes (**V**) and planar trimetalloborides (**VI**) is most

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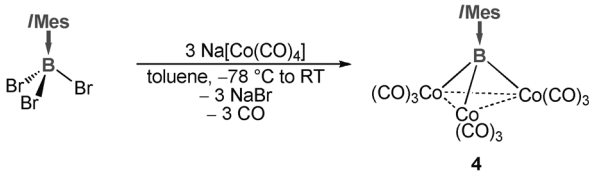
[**] This work was supported by the Deutsche Forschungsgemeinschaft.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302828.

likely a Lewis base-stabilized species of the type shown in Figure 1. To date, definite evidence for the existence of such a structural motif still remains to be provided, and we are only aware of two reports addressing this topic. Schmid et al. studied the reaction of NEt_3 and BBr_3 with $Tl[Co(CO)_4]$, which reportedly afforded tetrahedral $[(CO)_9Co_3(\mu_3\text{-}B{\cdot}NEt_3)]$ as a brown, highly sensitive solid. However, no structural data are available, and the chemical shift of the observed ^{11}B NMR resonance ($\delta = -2$ ppm) is rather uncommon for a boron atom coordinated to three transition-metal centers.[6] Also, the bonding situation in the related borataketenylidene cluster $[(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}BCO)]$ is rather difficult to describe. While spectroscopic parameters and reactivity of the exohedral CO group suggested the presence of a C–O triple bond and pure Lewis base coordination behavior, X-ray diffraction, photoelectron spectroscopy, and quantum-chemical calculations implied a strong double-bond character of the B–C bond.[7]

Our present approach in realizing an electron-precise μ_3 boride complex with tetrahedral geometry at boron makes use of the well-known ability of *N*-heterocyclic carbenes (NHCs) to stabilize uncommon main-group-element and transition-metal species.[8] We reasoned that *I*Mes·BBr_3 (*I*Mes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)[8b] is an ideal precursor for this purpose, because 1) the anticipated tetrahedral geometry is preformed with the required Lewis base already attached to boron; 2) a straightforward reaction pathway by stoichiometric salt metathesis is conceivable; and 3) the bulky NHC provides effective electronic and kinetic stabilization of the boron center.

To this end, *I*Mes·BBr_3 was treated with three equivalents of $Na[Co(CO)_4]$ in toluene at −78 °C. After reaching ambient temperature, the reaction proceeded smoothly and with high selectivity to afford the μ_3 boride species **4** quantitatively within 10 h (Scheme 2).[9] No intermediates can be observed



Scheme 2. Synthesis of tetrahedral μ_3 boride **4**.

by ^{11}B NMR spectroscopy of the reaction mixture. Instead, the ^{11}B NMR signal of *I*Mes·BBr_3 gradually and quantitatively devolves into a single new resonance for **4** ($\delta = 89$ ppm) during the course of the reaction. The chemical shift of **4** is not surprising and agrees very well with the coordination of three transition metals and an exohedral ligand to the boron center. Thus, related μ_3 borylenes **1** ($\delta = 144$ ppm)[3] and **2** ($\delta =$ 131 ppm, R = H; $\delta = 117$ ppm, R = CN; $\delta = 88$ ppm, R = OEt; $\delta = 78$ ppm, R = OMe)[4] appear in a similar range in the ^{11}B NMR spectra, while the coordination of the Lewis base causes a dramatic upfield shift with respect to planar trimetalloboride **3** ($\delta = 196$ ppm).[5e] By contrast, the ^{11}B NMR chemical shift of **4** contrasts significantly with the value obtained for $[(CO)_9Co_3(\mu_3\text{-}B{\cdot}NEt_3)]$ ($\delta = -2$ ppm),[6] which challenges its originally proposed structure. After workup, **4** was eventually isolated as dark red crystals in moderate yields (28%), which proved indefinitely stable at room temperature under an inert atmosphere. Yields are reproducible and cannot be increased, even though ^{11}B NMR spectroscopy suggested clean and quantitative conversion of *I*Mes·BBr_3 into **4**. The identity of **4** is easily verified by NMR/IR spectroscopy, elemental analysis, and X-ray diffraction (Figure 2).[9]

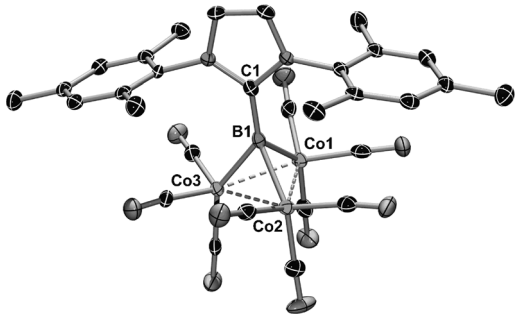


Figure 2. Molecular structure of **4**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–B1 1.569(5), B1–Co1 2.024(4), B1–Co2 2.031(4), B1–Co3 2.029(3), Co1–Co2 2.510(2), Co2–Co3 2.487(2), Co3–Co1 2.491(2); Co1-B1-Co2 76.5(1), Co3-B1-Co2 75.5(1), Co1-B1-Co3 75.8(1), C1-B1-Co1 132.6(2), C1-B1-Co2 134.3(2), C1-B1-Co3 137.1(2), Co3-Co1-Co2 59.6(1), Co3-Co2-Co1 59.8(1), Co2-Co3-Co1 60.6(1).

The molecular structure in the solid state nicely illustrates the μ_3 bridging boride motif, with the NHC-stabilized boron atom symmetrically located above a three-membered Co_3 ring, in which each cobalt atom is further substituted by three terminal carbonyl ligands. This scaffold is well-known for the related Group 14 species, that is, μ_3 carbyne[10] and μ_3 silylidyne complexes.[11] The C1–B1 axis is oriented perpendicular to the Co_3 plane with only marginal bending towards the Co1–Co2 linkage. B–Co distances are similar (2.024(4)–2.031(4) Å) and strongly resemble those found in **1** (2.018(8)–2.065(8) Å).[3] However, values are significantly larger than in di- (μ_2) and trinuclear (μ_3) cobalt borylene complexes $[(\eta^5\text{-}C_5H_5)(OC)Co\{\mu\text{-}BN(SiMe_3)_2\}W(CO)_5]$ (1.913(3) Å), $[\{(\eta^5\text{-}C_5H_5)(OC)Co\}_2\{\mu\text{-}BN(SiMe_3)_2\}]$ (1.952(2) Å),[2l] and **3** (1.903(2) Å),[5e] but smaller than in phosphine-stabilized $[\{Co(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}BH{\cdot}PMe_3)]$ (2.108(11)–2.112(9) Å).[12] Moreover, short Co–Co bond lengths (2.487(2)–2.510(2) Å) in **4**, which are of similar magnitude than in **1** (2.473(2)–2.561(1) Å)[3] and $[\{Co(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}BH{\cdot}PMe_3)]$ (2.486(2) Å),[12] clearly imply the presence of metal–metal bonding interactions. The B–C bond (1.569(5) Å) is rather short for a B–C single bond (1.61 Å), and suggests at least partial double-bond character (compare with the ELF).

The spectroscopic parameters of **4** in solution (C_6D_6) are consistent with its solid-state structure, while a single ^{13}C NMR resonance for the carbonyl ligands ($\delta =$ 206.2 ppm) indicates fluxional behavior. The infrared spectrum of **4** features six distinct bands between 1963 to

2098 cm^{-1}, which is in agreement with related trinuclear complexes featuring μ_3 carbyne and μ_3 silylidyne ligands.[10,11]

Density functional theory (DFT) calculations served to evaluate the actual bonding situation in **4** in more detail.[9] The optimization of the geometry at def2-SV(P)/B3LYP level of theory led to a structure containing three bridging carbonyl groups. Consequently, the experimentally determined geometry with optimized positions of hydrogen atoms was used for further evaluation (**4′**). Analysis of the Kohn–Sham orbitals shows that both σ- and π-type orbitals are involved in the Co–B bonding interactions. Thus, it is the HOMO−26 that illustrates the σ-type overlap of a sp_z-hybrid of boron with d_{z^2}-type orbitals of the cobalt atoms. The π-type interaction of p_x and p_y orbitals of boron with d orbitals of cobalt atoms is evident in all five HOMOs (the HOMO is shown in Figure 3 as a representative example). NBO analysis of **4′** reveals a positive natural charge on the metal centers (0.44–0.46), while boron is negatively charged (−0.39). These results might appear surprising at first sight, as earlier studies on transition-metal–boron electron-precise compounds strongly suggested an opposite charge distribution.[13] In this case however, Lewis base coordination of the NHC must also be taken into account.

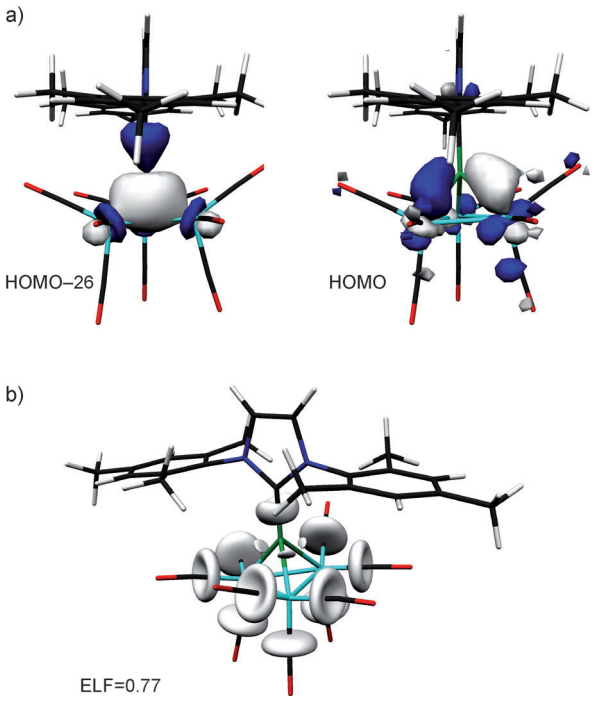


Figure 3. a) Kohn–Sham orbitals of the σ- (HOMO−26) and π-component (HOMO) of the BCo_3 interactions. b) Electron localization function plot (ELF = 0.77) for **4′**. The ELF contributions for remote ligands were omitted for clarity.

Recent theoretical work clearly demonstrated that such a dative interaction readily induces a negative natural charge at the boron center.[14] Despite the difference in charges, Wiberg bond indices[15] (WBI) for all B–Co bonds are relatively high (0.51–0.58), which underlines a pronounced covalent character of these interactions. By contrast, the WBIs of the Co–Co bonds feature much lower values of about 0.20. The localized character of the Co–B interactions is also reflected in the topology of the electron localization function (ELF).[16] Accordingly, ELF calculations on **4′** reveal the presence of three attractors located on the Co–B bonding axes, thus emphasizing the two-center character of these interactions (Figure 3). Furthermore, the ellipticity of the disynaptic valence basin (B,C) and its high population (2.7 e) also stress the significance of π components for the C–B bond, which indicates partial double-bond character.

Surprisingly, all attempts to further extend this experimental approach to other NHC ligands have consistently failed so far. Thus, no boron-containing reaction product was observed when *I*Me·BBr_3 (*I*Me = 1,3-dimethylimidazol-2-ylidene) was employed instead of *I*Mes·BBr_3. Obviously, steric factors play a major role in this transformation, and the much smaller ligand *I*Me is not able to stabilize the desired product effectively. Also, the NHC ligand may not be too large (such as *I*Dip·BBr_3; *I*Dip = 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene), or no reaction is observed at all.

To summarize, we succeeded in the isolation of a tetrahedral μ_3 boride complex **4** with an electron-precise bonding situation. Exploiting the concept of Lewis base (NHC) stabilization, the tetrahedral geometry of the μ_3-BCo_3 core could be retained in **4**, which is highly unusual for trimetalloboride species. DFT calculations were further used to verify the electron-precise bonding situation. Thus, **4** represents the missing link between tetrahedral μ_3 borylene (non-classical) and planar μ_3 boride (electron-precise) complexes.

Received: April 5, 2013
Published online: June 3, 2013

Keywords: boride ligands · boron · borylene ligands · carbenes · cobalt

[1] a) H. Braunschweig, R. D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924–3957; b) 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*, 2685–2722; c) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380–5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254–5274; d) D. L. Kays, S. Aldridge, *Struct. Bonding* **2008**, *130*, 29–122; e) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535–559; f) D. Vidovic, G. A. Pierce, S. Aldridge, *Chem. Commun.* **2009**, 1157–1171; g) H. Braunschweig, D. Rais, *Heteroat. Chem.* **2005**, *16*, 566–571; h) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1–51.

[2] a) H. Braunschweig, G. R. Whittell, *Chem. Eur. J.* **2005**, *11*, 6128–6133; b) H. Braunschweig, C. Kollann, F. Seeler, *Struct. Bonding* **2008**, *130*, 1–29; c) H. Braunschweig, C. Kollann, U. Englert, *Angew. Chem.* **1998**, *110*, 3355–3357; *Angew. Chem. Int. Ed.* **1998**, *37*, 3179–3180; d) D. L. Kays (née Coombs), A. Rossin, J. K. Day, L.-L. Ooi, S. Aldridge, *Dalton Trans.* **2006**, 399–410; e) 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; f) D. L. Kays (née Coombs), S. Aldridge, A. Rossin, C. Jones, D. J. Willock, *Organometallics* **2004**, *23*, 2911–2926; g) D. L. Coombs, S. Aldridge, C. Jones, D. J. Willock, *J. Am. Chem. Soc.* **2003**, *125*, 6356–6357; h) S. Aldridge, C. Jones, T. Gans-Eichler, A. Stasch, D. L. Kays, N. D.

Coombs, D. J. Willock, *Angew. Chem.* **2006**, *118*, 6264 – 6268; *Angew. Chem. Int. Ed.* **2006**, *45*, 6118 – 6122; i) H. Braunschweig, T. Wagner, *Angew. Chem.* **1995**, *107*, 904 – 905; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 825 – 826; j) H. Braunschweig, B. Ganter, *J. Organomet. Chem.* **1997**, *545*, 163 – 167; k) P. Bissinger, H. Braunschweig, T. Kupfer, K. Radacki, *Organometallics* **2010**, *29*, 3987 – 3990; l) H. Braunschweig, M. Forster, K. Radacki, F. Seeler, G. R. Whittell, *Angew. Chem.* **2007**, *119*, 5304 – 5307 – 5310; *Angew. Chem. Int. Ed.* **2007**, *46*, 5212 – 5214.

[3] a) J. Feilong, T. P. Fehlner, A. L. Rheingold, *Angew. Chem.* **1988**, *100*, 400 – 402; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 424 – 426; b) K. J. Deck, T. P. Fehlner, A. L. Rheingold, *Inorg. Chem.* **1993**, *32*, 2794 – 2795; c) K. J. Deck, P. Brenton, T. P. Fehlner, *Inorg. Chem.* **1997**, *36*, 554 – 558.

[4] R. Okamura, K.-i. Tada, K. Matsubara, M. Oshima, H. Suzuki, *Organometallics* **2001**, *20*, 4772 – 4774.

[5] a) H. Braunschweig, K. Radacki, D. Scheschkewitz, G. R. Whittell, *Angew. Chem.* **2005**, *117*, 1685 – 1688; *Angew. Chem. Int. Ed.* **2005**, *44*, 1658 – 1661; b) H. Braunschweig, K. Kraft, T. Kupfer, K. Radacki, F. Seeler, *Angew. Chem.* **2008**, *120*, 5009 – 5011; *Angew. Chem. Int. Ed.* **2008**, *47*, 4931 – 4933; c) H. Braunschweig, M. Burzler, R. D. Dewhurst, K. Radacki, *Angew. Chem.* **2008**, *120*, 5732 – 5735; *Angew. Chem. Int. Ed.* **2008**, *47*, 5650 – 5653; d) H. Braunschweig, K. Radacki, D. Rais, F. Seeler, *Angew. Chem.* **2006**, *118*, 1087 – 1090; *Angew. Chem. Int. Ed.* **2006**, *45*, 1066 – 1069; e) H. Braunschweig, R. D. Dewhurst, K. Kraft, K. Radacki, *Angew. Chem.* **2009**, *121*, 5951 – 5954; *Angew. Chem. Int. Ed.* **2009**, *48*, 5837 – 5840; f) H. Braunschweig, P. Brenner, R. D. Dewhurst, M. Kaupp, R. Müller, S. Östreicher, *Angew. Chem.* **2009**, *121*, 9916 – 9919; *Angew. Chem. Int. Ed.* **2009**, *48*, 9735 – 9738.

[6] G. Schmid, V. Bätzel, G. Etzrodt, R. Pfeil, *J. Organomet. Chem.* **1975**, *86*, 257 – 262.

[7] a) S. G. Shore, D. Y. Jan, L. Y. Hsu, W. L. Hsu, S. Kennedy, J. Huffman, *J. Am. Chem. Soc.* **1983**, *105*, 5923 – 5924; b) R. D. Barreto, T. P. Fehlner, L. Y. Hsu, D. Y. Jan, S. G. Shore, *Inorg. Chem.* **1986**, *25*, 3572 – 3581; c) D. Y. Jan, D. P. Workman, L. Y. Hsu, J. A. Krause, S. G. Shore, *Inorg. Chem.* **1992**, *31*, 5123 – 5131; d) J.-H. Chung, E. P. Boyd, J. Liu, S. G. Shore, *Inorg. Chem.* **1997**, *36*, 4778 – 4781; e) D. J. H. Emslie, B. E. Cowie, K. B. Kolpin, *Dalton Trans.* **2012**, *41*, 1101 – 1117.

[8] a) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 12412 – 12413; b) Y. Wang, B. Quillian, P. Wei, Y. Xie, C. S. Wannere, R. B. King, H. F. Schaefer III, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 3298 – 3299; c) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326 – 12337; d) P. de Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.* **2009**, *253*, 862 – 892; e) D. P. Curran, A. Solovyev, M. M. Brahmi, L. Fensterbank, M. Malacria, E. Lacôte, *Angew. Chem.* **2011**, *123*, 10476 – 10500; *Angew. Chem. Int. Ed.* **2011**, *50*, 10294 – 10317.

[9] Details on the experimental procedure, the crystal structure determinations, and the theoretical calculations can be found in the Supporting Information.

[10] a) B. R. Penfold, B. H. Robinson, *Acc. Chem. Res.* **1973**, *6*, 73 – 80; b) G. H. Worth, B. H. Robinson, J. Simpson, *Organometallics* **1992**, *11*, 3863 – 3874; c) M. Pizzotti, C. Zucchi, A. Chiesi-Villa, R. Boese, G. Pályi, *J. Organomet. Chem.* **2005**, *690*, 4740 – 4744; d) W. Cen, K. J. Haller, T. P. Fehlner, *Inorg. Chem.* **1993**, *32*, 995 – 1000.

[11] P. Gusbeth, H. Vahrenkamp, *Chem. Ber.* **1985**, *118*, 1143 – 1153.

[12] M. Shimoi, S. Ikubo, Y. Kawano, K. Katoh, H. Ogino, *J. Am. Chem. Soc.* **1998**, *120*, 4222 – 4223.

[13] a) G. Frenking, N. Froehlich, *Chem. Rev.* **2000**, *100*, 717 – 774; b) Y. Chen, G. Frenking, *J. Chem. Soc. Dalton Trans.* **2001**, 434 – 440; c) H. Braunschweig, M. Burzler, T. Kupfer, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 7932 – 7934; *Angew. Chem. Int. Ed.* **2007**, *46*, 7785 – 7787; d) K. Pandey, H. Braunschweig, R. D. Dewhurst, *Eur. J. Inorg. Chem.* **2011**, 2045 – 2056.

[14] a) T. Yasue, Y. Kawano, M. Shimoi, *Angew. Chem.* **2003**, *115*, 1769 – 1772; *Angew. Chem. Int. Ed.* **2003**, *42*, 1727 – 1730; b) R. Tonner, G. Frenking, *Chem. Eur. J.* **2008**, *14*, 3273 – 3289; c) J. Hioe, A. Karton, J. M. L. Martin, H. Zipse, *Chem. Eur. J.* **2010**, *16*, 6861 – 6865.

[15] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083 – 1096.

[16] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397 – 5403.

